

## Redox Reactions for Group 5 Elements, Including Element 105, in Aqueous Solutions

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Standard redox potentials  $E^\circ(M^{z+x}/M^{z+})$  in acidic solutions for group 5 elements including element 105 (Ha) and the actinide, Pa, have been estimated on the basis of the ionization potentials calculated via the multiconfiguration Dirac–Fock method. Stability of the pentavalent state was shown to increase along the group from V to Ha, while that of the tetra- and trivalent states decreases in this direction. Our estimates have shown no extra stability of the trivalent state of hahnium. Element 105 should form mixed-valence complexes by analogy with Nb due to the similar values of their potentials  $E^\circ(M^{3+}/M^{2+})$ . The stability of the maximum oxidation state of the elements decreases in the direction  $103 > 104 > 105$ .

## I. Introduction

During the past few years, there has been a growing interest in actinide and transactinide chemistry. Besides the importance of the lighter elements and their compounds in applied research, there is a basic interest in the detailed mapping of the periodic table of the elements. The high degree of interest in this region of the periodic table comes from the fact that in the heavy elements increasingly large relativistic effects become very important and can influence the electronic structure, which may affect physicochemical properties and chemical behavior.

These fundamental properties are ground-state electronic configurations, atomic (ionic) radii, and ionization potentials. Changes in these characteristics may influence the stability of different oxidation states, enthalpies of hydration or sublimation, complexing behavior in aqueous solutions, and many other properties.

Relativistic atomic multiconfiguration Dirac–Fock calculations<sup>1,2</sup> (MCDF) have shown that the relativistic stabilization of  $s_{1/2}$  and  $p_{1/2}$  orbitals for the heavy elements causes the ground-state electronic configurations for elements 103 and 104 to be different from that expected on the basis of a straightforward extrapolation of the periodic system: Lr turned out to have a  $7s^27p_{1/2}$  ground-state electronic configuration instead of the expected  $6d^7s^2$ , and element 104  $6d^7s^27p_{1/2}$  instead of  $6d^27s^2$ . For element 105, MCDF calculations<sup>3</sup> give, as was expected, the ground-state electronic configuration  $6d^37s^2$ .

A number of chemical experiments have been carefully planned and conducted to study the physicochemical properties of the heavy elements and, in particular, to attempt to observe the influence of relativistic effects on them. These include experiments<sup>4,5</sup> on the volatility of elements 103, 104, and 105 and their halides using the gas chromatography technique and on solution chemistry of element 105 through a chromatographic solvent extraction.<sup>6</sup>

These experiments have revealed an interesting chemical behavior of the heavy elements and have been considered theoretically in our previous work.<sup>7</sup>

The influence of the relativistic effects on the stability of oxidation states is one of the interesting aspects of experimental investigations. Thus, it has been suggested<sup>8</sup> that the  $7s^2$  closed shell in Lr might be sufficiently stabilized by the relativistic effects

to make it an “inert core” so that only the  $7p_{1/2}$  (or  $6d$ ) electron may be removed under reducing conditions, thereby producing monovalent Lr. Nevertheless, there was no experimental evidence for the reduction of  $Lr^{3+}$  in aqueous solution,<sup>9</sup> although in the similar experiments  $Md^{3+}$  was reduced to  $Md^{2+}$ . The resulting limit for the reduction potential of the  $Lr^{3+}/Lr^{1(2)+}$  couple was found to be  $E^\circ < -0.44$  V. Attempts to reduce  $Lr^{3+}$  to  $Lr^+$  in ethanol with  $Sm^{2+}$  have yielded only a limit of  $E^\circ < -1.56$  V, and no reduction of  $Lr^{3+}$  has been observed.<sup>10</sup>

In ref 11, it was expressed that the +1 oxidation state of element 104 should show a higher stability as compared to the analogues Zr and Hf due to a lower value of the first ionization potential and a  $d^2sp$  ground-state electronic configuration with a presumably delocalized p electron. In refs 12 and 13, estimates of the standard electrode potentials for elements 103 and 104 are given based on an ionic model.

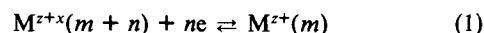
In this paper, we present the results of an evaluation of redox potentials for group 5 elements in acidic solutions, including element 105, based on our MCDF calculations<sup>3</sup> of the ionization potentials. These predicted thermodynamic properties will contribute to our knowledge about the chemical behavior of element 105 in solutions.

## II. Characteristics of the Redox Potentials

For niobium and tantalum, all the formal oxidation states from +5 to –2 have been reported.<sup>14</sup> The small difference between energy levels of the d and s electrons gives rise to a wide range of oxidation states. The oxidation states +4, +3, and +2 for Nb and Ta are nevertheless less characterized than the corresponding ones for vanadium.

The complete picture of the reduction–oxidation properties of group 5 elements should include potentials for the following couples:  $M^{5+}/M$ ,  $M^{5+}/M^{4+}$ ,  $M^{4+}/M^{3+}$ ,  $M^{3+}/M^{2+}$ , and  $M^{2+}/M^{1+}$ .

For characterizing an oxidation state, the oxidation–reduction potential  $E^\circ$  is of crucial importance. For the reaction



the redox potential  $E^\circ(M^{z+x}/M^{z+})$  defines all the changes when an ion of charge  $z+x$  and valency  $m+n$  comes over to a state with charge  $z+$  and valency  $m$ . (We will equate here the valency to the effective charge for the species in solutions, which is generally not the case.)

For reaction 1 involving electron e, the change of the free energy  $\Delta G$  is expressed as

$$\Delta G = -nFE \quad (J \text{ mol}^{-1}) \quad (2)$$

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where  $F$  is the Faraday constant (the charge of a mole of electrons), equal to  $96487 \text{ C mol}^{-1}$ . In other units, eq 2 has the form

$$\Delta G = -n(23\,060)E \quad (\text{cal mol}^{-1})$$

The standard potential  $E^\circ$  can be calculated using eq 2 when the activities of all species in solution are equal to 1.

On the other hand, the change of the free energy in the redox reaction (1) can be expressed in the following form:<sup>15</sup>

$$\Delta G = -[IP + \Delta G_{\text{hyd}}] \quad (3)$$

where  $\Delta G_{\text{hyd}}$  is the change in hydration energy when an ion in valent state  $m + n$  comes over to valent state  $m$  during the reduction process.

The ionization energy

$$IP = I \pm \Delta E \quad (4)$$

where  $I$  is the one-particle ionization energy for  $M^{z+} \rightarrow M^{z+1}$  and  $\Delta E$  is the energy necessary for the reconstruction (or a change) of an electronic configuration of the metal ion when it is transformed from valent state  $m$  to valent state  $m + n$ .

As an example, we consider here the process  $\text{Ta}^{2+}(\text{d}^3) \rightarrow \text{Ta}^{3+}(\text{d}^2)$ . In this case, there is no reconstruction of the electronic configuration, and in eq 4,  $\Delta E = 0$  so that  $IP = I$ . For the process  $\text{Ta}^+(\text{d}^3\text{s}) \rightarrow \text{Ta}^{2+}(\text{d}^3)$ , there is a reconstruction of the electronic configuration and  $IP = I + \Delta E$ , where  $\Delta E = E(\text{d}^4) - E(\text{d}^3\text{s})$ .

On the example of the actinide series, it was shown<sup>15-17</sup> that the  $\Delta E$ 's correlate linearly with the redox potentials and define all the changes in their values. In ref 17, a linear dependence of the redox potentials on the energies of the electron-transfer spectra corresponding to the changes in the electronic configurations has been established. Ionization potentials  $I$  and  $\Delta G_{\text{hyd}}$  were shown<sup>15</sup> to be smooth functions of the atomic number (e.g., for the lanthanide and actinide series) and contribute only to the absolute values of  $\Delta G$ .

The fact that  $\Delta G_{\text{hyd}}$  is a smooth function of the atomic number for the group 5 elements can be seen from the following.

According to the Born theory of ionic solvation,<sup>18</sup>  $\Delta G_{\text{hyd}}(M^{z+})$  is a function of ionic charge  $z$  and the radius of an ion  $r_{M^{z+}}$ :

$$\Delta G_{\text{hyd}} = A(z)/\epsilon[r_{M^{z+}} + r_x(z)] \quad (5)$$

where  $\epsilon$  is the dielectric constant of water or an aqueous solution and  $r_x(z)$  is a radius parameter to be added to the crystal ionic radius and which depends on  $z$ . The change in the hydration energy when the ion is transformed from oxidation state  $z$  to oxidation state  $z + x$  is

$$\Delta G_{\text{hyd}} = \Delta G_{\text{hyd}}(M^{z+x}) - \Delta G_{\text{hyd}}(M^{z+}) = \frac{A(z+x)/\epsilon[r_{M^{z+x}} + r(z+x)] - A(z)/\epsilon[r_{M^{z+}} + r(z)]}{(6)}$$

One can see from the results of the MCDF calculations<sup>3</sup> that the differences in ionic radii of V, Nb, Ta, and Ha between one oxidation state and any other state are very similar. Assuming that the same is valid for  $r(z+x)$  and  $r(z)$ ,  $\Delta G_{\text{hyd}}$  (eq 6) can be assumed as a smooth function of the atomic number.

Thus, from the foregoing, it follows that the redox potentials  $E^\circ(M^{z+x}/M^{z+})$  should be proportional to the values of the ionization potentials  $IP$  in which the changes in electronic configurations are included.

The validity of such a correlation is well seen on the example of  $E^\circ(\text{II} - \text{III})$  for early actinides,<sup>15</sup> where the IPs already contain the reconstruction of the electronic configurations:  $IP = E_{A_n^{z+}}(\text{df}^2) - E_{A_n^{z+}}(\text{f}^2)$ . Also in same ref 15, the redox potentials for all members of the lanthanide and actinide series have been estimated using the methodology outlined.

In the present work, we will estimate the unknown values of the redox potentials for group 5 elements V, Nb, Ta, and Ha, along with a pseudomember of group 5—Pa—using the correlation between experimental  $E^\circ(M^{z+x}/M^{z+})$  and the calculated<sup>3</sup> IPs, which have been normalized and extrapolated to the experimentally known values.<sup>19</sup> These calculated IPs are actually the differences between the energies of the electronic configurations corresponding to the reduced and the oxidized states. For the oxidation processes  $M^0/M^{5+}$ ,  $M^{4+}/M^{5+}$ ,  $M^{3+}/M^{4+}$ , and  $M^{2+}/M^{3+}$

TABLE I: Standard Free Energies of Formation (in kcal mol<sup>-1</sup>), Ionization Potentials [0 → 5+] (in eV), and Standard Reduction Potentials (in V) for the M<sup>5+</sup>/M Couple for the Pentoxides of Group 5 Elements

compd	$\Delta G_f^\circ$ <sup>a</sup>		IP[0 → 5+] <sup>j</sup>	$E^\circ(M^{5+}/M)$ <sup>a</sup>	
V <sub>2</sub> O <sub>5</sub> (c)	-344.0 <sup>a</sup>	-341.1 <sup>b</sup>	162.64	-0.25 <sup>a</sup>	-0.242 <sup>h</sup>
	-339.2 <sup>c</sup>	-339.3 <sup>d</sup>			
VO <sub>2</sub> <sup>+</sup> (aq)	-140.3 <sup>d</sup>			-0.236 <sup>c</sup>	-0.233 <sup>h</sup>
Nb <sub>2</sub> O <sub>5</sub> (c)	-432.0 <sup>a</sup>	-421.8 <sup>e</sup>	135.05	-0.65 <sup>a</sup>	-0.601 <sup>h</sup>
	-422.6 <sup>c</sup>	-422.1 <sup>d</sup>			
Ta <sub>2</sub> O <sub>5</sub> (c)	-470.6 <sup>a</sup>	-456.4 <sup>f</sup>	132.03	-0.81 <sup>a</sup>	-0.752 <sup>h</sup>
	-457.0 <sup>c</sup>	-456.8 <sup>d</sup>			
Pa <sub>2</sub> O <sub>5</sub> (c)	-514.05 <sup>g</sup>		110.14 <sup>i</sup>	(-1.24) <sup>h</sup>	
PaO <sub>2</sub> <sup>+</sup> (aq)	-228.7 <sup>k</sup>			-1.0 <sup>g</sup>	
PaOOH <sup>2+</sup>	-250.95 <sup>c</sup>			-1.0 <sup>c</sup>	-1.21 <sup>h</sup>
Ha <sub>2</sub> O <sub>5</sub> (c)	-474.90 <sup>k</sup>		126.38	(-0.81) <sup>k</sup>	(-0.90) <sup>k</sup>

<sup>a</sup>Reference 20. <sup>b</sup>Reference 21. <sup>c</sup>Reference 22. <sup>d</sup>Reference 23. <sup>e</sup>Reference 24. <sup>f</sup>Reference 25. <sup>g</sup>Reference 26. <sup>h</sup>Reference 27, the most recent and revised values. <sup>i</sup>Reference 28. <sup>j</sup>Reference 3. <sup>k</sup>Estimated (this work). (Values in parentheses in this table and the following ones are the estimated values.)

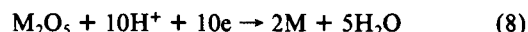
of V, Nb, Ta, and Ha, these IPs are the energy transitions between the electronic configurations  $d^3s^2/d^0$  ( $d^4s/d^0$  for Nb),  $d^1/d^0$ ,  $d^2/d^1$ , and  $d^3/d^2$ , respectively. For these transitions, there are no reconstructions of the electronic configurations. For the  $\text{Pa}^0/\text{Pa}^{5+}$ ,  $\text{Pa}^{4+}/\text{Pa}^{5+}$ ,  $\text{Pa}^{3+}/\text{Pa}^{4+}$  and  $\text{Pa}^{2+}/\text{Pa}^{3+}$  oxidation processes, the IPs are the energy transitions between  $f^2ds^2/f^0$ ,  $f^1/f^0$ ,  $f^2/f^1$ , and  $f^2d/f^2$  electronic configurations, respectively. The energy transitions between the electronic configuration corresponding to the  $M^+/M^{2+}$  and  $M^0/M^+$  oxidation processes have also been calculated in ref 3, but we will not use these data here because of the absence of the experimental data for  $E^\circ(M^+/M^{2+})$  and  $E^\circ(M^0/M^+)$ .

### III. Redox Reactions of V, Nb, Ta, Ha, and Pa in Aqueous Solutions

A. Reduction Reaction  $M^{5+} \rightarrow M$ . Reaction 1 for the potential  $E^\circ(M^{5+}/M)$  can be written as



The known reduction process corresponding to reaction 7 for V, Nb, and Ta is the reaction of their pentoxides with a strong (e.g., hydrochloric) acid:



The free energy  $\Delta G^\circ$  of reaction 8 is the difference between the free formation energies of the components in the right and left parts of this reaction:

$$\Delta G^\circ = 2\Delta G_f^\circ(M) + 5\Delta G_f^\circ(H_2O) - \Delta G_f^\circ(M_2O_5) - 10\Delta G_f^\circ(H^+) - 10\Delta G_f^\circ(e) \quad (9)$$

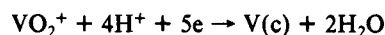
The standard formation energies of an element M, e, and  $H^+$  are set equal to zero. The value  $\Delta G_f^\circ(H_2O)$  is  $-56\,690 \text{ cal mol}^{-1}$ .<sup>20</sup> Thus, for reaction 8 using eq 2,  $E^\circ(M_2O_5/M)$  can be defined as

$$E^\circ(M_2O_5/M) = -\frac{5(-56\,690) - \Delta G_f^\circ(M_2O_5)}{(10)(23\,060)} \quad (10)$$

where one has to know the value of  $\Delta G_f^\circ(M_2O_5)$ .

In Table I, we present the data on  $\Delta G_f^\circ(M_2O_5)$  from different sources and, based on them the corresponding standard potentials  $E^\circ(M_2O_5/M)$ .

For the process  $V^{5+}/V$ , the standard potential of the reaction

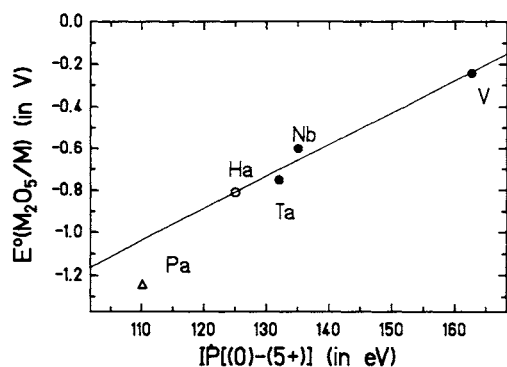


has been measured, with its value being listed in Table I.

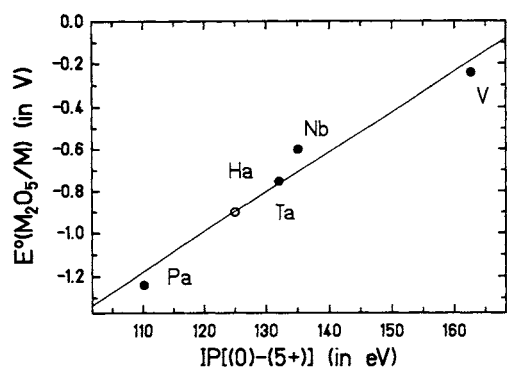
For protactinium, the potential can be determined through the reaction



since the hydrated oxide in solution,  $\text{Pa}_2\text{O}_5(\text{aq})$ , is thought to be  $\text{PaO}_2^+$ . The standard potential for reaction 11 is  $-1.0 \text{ V}$ .<sup>22</sup> In



**Figure 1.** Correlation between ionization potentials [0 → 5+] and the standard potentials  $E^\circ(\text{M}_2\text{O}_5/\text{M})$  for group 5 elements. (Pa point is not included in the correlation.) Filled circles are experimental values (see Table I); open circles are estimated values (from this work); open triangle is Pa point which is not included in the correlation.



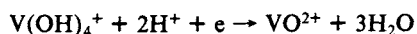
**Figure 2.** Correlation between ionization potentials [0 → 5+] and the standard potentials  $E^\circ(\text{M}_2\text{O}_5/\text{M})$  for group 5 elements. (Pa point is included in the correlation.) Filled circles are experimental and estimated<sup>26</sup> values (see Table I); open circles are estimated values (this work).

ref 27, the value of the standard potential for the  $\text{PaOOH}^{2+}/\text{Pa}(\text{c})$  couple is given as  $-1.25$  V, and an estimate has been done of the potential for the  $\text{Pa}_2\text{O}_5/\text{Pa}(\text{c})$  couple as  $-1.24$  V.

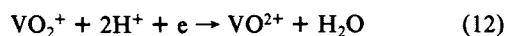
The ionization potentials  $\text{IP}[0 \rightarrow 5+]$  obtained as a result of the MCDF calculations<sup>3</sup> are also listed in Table I. From a linear correlation with a least-squares fit between the known  $E^\circ(\text{M}_2\text{O}_5/\text{M})$  for V, Nb, and Ta and  $\text{IP}[0 \rightarrow 5+]$  of the group 5 elements (Figure 1), one obtains  $E^\circ(\text{Ha}_2\text{O}_5/\text{Ha})$  equal to  $-0.81$  V. Including the value  $E^\circ(\text{Pa}_2\text{O}_5/\text{Pa}) = -1.24$  V in this correlation gives  $E^\circ(\text{Ha}_2\text{O}_5/\text{Ha}) = -0.9$  V (Figure 2). Using the value of the potential  $\text{Ha}_2\text{O}_5/\text{Ha}$  as  $-0.81$  V, one can calculate the free formation energy of  $\text{Ha}_2\text{O}_5$  as  $-474.85$  kcal mol<sup>-1</sup>. Thus, the stability of the pentavalent state in solutions increases in the direction  $\text{V} < \text{Nb} < \text{Ta} < \text{Ha} < \text{Pa}$ , with  $E^\circ(\text{Ha}_2\text{O}_5/\text{Ha})$  being between the corresponding values for Ta and Pa.

**B. Reduction Reaction  $\text{M}^{5+} \rightarrow \text{M}^{4+}$ .** For the process  $\text{M}^{5+} \rightarrow \text{M}^{4+}$ , the standard potentials have been measured<sup>22,26,27</sup> for V, Nb, and Pa, with that of protactinium being a tentative one (Table II).

At 1 M  $[\text{H}^+]$  concentration in aqueous solution, V(V) is a moderately good oxidizing agent, and the potential  $E^\circ(\text{MO}_2^+/\text{MO}^{2+})$  is equal to 1.0 V for the reactions



or



The following thermodynamic data have been obtained for the  $\text{VO}^{2+}$  ion in aqueous solution:<sup>23</sup>  $\Delta H_f^\circ = -116.3$  kcal mol<sup>-1</sup>,  $\Delta G_f^\circ = -106.7$  kcal mol<sup>-1</sup>, and  $\Delta S_f^\circ = -32.0$  cal mol<sup>-1</sup> K<sup>-1</sup>. Similarly, the reduction of Pa(V)

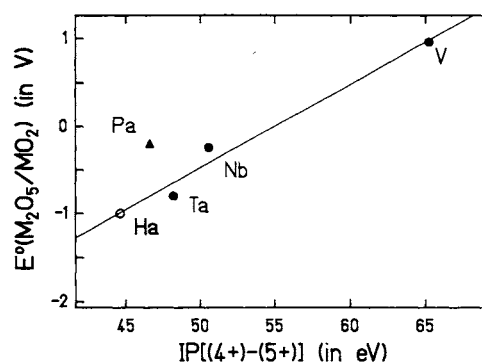


was studied,<sup>26</sup> where  $\text{PaO}^{2+}$  is a hypothetical species. The value

**TABLE II: Fifth Ionization Potentials [4+ → 5+] (in eV), Standard Free Energies of Formation (in kcal mol<sup>-1</sup>) for  $\text{MO}_2^+$  and  $\text{MO}^{2+}$  Species, and Standard Reduction Potentials for the  $\text{M}_2\text{O}_5/\text{MO}_2$  and  $\text{MO}_2^+/\text{MO}^{2+}$  Couples (in V) for Group 5 Elements**

	V	Nb	Ta	Ha	Pa
$\text{IP}[4+ \rightarrow 5+]$ <sup>a</sup>	65.23	50.55	48.19	44.62	46.6 <sup>b</sup>
$E^\circ(\text{M}_2\text{O}_5/\text{MO}_2)$ <sup>c</sup>	0.957 <sup>d</sup>	-0.248	(-0.8)	(-1.0) <sup>e</sup>	(-0.2)
$E^\circ(\text{MO}_2^+/\text{MO}^{2+})$ <sup>c</sup>	1.00	(-0.2)	(-1.0) <sup>f</sup>	(-1.13) <sup>e</sup>	-0.1
$\Delta G_f^\circ(\text{MO}_2^+)$ <sup>e</sup>	-140.3 <sup>g</sup>	-163.0	-201.4 <sup>g</sup>	-244.0	-228.7
$\Delta G_f^\circ(\text{MO}^{2+})$ <sup>e</sup>	-106.7 <sup>g</sup>	-101.7	-121.65	-161.3	-169.7

<sup>a</sup> Reference 3. <sup>b</sup> Reference 28. <sup>c</sup> Reference 27. <sup>d</sup> For the  $\text{V}_2\text{O}_5/\text{VO}^{2+}$  couple, ref 27. <sup>e</sup> Estimated (this work). <sup>f</sup> For the  $\text{M}(\text{OH})_4^+/\text{M}(\text{OH})_2^{2+}$  couple, ref 27. <sup>g</sup> Reference 23.



**Figure 3.** Correlation between ionization potentials [4+ → 5+] and the standard potentials  $E^\circ(\text{M}_2\text{O}_5/\text{MO}_2)$  for group 5 elements. Filled circles are experimental and estimated<sup>26</sup> values (see Table II); open circles are estimated values (this work). (Pa point does not fit the curve.)

given for  $E^\circ(\text{PaO}_2^+/\text{PaO}^{2+})$  of reaction 13 is  $-0.1$  V. In ref 27, the experimental value of the potential for the  $\text{PaOOH}^{2+}/\text{Pa}^{4+}$  couple is given as  $-0.1$  V and an estimated potential for the  $\text{Pa}_2\text{O}_5/\text{PaO}_2$  couple as  $-0.2$  V. Our earlier estimate<sup>30</sup> of  $E^\circ(\text{Pa}^{5+}/\text{Pa}^{4+})$  was  $-0.34$  V.

Comparing pentavalent vanadium and protactinium, one sees that Pa(V) [ $\text{PaO}_2^+$ ,  $\text{PaO}^{3+}$ ,  $\text{PaOOH}^{2+}$ ,  $\text{PaO}(\text{OH})_2^+$ ] is stable in aqueous solutions and it is difficult to reduce, while V(V) [ $\text{VO}_2^+$ ,  $\text{VO}^{3+}$ ,  $\text{V}(\text{OH})_4^+$ ] is unstable and it is easily reduced.

To evaluate the standard potentials  $E^\circ(\text{M}^{5+}/\text{M}^{4+})$  for Nb, Ta, and Ha, we have used again the linear correlation (Figure 3) between the known redox potentials for V and Nb, the estimated ones for Ta and Pa, and the fifth ionization potentials, obtained as a result of MCDF calculations<sup>3</sup> (Table II). The resulting value of  $E^\circ(\text{M}_2\text{O}_5/\text{MO}_2)$  for Ha is presented in Table II.

The Pa point is not included in the correlation, because it does not fit the plot in Figure 3. If the estimated value of  $E^\circ(\text{Ta}_2\text{O}_5/\text{TaO}_2)$  [ $-0.8$  V<sup>27</sup>] is not used, then the correlation based only on the two experimental points (V and Nb) gives the values  $E^\circ(\text{Ta}_2\text{O}_5/\text{TaO}_2) = -0.45$  V and  $E^\circ(\text{Ha}_2\text{O}_5/\text{HaO}_2) = -0.75$  V.

These data show that the stability of the tetravalent state in solution decreases from V to Ha:  $\text{V} \gg \text{Pa} > \text{Nb} > \text{Ta} > \text{Ha}$ . Thus, if the cation  $\text{PaO}^{3+}$  (or  $\text{PaO}_2^+$ ) in solution is difficult to reduce, then  $\text{Ha}^{5+}$  will be even more difficult to reduce.

For potentials  $E^\circ(\text{MO}_2^+/\text{MO}^{2+})$ , the values are known only for V and Pa. For Nb and Ta, we can assume that their potentials for the hydrolyzed species,  $E^\circ[\text{Nb}(\text{OH})_4^+/\text{Nb}(\text{OH})_2^{2+}] = -0.2$  V and  $E^\circ[\text{Ta}(\text{OH})_4^+/\text{Ta}(\text{OH})_2^{2+}] = -1.0$  V,<sup>27</sup> would correspond roughly to the potentials for the  $\text{NbO}_2^+/\text{NbO}^{2+}$  and  $\text{TaO}_2^+/\text{TaO}^{2+}$  couples. These cations,  $\text{MO}_2^+$  and  $\text{MO}^{2+}$ , obviously do not occur in aqueous solutions, as they will decompose. Nevertheless, we will use them to make a complete picture of the redox potentials. Such a choice can be justified because in solution chemistry unstable species which are immediately decomposed by water are used very often and, in addition, the real situation about which compound is present in a solution under which conditions is very complicated. Even for vanadium, there are hydrolyzed forms along with the pure cationic ones, and for protactinium, hydrolysis is extremely complicated.<sup>31</sup>

The correlation between the known potentials for the  $\text{MO}_2^+/\text{MO}^{2+}$  couple for V and Pa, along with the estimates for

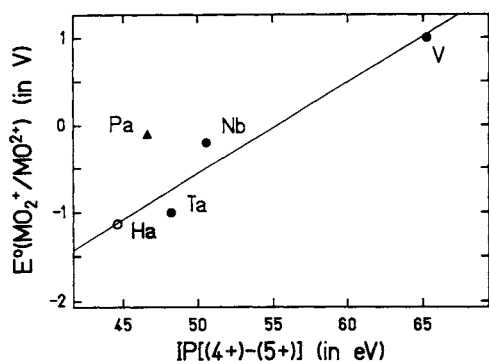
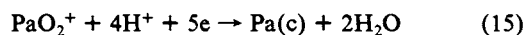


Figure 4. Correlation between ionization potentials [4+ → 5+] and the standard potentials  $E^\circ(\text{MO}_2^+/\text{MO}_2)$  for group 5 elements. Filled circles are experimental and estimated<sup>26</sup> values (see Table II); open circles are estimated values (this work). (Pa point does not fit the curve.)

Nb and Ta and the ionization potentials [5+ → 4+], gives a potential of -1.13 V for  $\text{HaO}_2^+/\text{HaO}^{2+}$  (see Figure 4 and Table II). From a knowledge of these potentials, the formation energies of the cations involved can be evaluated. This can be done using the following equation:

$$E^\circ(\text{MO}_2^+/\text{MO}_2) = \frac{\Delta G_f^\circ(\text{MO}_2^+) + \Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{MO}_2)}{23\,060} \quad (14)$$

$\Delta G_f^\circ(\text{PaO}_2^+)$  can be determined from the reaction



using the relation

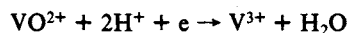
$$E^\circ(\text{PaO}_2^+/\text{Pa}) = \frac{2(-56\,690) - \Delta G_f^\circ(\text{PaO}_2^+)}{(5)(23\,060)} = -1 \text{ V}$$

Thus, one obtains  $\Delta G_f^\circ(\text{PaO}_2^+)$  equal to 228.7 kcal mol<sup>-1</sup>.

$\Delta G_f^\circ(\text{TaO}_2^+)$  was determined from eq 14 using the experimental value<sup>23</sup>  $\Delta G_f^\circ(\text{TaO}_2^+) = -201.4$  kcal mol<sup>-1</sup>. The  $\Delta G_f^\circ(\text{MO}_2^+)$ 's for Nb and Ha have been determined on the basis of the linear correlation between  $\Delta G_f^\circ(\text{MO}_2^+)$  and the atomic numbers of the elements. These  $\Delta G_f^\circ(\text{MO}_2^+)$  values obtained and  $E^\circ(\text{MO}_2^+/\text{MO}_2)$  were used to calculate the unknown free energies of formation of  $\text{MO}_2^+$  for Nb and Ha. The results are presented in Table II.

From the estimated values of the redox potentials  $E^\circ(\text{M}_2\text{O}_5/\text{MO}_2)$  and  $E^\circ(\text{MO}_2^+/\text{MO}_2)$ , one can see that the stabilities of the tetravalent states of V and Ha represent two extremes in the group. Thus, aqueous solutions of the oxovanadium(V) ion in the presence of a strong acid are stable for months, Pa(IV) is unstable and it rapidly oxidizes to the pentavalent state, and Ha(IV) will be even less stable than Pa(IV).

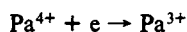
C. Reduction Reaction  $\text{M}^{4+} \rightarrow \text{M}^{3+}$ . For the reaction



$$E^\circ(\text{V}^{4+}/\text{V}^{3+}) = 0.337 \text{ V}^{27}$$

The reduction potential  $E^\circ(\text{NbO}_2/\text{Nb}^{3+})$  has been estimated<sup>27</sup> as -0.4 V and  $E^\circ(\text{TaO}_2/\text{Ta}^{3+})$  as -1.1 V.

For the reaction



the values  $E^\circ(\text{Pa}^{4+}/\text{Pa}^{3+}) = -1.9$  V and  $E^\circ(\text{PaO}_2/\text{Pa}^{3+}) = -2.0$  V have been estimated.<sup>27</sup> In an earlier study,<sup>30</sup>  $E^\circ(\text{Pa}^{4+}/\text{Pa}^{3+})$  was found to be -1.8 V. A linear correlation of the fourth ionization potentials<sup>3</sup> with  $E^\circ(\text{MO}_2/\text{M}^{3+})$  for V, Nb, Ta, and Pa (Figure 5) results in  $E^\circ(\text{HaO}_2/\text{Ha}^{3+}) = -1.38$  V (see Table III).

From the data of Table III, one can see that the stability of the trivalent state in aqueous solutions decreases in the succession V > Nb > Ta > Ha > Pa. The complex  $[\text{V}(\text{OH})_6]^{3+}$  exists in solution with a blue color, but it is slowly oxidized by air. Protactinium(III) is not known in solution.

TABLE III: Fourth Ionization Potentials [3+ → 4+] (in eV) and Standard Reduction Potentials for the  $\text{MO}_2/\text{M}^{3+}$  Couple (in V) for Group 5 Elements

	V	Nb	Ta	Ha	Pa
$\text{IP}[3+ \rightarrow 4+]^a$	46.71	38.26	36.73	34.19	31.00 <sup>b</sup>
$E^\circ(\text{MO}_2/\text{M}^{3+})^c$	0.337 <sup>d</sup>	(-0.4)	(-1.1)	(-1.38) <sup>e</sup>	(-2.0)

<sup>a</sup> Reference 3. <sup>b</sup> Reference 28. <sup>c</sup> Reference 27. <sup>d</sup> For the  $\text{VO}^{2+}/\text{V}^{3+}$  couple. <sup>e</sup> Estimated (this work).

TABLE IV: Third Ionization Potentials [2+ → 3+] (in eV) and Standard Reduction Potentials for the  $\text{M}^{3+}/\text{M}^{2+}$  couple (in V) for Group 5 Elements

	V	Nb	Ta	Ha	Pa
$\text{IP}[2+ \rightarrow 3+]^a$	29.31	25.04	23.84	24.65	18.80 <sup>b</sup>
$E^\circ(\text{M}^{3+}/\text{M}^{2+})$	-0.255 <sup>c</sup>	(-0.9) <sup>d</sup>	(-1.35) <sup>e</sup>	(-1.20) <sup>e</sup>	(-2.60) <sup>f</sup>

<sup>a</sup> Reference 3. <sup>b</sup> Reference 28. <sup>c</sup> Reference 27. <sup>d</sup> For the  $\text{Nb}^{3+}/\text{NbO}$  couple, ref 27. <sup>e</sup> Estimated (this work). <sup>f</sup> Reference 12.

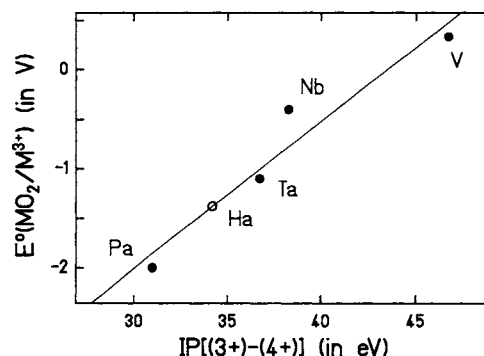


Figure 5. Correlation between ionization potentials [3+ → 4+] and the standard potentials  $E^\circ(\text{MO}_2/\text{M}^{3+})$  for group 5 elements. Filled circles are reference values (see Table III); open circles are estimated values (this work).

D. Reduction Reaction  $\text{M}^{3+} \rightarrow \text{M}^{2+}$ . There are nearly no data for the process  $\text{M}^{3+} \rightarrow \text{M}^{2+}$ . For vanadium, the reduction potential  $E^\circ(\text{M}^{3+}/\text{M}^{2+})$  has been given as -0.255 V.<sup>27</sup> The estimate of  $E^\circ(\text{Nb}^{3+}/\text{NbO})$  is -0.9 V.

Estimates of the standard potential for the  $\text{Pa}^{3+}/\text{Pa}^{2+}$  couple vary over quite a wide range: -5.2,<sup>15</sup> -4.7,<sup>32</sup> and -2.6.<sup>12</sup> Because Pa is an important point for the correlation of the redox potentials in group 5, we will analyze the reasons for such a large discrepancy in the values of this potential. In refs 15 and 32, it was supposed that both complex ions in solutions,  $\text{Pa}^{2+}$  and  $\text{Pa}^{3+}$ , have  $f^q$  electronic configuration with  $q = 3$  and  $q = 2$ , respectively. In ref 12, the potential for the  $\text{Pa}^{3+}/\text{Pa}^{2+}$  couple was estimated assuming that the electronic configuration for  $\text{Pa}(\text{H}_2\text{O})_n^{2+}$  is  $f^2d$ . It is clear that ionization potentials are different for the electronic configurations  $f^3$  and  $f^2d$ , which will result in different values of the redox potentials.

If it is true that the electronic configuration of  $\text{Pa}^{2+}$  is  $f^2d$ , then Pa should be an analogue of the group 5 d elements in lower oxidation states. If also the estimate  $E^\circ(\text{Pa}^{3+}/\text{Pa}^{2+}) = -2.6$  V is correct, one can raise a question about obtaining the divalent protactinium in solutions or in the molten phase under special conditions because the value of the potential is close to that for the couple  $\text{Am}^{3+}/\text{Am}^{2+}$  equal to -2.3<sup>32</sup> or -2.5 V.<sup>15</sup> It was reported<sup>33</sup> that in the solid state, PaO like all other AnO's has not been obtained in a pure form. It has been identified by X-ray study as a surface layer on protactinium metal. Thus, in principle,  $\text{Pa}^{2+}$  exists in the solid state under the special conditions (as, e.g.,  $\text{NpO}$  only on the surface of  $\text{NpO}_2$ ), one can suppose that at the specific value of the potential in solutions or in the molten phase,  $\text{Pa}^{2+}$  in the electronic configuration  $f^2d$  can be obtained. However, we must admit that neither our calculations<sup>15</sup> of  $\text{PaCl}_6^{4-}$  or  $\text{PaCl}_6^{3-}$  nor calculations of other authors, nor the spectral studies, have ever shown the inversion of the nonbonding and antibonding levels in the protactinium (or other actinide) compounds so that 6d levels went below 5f ones or mixed with them,

TABLE V: Ionization Potentials [0 → 3+] (in eV) and Standard Reduction Potentials for the M<sup>3+</sup>/M Couple (in V) for Group 5 Elements

	V	Nb	Ta	Ha	Pa
IP[0 → 3+] <sup>a</sup>	50.70	46.24	47.11	47.56	36.39 <sup>b</sup>
E°(M <sup>3+</sup> /M)	-0.87, <sup>c</sup> (-0.84) <sup>e</sup>	-1.10, <sup>c</sup> (-0.8) <sup>d</sup>	(-0.6) <sup>d</sup>	(-0.56) <sup>e</sup>	(-1.34) <sup>d</sup>
E°(M <sup>3+</sup> /M)	-0.87, <sup>c</sup> (-0.84) <sup>e</sup>	-1.10, <sup>c</sup> (-0.8) <sup>d</sup>	(-0.74) <sup>f</sup>	(-0.64) <sup>f</sup>	(-1.34) <sup>d</sup>

<sup>a</sup> Reference 3. <sup>b</sup> Reference 28. <sup>c</sup> Reference 20. <sup>d</sup> Reference 27. <sup>e</sup> Estimated (this work) using eq 16 with E°(Ta<sub>2</sub>O<sub>5</sub>/TaO<sub>2</sub>) = -0.8 V and E°(Ha<sub>2</sub>O<sub>5</sub>/HaO<sub>2</sub>) = -1.0 V. <sup>f</sup> Estimated (this work) using eq 16 with E°(Ta<sub>2</sub>O<sub>5</sub>/TaO<sub>2</sub>) = -0.45 V and E°(Ha<sub>2</sub>O<sub>5</sub>/HaO<sub>2</sub>) = -0.75 V. <sup>g</sup> Calculated using the relation 3E°(M<sup>3+</sup>/M) = E°(M<sup>3+</sup>/M<sup>2+</sup>) + 2E°(M<sup>2+</sup>/M).

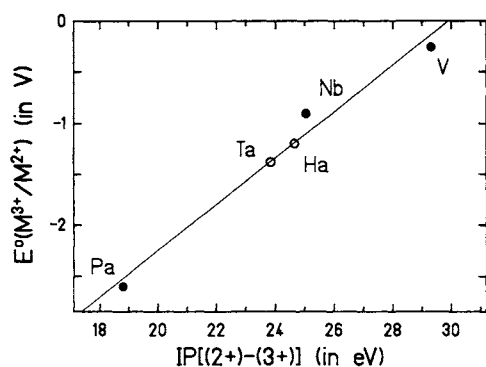


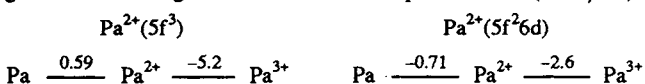
Figure 6. Correlation between ionization potentials [2+ → 3] and the standard potentials E°(M<sup>3+</sup>/M<sup>2+</sup>) for group 5 elements. Filled circles are reference values (see Table IV); open circles are estimated values (this work).

leading to the f<sup>0</sup>d electronic configuration. Bonding molecular orbitals of d character in actinide compounds are indeed occupied by electrons, while the antibonding ones stay vacant.

No information about the low oxidation states for Ta in solutions is available.

An evaluation of the potentials E°(M<sup>3+</sup>/M<sup>2+</sup>) for Nb, Ta, and Ha can be done on the basis of the correlation between these values and the third ionization potentials (Figure 6), using the values of E°(V<sup>3+</sup>/V<sup>2+</sup>) and E°(Nb<sup>3+</sup>/NbO) and an estimate<sup>12</sup> of E°(Pa<sup>3+</sup>/Pa<sup>2+</sup>) of -2.6 V. This evaluation is, of course, a very crude one since the uncertainty in the E°(Pa<sup>3+</sup>/Pa<sup>2+</sup>) estimate is large. The resulting values of the redox potentials are given in Table IV, which show that the stability of the divalent state changes in the following order: V > Nb > Ha > Ta > Pa.

On the basis of the two values of the potential Pa<sup>3+</sup>/Pa<sup>2+</sup>, we give the following two schemes for the potential E°(Pa<sup>2+</sup>/Pa):



Using the relation 3E°(M<sup>3+</sup>/M) = 2E°(M<sup>2+</sup>/M) + E°(M<sup>3+</sup>/M<sup>2+</sup>), the estimated potentials E°(M<sup>2+</sup>/M) along with the measured ones for V, Nb, Ta, Ha, and Pa are -1.125, -0.733, (-0.225), (-0.24), and (0.59) or (-0.83) V, respectively.

**E. Reduction Reaction M<sup>3+</sup> → M.** We can evaluate the potential E°(M<sup>3+</sup>/M) more accurately using the thermodynamic formula

$$E^\circ(\text{M}^{3+}/\text{M}) = \frac{1}{3}[5E^\circ(\text{M}^{5+}/\text{M}) - E^\circ(\text{M}^{4+}/\text{M}^{3+}) - E^\circ(\text{M}^{5+}/\text{M}^{4+})] \quad (16)$$

The resulting potentials are listed in Table V. A second set of standard potentials, M<sup>3+</sup>/M, which have been calculated using eq 16 but with E°(Ta<sub>2</sub>O<sub>5</sub>/TaO<sub>2</sub>) = -0.45 V and E°(Ha<sub>2</sub>O<sub>5</sub>/HaO<sub>2</sub>) = -0.75 V are also presented in this table.

**F. Mixed-Valence Low Oxidation States of Group 5 Elements.** There are some examples of the stability of low oxidation states of group 5 elements in solutions.<sup>34</sup> The cation [Nb<sub>6</sub><sup>2.17+</sup>Cl<sub>12</sub>]<sup>+</sup> is stable in HCl solution. It is a cluster of O<sub>h</sub> symmetry with the valency of niobium between 2 and 3. Another ion [Nb<sub>6</sub><sup>3.66+</sup>O<sub>3</sub>(SO<sub>4</sub>)<sub>12</sub>]<sup>8-</sup> exists in solution, and the valency of niobium is between 3 and 4. It can be prepared through cathode reduction with H<sub>2</sub>SO<sub>4</sub> at a pH between 8.8 and 14:

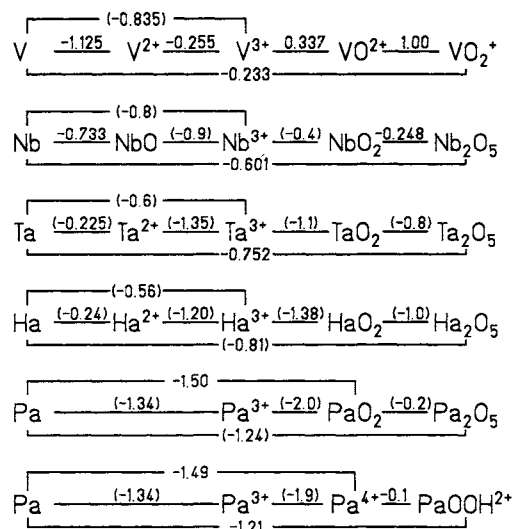
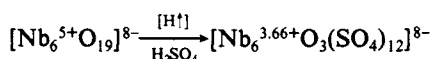


Figure 7. Standard redox potentials for group 5 elements and Pa. For the E°(M<sub>2</sub>O<sub>5</sub>/MO<sub>2</sub>) potentials, the more reliable values of Table II have been used, and for E°(M<sup>3+</sup>/M), those from Table V have been used. (Figures in parentheses are the estimated values.)

TABLE VI: Standard Reduction Potentials E°(M<sup>z+</sup>/M<sup>(z-1)+</sup>) (in V) for Heavy Elements

element	E°(M <sup>3+</sup> /M <sup>2+</sup> ) <sup>a</sup>	E°(M <sup>4+</sup> /M <sup>3+</sup> ) <sup>a</sup>	E°(M <sup>5+</sup> /M <sup>4+</sup> ) <sup>b</sup>
102(No)	1.3	6.6	
103(Lr)	-2.6	8.1	
104	-1.7	-1.5	
105(Ha)	-1.20 <sup>b</sup>	-1.38 <sup>b</sup>	-1.0

<sup>a</sup> Reference 10. <sup>b</sup> Estimated (this work).

These examples show the possibility of forming mixed-valence complexes of Nb under certain circumstances. Apparently, the same can be true for Ha because they have similar values of potentials E°(M<sup>3+</sup>/M<sup>2+</sup>). In complexes [Ta<sub>6</sub><sup>5+</sup>O<sub>19</sub>]<sup>8-</sup> and [Nb<sub>6</sub><sup>5+</sup>O<sub>19</sub>]<sup>8-</sup>, the metals are not reduced to lower oxidation states. The cation [Ta<sub>6</sub>Cl<sub>6</sub>]<sup>+</sup> exists, but it is unstable in solution.

#### IV. Conclusions

A complete picture of the redox potentials for the group 5 elements and Pa is shown in Figure 7.

For the group 5 elements, the stability of the pentavalent state increases in going from V to Ha, while that of the tetra- and trivalent states decreases in this direction. The divalent state of Ha should be slightly less stable than that of Nb, and Ha would be expected to form mixed-valence complexes, as does Nb. The present estimates show that there will be no extra stability of the trivalent state of hahnium, as could be expected from the ground-state electronic configuration of Ha d<sup>3</sup>s<sup>2</sup>.

Comparing the standard reduction potentials E°(M<sup>3+</sup>/M<sup>2+</sup>), E°(M<sup>4+</sup>/M<sup>3+</sup>), and E°(M<sup>5+</sup>/M<sup>4+</sup>) for elements 102 to 105 (Table VI), one can see that the potentials corresponding to the reduction from the maximum oxidation state to the next one decrease in going from Lr (-2.6 V) to Ha (-1.0 V). Thus, trivalent Lr is more stable than tetravalent element 104, and tetravalent element 104 is more stable than pentavalent hahnium.

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