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S 49. *Oxidation States of the Rare-earth and Actinide Elements.*

By ROBERT E. CONNICK.

The existence of a wide variety of oxidation states and the ease of oxidation to higher states of the actinide elements compared with the rare-earth elements is discussed in terms of ionisation potentials and free energies of hydration.

The " stability " of the +3 oxidation state of the rare earths is not to be regarded as characteristic of *f* electrons in general.

Trends in the oxidation potentials of the 2—3 and 3—4 couples of the rare earths are interpreted in terms of the binding energy of the *f* electrons. Similar correlations are made for the actinide elements; hydrolysis enters as an additional complication in the case of the 4—5 and 4—6 couples.

The electron configuration of thorium in the +2 oxidation state is probably $6d^2$. On the basis of the present evidence it is not possible to decide between an *f* and a *d* configuration for the +3 state.

The oxidation potentials and electron configurations of protoactinium are briefly considered.

THERE is a marked similarity in the chemical properties of corresponding oxidation states of the rare earth and actinide* elements (with the exception of protoactinium). This arises from the stabilization of the 5*f* orbitals in the neighbourhood of thorium,† resulting in the occurrence of a group of elements analogous to the rare earths. The two series of elements do differ, however, in the much greater variety of oxidation states exhibited by the actinides (see Table I) and the greater ease of oxidation to higher states of the latter.

Factors determining Oxidation Potentials.—The existence of an oxidation state of an element is contingent upon its reacting only slowly, if at all, with its surroundings. In acidic aqueous solution, to which the following discussion will be largely confined, the reactivity of water imposes the following limitations for the type of ions under consideration. An oxidation state will exist only if all its oxidation potentials to higher states are more positive than *ca.* −2·0 volts and all its reduction potentials to lower states are more negative than *ca.* +1·5 volts. In the case of solid compounds these limits are often wider but depend rather specifically on the particular compounds. The +4 oxide sometimes exists where the +4 ion does not in aqueous solution; lower oxidation states frequently exist in solids although " unstable " in solution.

For simple ions in aqueous solution the oxidation–reduction potential connecting two oxidation states may be broken up into steps involving hydration energies and ionisation potentials. Thus for the reaction

$$M^{+x}_{aq} + H^{+}_{aq} = M^{x+1}_{aq} + \tfrac{1}{2}H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the following steps may be written :

$$M^{+x}_{g} = M^{+x}_{aq} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2) \qquad\qquad H^{+}_{aq} = H^{+}_{g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$M^{+x}_{g} = M^{x+1}_{g} + e^{-} \quad . \quad . \quad . \quad . \quad (3) \qquad\qquad e^{-} + H^{+}_{g} = H_{g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$M^{x+1}_{g} = M^{x+1}_{aq} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4) \qquad\qquad H_{g} = \tfrac{1}{2}H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The free energy of reaction (1) is

$$\Delta F_1 = -\Delta F_2 + \Delta F_3 + \Delta F_4 + \Delta F_5 + \Delta F_6 + \Delta F_7$$

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* The term " actinide elements " is used here to designate the elements from actinium to curium, inclusive. The rare earths (or lanthanides) are assumed to start with lanthanum and end with lutecium.

† It has recently been shown that gaseous Th^{+3} has a 5*f* ground configuration, rather than 6*d* (Klinkenberg and Lang, private communication; to be published in *Physica*).

which may be written as

$$\Delta F_1 = -\Delta F_2 + I + \Delta F_4 + \Delta F_5 - I_H + \Delta F_7$$

where I and I_H are the ionization potentials of the gaseous ion M^{+x} and the hydrogen atom, respectively.

For standard conditions

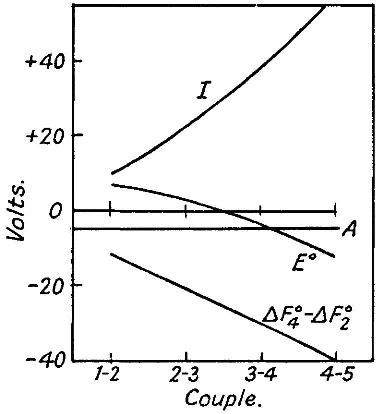
$$\Delta F_1{}^\circ = -\Delta F_2{}^\circ + \Delta F_4{}^\circ + I + A$$

where A is a constant. If all quantities are expressed in electron volts, $-\Delta F_1{}^\circ$ gives the standard oxidation–reduction potential of the couple, E°, *i.e.*,

$$-E^\circ = \Delta F_4{}^\circ - \Delta F_2{}^\circ + I + A \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

It is of interest to see the order of magnitude of each term in equation (8). Fig. 1 is a rough plot of these values for the successive oxidation–reduction couples of neodymium (plotted as abcissa). Complete curves have been drawn rather than individual points, since these quantities in general show continuous trends with increasing oxidation number.

FIG. 1.



Semi-quantitative plot for neodymium of quantities which determine oxidation potentials of couples.

The orders of magnitude of the ionization potentials and hydration energies are known for a few of the rare earths so that the qualitative shape and position of the I and the $\Delta F_4{}^\circ - \Delta F_2{}^\circ$ curves are known, but the individual values of these quantities have not been determined with anything approximating to the accuracy necessary to give even rough values for the oxidation potentials of the couples. This is true of all rare-earth and actinide elements. Therefore the shape and position of the E° curve in Fig. 1 was actually fixed by a knowledge of the chemistry of neodymium and the neighbouring elements. The 2—3 potential must be considerably more positive than $+1{\cdot}5$ volts and the 3—4 potential considerably more negative than $-2{\cdot}0$ volts. This places lower limits on the negative of the slope of E° as it crosses the abcissa axis and, as judged from the cerium 3—4 and the samarium 2—3 potentials, the crossing point is roughly mid-way between the 2—3 and 3—4 couples. The 1—2 couple is fairly well fixed by estimated ionization-potential and hydration-energy values because these quantities are relatively small in this case. The remainder of the E° curve is primarily an extrapolation from the above but one which is considered reasonable and is consistent with known chemical facts.

If the ionisation potentials and free energies of hydration were known accurately or could be predicted theoretically, it would be possible to calculate all the oxidation–reduction properties of these elements. Unfortunately such is not the case, and it appears that most of this information will be very difficult to obtain. Therefore Fig. 1 and much of what follows is in the nature of an interpretation of oxidation–reduction behaviour in terms of hydration energies and ionization potentials rather than a prediction from these quantities.

The Stability of the $+3$ *Oxidation State of the Rare Earths.*—In Fig. 1 the E° curve was drawn to correspond to the fact that only the $+3$ oxidation state of neodymium is stable with respect to reaction with water. For the 1—2 and 2—3 couples the hydration energy and A terms more than compensate the ionization energy term and oxidation to the +3 state occurs readily. The ionization potential, which is a steeper function of the degree of oxidation than the hydration-energy term, becomes dominant by the time the 3—4 couple is reached and the oxidation potential becomes strongly negative. As is discussed below, the corresponding curves for the other rare earths are not greatly shifted from the neodymium curve; thus, in every case the +3 oxidation state exists in aqueous solution and its oxidation or reduction is either very difficult or impossible.

The ionization potentials and hydration energies for 4*f* electrons will be different than for 5*f* electrons. Therefore it is not to be expected that the resulting E° values of the two series will correspond or that the same oxidation states will necessarily exist. It is clear that the great " stability " of the +3 state of the rare earths is peculiar only to 4*f* electrons and results from the fact that the ionization potentials and free energies of hydration happen to combine to give very positive values for the oxidation potential of the 2—3 couple and very negative values for the 3—4 couple.

At one time it was believed that the electronic configuration of the rare-earth atoms was $f^n d^1 s^2$ and that the " stability " of the +3 state was to be correlated with the removal of the two *s* and one *d* electron. It is now known that of the elements studied the majority do not

TABLE I.

Oxidation states of rare-earth and actinide elements.

	Oxidation number.				Oxidation number.				Oxidation number.				
La		3		Tb		3	(4)	Ac		3			
Ce		3	4	Dy		3		Th	[2][a]	[3][a]	4		
Pr		3	(4)	Ho		3		Pa			(4)[b]	5	
Nd		3		Er		3		U		3	4	5	6
Pm		3		Tm		3		Np		3[c]	4[c]	5[c]	6[c]
Sm	2	3		Yb	2	3		Pu		3	4	5	6
Eu	2	3		Lu		3		Am	2[d]	3[d, e, f]	(4)[f, g]	5[h]	
Gd		3						Cm		3[d, h]			

Parentheses indicate that only the oxide has been prepared. Sub-normal oxides of semi-metallic character have been omitted.

[a] Only ThI_2 and ThI_3 known (Anderson and D'Eye this vol., p. S 244; Hayek and Rehner, *Experientia*, 1949, **5**, 114).
[b] Zachariasen, quoted by Thompson, in U.S.A.E.C. Declassified Document AECD-1897, Feb. 1948.
[c] Hindman, Magnusson, and La Chapelle, *J. Amer. Chem. Soc.*, 1949, **71**, 687.
[d] Thompson, James, and Morgan AECD–1907, Jan. 21, 1948.
[e] Cunningham, AECD–1879, Dec. 1947.
[f] Sherman Fried, AECD–1930, March 1948.
[g] Zachariasen, *Physical Rev.*, 1948, **73**, 1104.
[h] Werner and Perlman, AECD–1898, March 1948.

TABLE II.

*Electron configurations in rare-earth atoms and ions.**

	M.	M$^+$.	M^{++}.	M^{+++}.
La	$5d^1 6s^2$	$5d^2$	$5d$	—
Ce	—	$4f^2 6s^1$	—	$4f^1$
Pr	—	—	—	—
Nd	$4f^4 6s^2$	$4f^4 6s^1$	—	—
Pm	—	—	—	—
Sm	$4f^6 6s^2$	$4f^6 6s^1$	—	—
Eu	$4f^7 6s^2$	$4f^7 6s^1$	$4f^7$	—
Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1 6s^1$	—	—
Tb	$4f^8 5d^1 6s^2$ †	$4f^8 5d^1 6s^1$ †	—	—
Dy	—	—	—	—
Ho	—	—	—	—
Er	—	—	—	—
Tm	$4f^{13} 6s^2$	$4f^{13} 6s^1$	—	—
Yb	$4f^{14} 6s^2$	$4f^{14} 6s^1$	—	—
Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 6s^2$	$4f^{14} 6s$	—

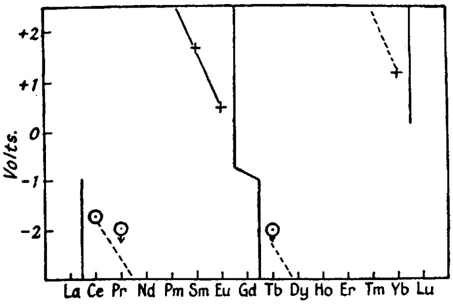
* Except for Tb, the data are from a table by Meggers (*Science*, 1947, **105**, 514).
† Klinkenberg (*Physica*, 1947, **13**, 1).

have this structure, as is shown in Table II. Probably most of the atoms whose structures have not been determined actually are of the $4f^n6s^2$ type.

Obviously the " stability " of the $+3$ state is not apparent from the configurations of Table II. Sometimes the third electron is a *d* and sometimes an *f* type. The effective nuclear charge acting on the *d* electron remains roughly constant but increases for the *f* electrons in proceeding through each half-filling of the shell. Therefore the third electron is of the *d* type at the beginning but changes to the *f* type because of the increasing binding energy of the latter. In either case, whether the third electron is of the *d* or *f* type, the hydration-energy term outweighs the ionisation potential so that oxidation to the $+3$ state occurs readily in aqueous solution. With the fourth electron this is no longer true and further oxidation is very difficult.

$+2$ *and* $+4$ *Oxidation States of Rare Earths.*—The E° curves of the other rare earths will be shifted relatively to the neodymium curve of Fig. 1. They may be expected to have the same general shape (except for a discontinuity at half-filling of the 4*f* shell) because the binding energy of the *f* electrons probably increases rather uniformly in going from element to element (except at half-filling of the shell) and because the hydration energies also should change uniformly as a result of the predominantly electrostatic nature of this effect and the continuous variation in radius. Experimentally the E° curves shift to more positive values as the atomic number increases (with a break when the *f* shell is half-filled). This trend can be explained in the following way.[*] Neighbouring elements in the same oxidation state differ only in the second having one more *f* electron and one unit greater nuclear charge than the first. All *f* electrons are bound more strongly in the second element because the nuclear screening of one *f* electron by another is relatively ineffective. In addition the radius is somewhat smaller, again leading to a higher ionisation potential. The hydration energies are also made larger by the decrease in radius but, as might be expected, this increase is small compared to that of the ionization potentials. The result is a shift of E° towards more negative values.

FIG. 2.



Oxidation potentials of rare earth elements: ⊙ 3–4 couple; + 2–3 couple.

The trends in E° for the 2—3 and 3—4 couples are shown in Fig. 2. An electron cannot be removed from La^{+3} in aqueous solution since it contains no *f* electrons and the inert-gas structure is very stable. With Ce^{+3} the first 4*f* electron is held rather loosely and the oxidation potential is $-1{\cdot}72$ volts. With Pr^{+3} the two 4*f* electrons are now held more strongly, because of the higher nuclear charge, and a $+4$ state is not obtainable in water. In Fig. 2 the arrow on the praseodymium point indicates the potential is more negative than $-2{\cdot}0$ volts. A higher oxide can be prepared, so the oxidation potential cannot be far outside the water stability range. There is no definite evidence (Klemm, *loc. cit.*; Pagel and Brinton, *J. Amer. Chem. Soc.*, 1929, **51**, 42; Marsh, *J.*, 1946, 15) of a $+4$ or higher oxidation state of neodymium or of the other elements through gadolinium, as would be expected from the increased strength of binding of the *f* electrons.

The dotted lines through the cerium and the terbium point show the slope of the 3—4 potential versus atomic number for the actinide elements; it is not necessarily the same for the rare earths.

At Tb^{+3} the 4*f* shell is half-filled with one electron left over. This electron is forced to pair up with one of the other *f* electrons, a configuration which is well known to be less stable than when all electrons are unpaired. Consequently a fourth electron is more readily removed than

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[*] For a somewhat different treatment based on " stable " configurations of La^{+3}, Gd^{+3}, and Lu^{+3}, see Klemm, *Z. anorg. Chem.*, 1929, **184**, 345; 1930, **187**, 29; 1932, **209**, 321.

with the previous elements and terbium forms a higher oxide, although the +4 state does not exist in aqueous solution. Following terbium the trend in ionization potentials precludes the existence of the +4 state through lutecium.

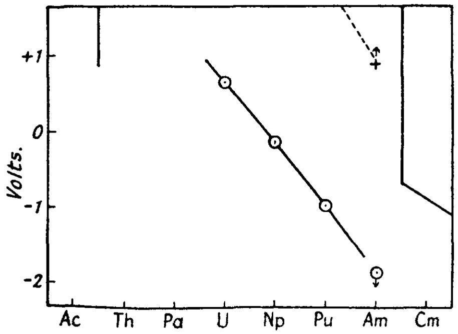
The increase in binding energy of the *f* electrons in proceeding through the series should also be reflected in a decrease in the 2—3 potential. From the data of Fig. 2 this is seen to be the case. Just when the 2—3 potential is getting well inside the water-stability range at europium it undergoes a large shift to more positive values because of the decrease in binding energy of the *f* electrons following half-filling of the shell. It is again just coming into the water stability range at ytterbium when the shell becomes completely filled.

From Fig. 1 it would be predicted that the 4—5 potential would always be too negative to permit the existence of the +5 oxidation state of the rare earths in aqueous solution, and similarly the 1—2 potential is too positive.

2—3 *and* 3—4 *Couples of the Actinide Elements.*—Experimentally the actinide elements have their $E°$ values shifted in a positive direction relatively to the rare earths. The fact that they are shifted is not surprising since, as previously discussed, the combinations of ionization potentials and hydration energies giving rise to the predominantly stable +3 state in the rare earths are peculiar only to the 4*f* electrons and are not expected to be the same necessarily for the 5*f* series. That the shift is towards more positive values is probably not predictable theoretically at the present time. It has been stated by some that such a shift should occur because the ionization potentials will be smaller for 5*f* than for 4*f* electrons; but it is clear from Fig. 1 that the free energy of hydration term, which is the difference of two hydration energies, works in the opposite direction and the actual $E°$ value is the relatively small difference of these two large terms, along with the constant A term.

The trends in the 2—3 and 3—4 couples shown by the actinides (see Fig. 3) are similar to those for the rare earths and the same discussion applies. The shift in potential with increasing atomic number is nicely shown by the 3—4 couple which here crosses right through the water stability region. The dotted line through the 2—3 americium point merely indicates the slope observed for the rare earths.

FIG. 3.



Oxidation potentials of actinide elements: ⊙ 3–4 couple; + 2–3 couple.

4—5 *and* 4—6 *Couples of the Actinide Elements.*—From Fig. 1 it might be predicted that the oxidation potential for the 4—5 couple should be much more negative than for the 3—4 couple. This is not the case, as is shown by comparison of Figs. 3 and 4. The curve of Fig. 1 applies to simple, hydrated ions, however, and experimentally it is found that the +5 ions of these elements are hydrolyzed in aqueous solution (as well as hydrated) to form MO_2^+. The formation of this species shows that it is more stable than a hypothetical +5 hydrated ion and therefore the 4—5 potentials should be more positive than predicted from Fig. 1.

The trend in the potential with increasing atomic number is not as great as with the 3—4 couple. Probably the effect of the tighter binding of the *f* electrons with increasing nuclear charge is being partly compensated for by an increase in the strength of the bonds to the two oxygens. The $E°$ values do not vary nearly linearly as with the 3—4 couple and there are not sufficient data to determine whether they lie on a smooth curve. Irregularities might arise from sensitivity of the metal–oxygen bond energies to the specific number and arrangement of non-bonding *f* electrons, or it may be fortuitous that the data for the 3—4 couple show such a uniform trend.

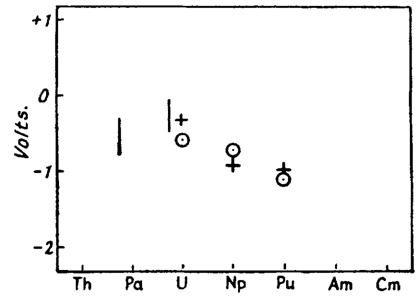
The actinides in the +6 oxidation state in acidic solution exist in the form of the ion MO_2^{++}. To avoid the introduction of differences in the metal–oxygen bond energies the potential of the 4—6 rather than 5—6 couple has been plotted in Fig. 4. The general discussion for the 4—5 couple applies here also.

+2 *and* +3 *Oxidation States of Thorium.*—Quite recently Anderson and D'Eye (this vol., p. S 244) have prepared ThI_2 and ThI_3, the latter also having been prepared by Hayek and Rehner (*Experientia*, 1949, **5**, 114). It is of interest to know the *l* value of the valency electrons of thorium in these compounds.

It has been shown (De Bruin, Klinkenberg, and Schuurmans, *Z. Physik*, 1944, **122**, 23; 1941, **118**, 58) spectroscopically that the ground electronic configurations of the valency electrons in gaseous Th^{+2} and Th^{+3} are $6d^2$ and $5f^1$, respectively. With Th^{+2} the $6d^15f^1$ state lies only a fraction of a volt above the ground level and the $5f^2$ level lies approximately 2 volts above. In the case of Th^{+3} the $6d^1$ state is approximately 1 volt less stable than the ground state. Since these various configurations do not differ greatly in energy, it is possible that any of them might be sufficiently stabilized in a condensed phase relatively to the gas phase to become the ground configuration.

In the case of Ce^{+3} the *d* configuration is stabilized relatively to the *f* in going from the gas to a condensed phase. The separation in levels is 49,737 cm.$^{-1}$ in the gaseous ion (Lang, *Canadian J. Res.*, 1936, **14**, *A*, 127) while the low-frequency limit of the absorption of the aqueous ion, which has been ascribed to excitation to the *d* configuration (see *e.g.*, Bose and Mukherji, *Phil. Mag.* 1938, **26**, 757) gives 34,000 cm.$^{-1}$. This stabilization is approximately 2 volts. The same effect being assumed to hold qualitatively for thorium, there should be no *f* electrons in ThI_2 and very likely none in ThI_3.

FIG. 4.



Oxidation potentials of actinide elements: ⊙ 4–5 couple; + 4–6 couple.

It is difficult to convert Anderson and D'Eye's data on the stability of ThI_3 with respect to disproportionation into Th and ThI_4 into an aqueous oxidation potential of the 3—4 couple. A rough estimate of this value using Brewer's general method (U.S.A.E.C. Declassified Document AECD-1899, Feb. 10, 1948) and the data for the corresponding uranium compounds (Brewer, Bromley, Gilles, and Lofgren, *ibid.*, MDDC-1543, Sept. 20, 1945) would indicate it to be of the same magnitude as the value extrapolated from the 3—4 potential curve of Fig. 3. Since the value corresponding to a *d* configuration would also be expected to lie in this region, the oxidation-potential data do not appear to offer a hopeful means of deciding between the two configurations.

The great reactivity of ThI_2 and ThI_3 with water provides no evidence as to the electron configurations, because *f*-type structures would be expected to reduce water rapidly on the basis of the data of Fig. 3, and the same is true of *d*-type structures, in analogy to the lower halides of zirconium and hafnium. The intense colour of the compounds is possible for any of the structures.*

Protoactinium.—Nothing is known of the electronic structure of the gaseous atom and ions of protoactinium. Its chemistry is only incompletely elucidated but it appears usually to exist in compounds in the +5 oxidation state. An oxide has been shown (Zachariasen, quoted by Thompson in U.S.A.E.C. Declassified Document AECD-1897, Feb. 1948) by *X*-ray analysis

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* At first sight it might be thought that ThI_3 should be nearly colourless like CeI_3 if it has an *f*-type configuration. In Ce^{+3} the *d* levels lie far above the *f*, giving transitions in the ultra-violet; however, they could lie much lower in the case of Th^{+3} so as to give absorption in the visible region.

to have the " dioxide " type structure which normally occurs in compounds approximating to the composition MO_2. Bouissieres and Haissinsky (this vol., p. S 256; *Compt. rend.*, 1948, **226**, 573) have recently reported the preparation in aqueous solution of an oxidation state below +5, probably +4. The reducing conditions used would indicate a 4—5 potential somewhat more negative than 0 volt.

Extrapolation of the 4—5 potentials of Fig. 4 to protoactinium is so uncertain that at best it may be predicted that the potential will probably be between 0 and −0·6 volt. Actually this extrapolated value should lie below the true value because it is clear from the chemistry of Pa(V) that it does not have a structure corresponding to UO_2^+, NpO_2^+, and PuO_2^+ but is more stable in a form resembling Cb(V) and Ta(V). This will make the oxidation potential of the 4—5 couple more positive than predicted from Fig. 4.

The presumed +4 state probably has an *f* type valency electron because, if it were *d*, reduction of Pa(V) to Pa(IV) should be very difficult by analogy with tantalum.

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[*Read, March* 28*th*, 1949.]