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COMPARATIVE CHEMISTRY OF THE LANTHANIDE AND ACTINIDE ELEMENTS

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COMPARATIVE CHEMISTRY OF THE LANTHANIDE AND ACTINIDE ELEMENTS

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In the discussion which follows, the elements of atomic number 57-71 inclusive are called "lanthanide elements"; similarly, those of atomic number 89-103 are called "actinide elements." Although this terminology has been the subject of criticism on both chemical and etymological grounds, it is adopted here for reasons of convenience. The question of its appropriateness, as compared with other terminologies which have been suggested, is not dealt with in this paper, in which it is intended only to present a comparison of properties of the elements. Since it is in oxidation-reduction behavior that the two series are least alike, this aspect of their comparative chemistries will receive most attention. The properties of the elements may be correlated with the electronic configurations of their atoms, and it is therefore appropriate to begin a discussion of the lanthanides and actinides by a consideration of their electronic configurations.

The ground state electronic configurations of the neutral gaseous atoms of the lanthanide elements have been known for some years. They may be represented by the following generalized configuration:

$$\text{Krypton configuration} + 4d^{10}\ 4f^{0-14}\ 5s^2\ 5p^6\ 5d^{0\ \text{or}\ 1}\ 6s^2 \qquad (I)$$

Only three of the elements — lanthanum, gadolinium and lutetium have an electron in the 5d subshell.

It will be recalled that the 4f electrons move in non-penetrating orbits and are thus shielded from the full charge of the nucleus. The 6s, 5s and 5p electrons provide considerable shielding of the "f" electrons from the influence of the external environment. The electrons in this shielded 4f subshell account

for the magnetic and spectroscopic properties exhibited by the lanthanide elements.

The recent atomic beam resonance studies of Nierenberg and his associates, at the Lawrence Radiation Laboratory in Berkeley has substantially increased our knowledge of the electronic configurations of the neutral atoms of the actinide elements. These investigations, supplemented by the earlier work of Klinkenberg, McNally, Racah, Meggers, and Fred and Tompkins permit the assignment of electronic configurations to all actinide elements through the first half of the series.

The configurations may be represented by the generalized formula:

$$\text{Xe configuration} + 5d^{10}\ 5f^{0-7}\ 6s^2\ 6p^6\ 6d^{0,1 \text{ or } 2}\ 6s^2. \qquad \text{(II)}$$

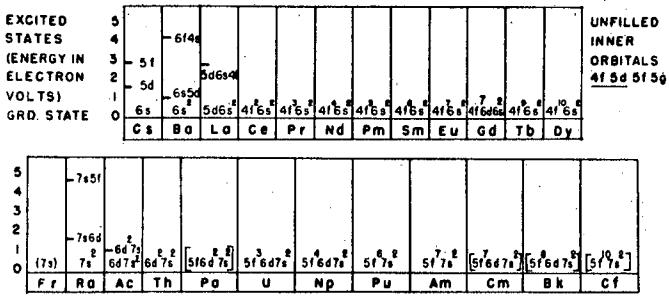
Neither the first nor the second member of the actinide series contains an f electron in the ground state configuration of the neutral gaseous atom. In the lanthanides, it is only the first member of the series which has no "f" electron.

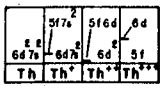
It has been shown, however, that in the doubly and trebly ionized atom of thorium, the second actinide element, f electrons are present in the ground state configuration. In fact, for all of the actinide elements in their ordinary states of oxidation, "f" electron configurations are more stable than "d" configurations.

There now exists a very substantial body of magnetic and spectroscopic data on actinide compounds which supports this view. This evidence will be examined later, in connection with the comparison of the magnetic and spectroscopic properties of the lanthanides and actinides.

Current knowledge of the electronic ground state configurations of the neutral gaseous atoms of the lanthanide and actinide elements is summarized in Slide No. 1. A few excited state configurations are given also, in order to

RELATIVE ENERGIES OF "d" AND "f" CONFIGURATIONS FOR ELEMENTS IN THE VICINITY OF LANTHANUM AND ACTINIUM





STABILIZATION OF 5f RELATIVE TO 6d CONFIGURATIONS WITH INCREASING IONIC CHARGE

illustrate the relative energies of alternative "d" and "f" configurations. For comparison, the data have been extended to include some antecedent elements.

The rapid stabilization of "f" relative to "d" configurations, which occurs between lanthanum and cerium is readily apparent. There are no "d" electrons in the neutral cerium atom.

In protoactinium, on the other hand, both "d" and "f" orbitals are occupied.

We wish now to consider the correlation between electronic configuration and oxidation-reduction behavior.

Unquestionably, the dominant feature of the chemistry of the lanthanide elements is their pronounced tendency to exhibit only the tripositive oxidation state in aqueous solution and in compounds. Although it is true that nearly half of the elements exhibit a higher or lower state, these states are relatively unstable. The persistence of tervalency in the series is indeed remarkable. It is this fact, of course, in combination with the uniformity of ionic radii, which is responsible for the astonishing similarity in the chemical properties of the elements of this transition series.

An adequate quantitative explanation of the dominance of a single oxidation state in this 15 element series does not exist. The problem is a very interesting one, however, and an explanation will be offered here. It is admitted, however, that the attempt will of necessity be based on incomplete - and indeed insufficient - fundamental data.

Before attacking the problem, perhaps some mention should be made of an earlier "explanation" of the trivalency of the rare earths, based on the assumption of a common electronic configuration of $5d\ 6s^2$ for the valence electrons of all of the elements. Aside from the fact that an "explanation" involving the ground state configuration has no quantitative significance by itself, the assumed configuration is now known to be exceptional rather than

common, as shown in the previous figure. Nevertheless, the idea that the $5d\ 6s^2$ configuration must play an important role in determining the trivalency of the lanthanides seems still to persist. There is no need to invoke this configuration in the explanation of trivalency. The obvious fact is that most lanthanide elements, in order to exhibit tervalency, must lose an electron from the 4f subshell. It follows, of course, that no exceptional amount of energy is involved in this process.

Clearly, what is important is not the electronic configuration, but the amount of energy required to reach a specified state of oxidation, relative to the energy of stabilization of that state in a particular environment. If the latter energy is greater, oxidation is energetically possible; if it is smaller, oxidation is energetically impossible.

The energy required to achieve a given state of oxidation in the cation is the energy necessary to convert the standard state of the element to the gaseous ion in the appropriate stage of ionization.

The energy of stabilization of the gaseous ion is its energy of hydration in solution, or, in a solid compound the energy of interaction of the cation with the anion lattice.

Since the oxidation of the cation must be accompanied by a concomitant reduction the energy of this latter process must be added in to obtain an overall energy balance.

The principles outlined above will be applied first to the problem of the stability of the tripositive ions of the lanthanide elements in acidic aqueous solution.

The tripositive state will be the only stable state, if the following two conditions hold simultaneously:

$$(1)\ M^{+4}_{(aq)} + 1/2\ H_2O_{(\ell)} = M^{+3}_{(aq)} + H^{+}_{(aq)} + 1/4\ O_{2(g)};\ \Delta F^{o} \leq 0.$$

$$(2)\ M^{+2}_{(aq)} + H^{+}_{(aq)} = M^{+3}_{(aq)} + 1/2\ H_{2(g)};\qquad \Delta F^{o} \leq 0.$$

Under these conditions the higher oxidation state will be spontaneously reduced by reaction with water, and the lower state spontaneously oxidized by hydrogen ion.

In practice, the conditions just specified are somewhat too restrictive, since the reactions are sufficiently slow to permit the unstable ions to persist in solution for appreciable lengths of time, unless the free energies are negative by about 25 Kcal.

In reaction (1) the rate determining step appears to be formation of atomic oxygen, the potential of the couple:

$$H_2O_{(\ell)} = H^{+} + O + e^{-}$$

being about -2.4 volts.

In reaction (2) the rate determining step appears to be the formation of atomic hydrogen, the potential of the couple:

$$H = H^{+} + e^{-}$$

being 2.1 volts.

The free energies of the reactions may be appreciably altered by hydrolysis or complex ion formation, but these complications will not be considered here.

Reaction (1) may be broken into the following steps which in sum are identical with it:

Reaction	Energy
(1a) $M^{+4}_{(aq)} = M^{+4}_{(g)}$	-Energy of hydration of $M^{+4}_{(g)}$
(1b) $M^{+4}_{(g)} + e^{-}_{(g)} = M^{+3}_{(g)}$	-Energy of ionization of $M^{+3}_{(g)}$
(1c) $M^{+3}_{(g)} = M^{+3}_{(aq)}$	Energy of hydration of $M^{+3}_{(g)}$
(1d) $1/2\ H_2O_{(\ell)} = 1/2\ H_2O_{(g)}$	Energy of vaporization of 1/2 mole $H_2O_{(\ell)}$
(1e) $1/2\ H_2O_{(g)} = 1/2\ H_{2(g)} + 1/4\ O_{2(g)}$	-Energy of formation of 1/2 mole $H_2O_{(\ell)}$
(1f) $1/2\ H_{2(g)} = H_{(g)}$	Energy of formation of 1 mole $H_{(g)}$
(1g) $H_{(g)} = H^{+}_{(g)} + e^{-}_{(g)}$	Energy of ionization of $H_{(g)}$
(1h) $H^{+}_{(g)} = H^{+}_{(aq)}$	Energy of hydration of $H^{+}_{(g)}$

The energy of reaction (1h) has been evaluated by Latimer and the energies of reactions (1d) through (1g) are well known. The sum of the energies of all but the first three reactions is 140 Kcal. The tetrapositive state will be unstable if the sum of the first three reactions is more negative than 125 Kcal.

The energies referred to in equations (1a) through (1h) are heats. Their sums, minus 15 Kcal, gives the free energy of the reaction at room temperature.

The energies of reactions (1a) and (1c) may be evaluated by application of the Born equation.

A value of 10 is employed here for the effective dielectric constant of the water of hydration, and the distance from the center of the ion to the center of the water dipole is taken to be the ionic radius plus 0.7 A. These values are reasonable approximations, but may be somewhat in error. They are, however, employed consistently in the calculation of all hydration energies considered in this paper.

The ionic radii used in the calculations are those given by Zachariasen. The calculated hydration energy of Ce^{+4} is -1480 kilocalories, and that of Ce^{+3} is -780 kilocalories. Using the value of 36.7 e.v., given by Latimer for the fourth ionization potential of cerium, the energy of reaction (1b) = -844 Kcal.

The sum of the energies of reactions (1a), (1b), and (1c) therefore amounts to -146 Kcals, and the total energy of reaction (1) to minus twenty-one kilocalories per mole. Tetrapositive cerium is thus calculated to be unstable with respect to reduction by water.

This is in agreement with observation. Ceric salts in perchloric acid solution (in which the cerium ion is uncomplexed) exhibit a slow spontaneous reduction to the cerous state.

In the case of cerium the oxidation potential of the cerous-ceric couple is known. The free energy of reaction (1) can be directly evaluated as -12 Kcal.

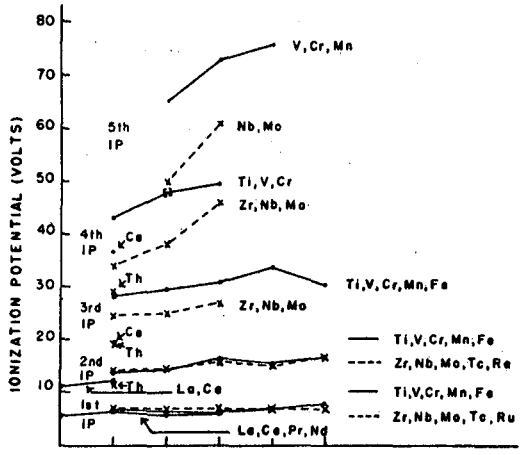
The value calculated from hydration energies and ionization potentials is thus in reasonably good agreement with direct measurement.

In the lanthanide and actinide elements tri and tetrapositive ions of the same element differ in radius by a nearly constant amount, independent of the particular element. Differences in hydration energies for the tri and tetrapositive ions vary, however, and must be calculated in each case. In general the effect of the lanthanide and actinide contractions is to stabilize the tetrapositive aqueous ion relative to the tripositive.

Since it is a matter of observation that exactly the opposite effect (increasing stabilization of the tripositive state) is noted, it is necessary to account for the decrease in stability of the higher state. It is reasonable to suppose that it is due to a more or less regular increase in the fourth ionization potential with increasing atomic number.

These ionization potentials have not been measured beyond cerium and their evaluation must of necessity be based on estimates, utilizing the available data on ionization potentials of elements in other regions of the periodic system. The data on the 3d and 4d transition elements appear to be most suitable and these data are presented in graphical form in the next slide (Slide No. 4), along

Slide 4



IONIZATION POTENTIALS OF SOME "d" AND "f" TRANSITION ELEMENTS

with the available information on the ionization potentials of the lanthanide and actinide elements.

The features of interest here are the following: first, the energy required to remove an electron from a given "d" subshell increases monotonically with increasing atomic number, except for the drop produced by the half filled subshell. (This behavior is noted throughout the periodic system and holds for "p" subshells as well as "d"). Second, in the two "d" transition series, the energies of the third and fourth ionizations are of smaller magnitude in the heavier elements, the difference being greater for the higher stage of ionization.

On the basis of these two effects it is possible to place limits on the rate of increase with atomic number of the fourth ionization potentials of the light lanthanides.

The rate per unit increase in atomic number will be greater than the one electron volt increase in the value of the third ionization between La and Ce, and less than the 8 electron volts average increase in the 4th ionization potential observed in the sequence: Zr, Nb, Mo.

For the light lanthanides, an average increase in the 4th ionization potential of 2 electron volts per unit increase in atomic number is taken as a conservative estimate.

Ionization energies and calculated hydration energies for the first half of the lanthanide series are presented in Table I (slide No. 5), along with calculated values for the free enrgy of reaction (1). The free energy values are consistent with experimental observation. All tetrapositive ions of the light lanthanides are thermodynamically unstable with respect to reduction by water in acidic aqueous solution. The calculated free energy of the reaction of ceric ion with water corresponds to a slow rate of reduction; that of the

reaction of Pr^{+4} ion is consistent with the observed instantaneous reduction by water. The calculated value of the $Pr^{+3} = Pr^{+4} + e^-$ couple of -3.5 v is in reasonable agreement with a calorimetrically determined value of ~ -2.8 v.

Table I

M^{+3} and M^{+4} Hydration and Ionization Energies for the Light Lanthanides

Element	Hydration energy $M^{+3}(g)$	Hydration energy $M^{+4}(g)$	4th ionization potential (Kcal)	Free energy of reaction (1) (Kcal)	Stability in solution
Ce	780	1480	846	-21	Metastable
Pr	790	1500	892*	-56	Unstable
Nd	799	1520	939*	-92	Unstable
Pm	809	1540	985*	-128	Unstable
Sm	814	1549	1031*	-170	Unstable
Eu	818	1558	1077*	-211	Unstable
Gd	823	1568	1123*	-252	Unstable

*Estimated value.

The question of the stability of the dipositive aqueous ions of the light lanthanides can be treated in the same way as that used for the tetrapositive ions.

Using the known value of the third ionization potential for cerium, the known radius of Ce^{+3} and an extrapolated value for the radius of Ce^{+2} a calculated value of -99 Kcal is obtained for the free energy of reaction (2) on application of the Born equation for the evaluation of hydration energies. Ce^{+2} is thus completely unstable in aqueous solution.

In order to estimate the stabilities of the dipositive states of succeeding lanthanide elements it is necessary to predict the rate of increase in the third ionization potential.

The increase in the third ionization potential between La and Ce is 0.9 electron volt. This may be somewhat less than the average increase in the third ionization potential for the series La-Gd, because it corresponds to ionization of the first electron added after the formation of an underlying closed shell. An average increase of 0.9 electron volt per element is used in estimating the ionization potentials, however.

Ionic radii of the dipositive ions of the light actinides may be obtained with an uncertainty of no more than 0.02 A by extrapolating from the known radii of Sm^{+2} and Eu^{+2}.

These radii give the calculated values of hydration energies listed in Table II. The hydration energies in conjunction with the estimated third ionization potentials give the listed energies for reaction (2).

Table II

Hydration Energies and Third Ionization Potential for the Light Lanthanides

Element	$M^{+2}(g)$ Hydration energy + Kcal	$M^{+3}(g)$ Hydration energy Kcal	Third Ionization potential volts - Kcal	ΔF reaction (2); Kcal	Stability in solution
La	326	771	442	-116	Unstable
Ce	330	780	464	-99	Unstable
Pr	334	790	484*	-85	Unstable
Nd	337	799	505*	-70	Unstable
Pm	341	809	526*	-55	Unstable
Sm	343	814	546	-38	Unstable
Eu	345	818	567	-19	Metastable

*Estimated values.

All of the dipositive aqueous ions of the light lanthanides are thus calculated to be unstable with respect to oxidation by hydrogen ion. The

calculated reaction energies are consistent with a slow rate of oxidation in the case of europium. The calculations are thus in fair agreement with observation, europous ion having sufficient stability to persist in aqueous solution for some time.

Hydration energies and ionization potentials are thus seen to account for the observed stability of the aqueous oxidation states of the light lanthanides in a consistent and logical fashion.

The extension of these considerations to the heavier elements of the second half of the series necessitates an estimation of the effect of a half filled subshell on the ionization potentials. The effect cannot be predicted with much accuracy.

In the 4d elements the half filled subshell produces a drop of about 6 ev in the third ionization potential. A similar drop at Gd followed by an increase of 0.9 ev per element for the second half of the series would indicate instability of the all aqueous dipositive ions of the heavy lanthanides, although the calculated energy of reaction (2) would predict the possibility that the oxidation of Yb^{+2} by H^{+} might be slow.

In the 3d and 4d transition elements the half filled subshell effect approximately doubles between the second and third ionization potentials - increasing from 3 to 6 e.v. The same rate of increase extended to the 4th ionization potential in the lanthanide elements would give a drop of 12 e.v. between Gd and Tb. This value is likely to be somewhat high, and an estimate of 10 e.v. probably is nearer the truth. Either value predicts instability of the tetrapositive state in aqueous solution for all heavy lanthanides, in agreement with observation.

The stability of solid compounds of the lanthanide ions may be calculated by methods similar to those outlined above, except that the relevant quantities are the crystal energies, energies of formation of the anions, and the

ionization potentials. In these calculations it is unnecessary to make arbitrary assignments of any new parameters. The ionization potentials used are the same as those already evaluated for the aqueous ions.

The method may be illustrated by a consideration of the treatment of the stabilities of the lanthanide dioxides.

Crystal energy calculations for CeO_2 and the cubic form of Ce_2O_3, and the use of the known value of the fourth ionization potential gives a calculated value of -58 Kcal for the energy of reaction (3). The sesquioxide of cerium is thus unstable with respect to oxidation to the dioxide in air. The calculated value is a few Kcal too negative to be consistent with the observed reduction of CeO_2 to Ce_2O_3 by hydrogen at elevated temperatures.

Extension of the calculations to the case of praseodymium gives a value of -22 Kcal, indicating a somewhat greater stability for PrO_2 than is actually observed.

At neodymium, the sesquioxide is calculated to be stable to oxidation by O_2. The sesquioxides of the succeeding elements through gadolinium also are stable.

At terbium, assuming a drop of 10 e.v. in the 4th ionization potential as estimated previously, terbium sesquioxide is calculated to be spontaneously oxidizable by $O_{2(g)}$, as is dysprosium sesquioxide.

The latter calculation does not correspond with experimental fact. The sesquioxides of the remaining elements are correctly calculated to be stable.

It would be of interest to extend the crystal energy calculations to the fluorides, but the tetrafluorides possess complicated crystal structures which have not been worked out in detail.

Tetrahalides other than the fluorides are unstable because of the smaller crystal energies for lattices formed with large monovalent anions.

(3) $1/2\ M_2O_{3(c)} + 1/4\ O_{2(g)} = MO_{2(c)}$.

Calculations similar to those described for the lanthanide elements have also been carried out for the actinide aqueous ions.

Data on the stabilities of the tetrapositive aqueous ions are summarized in Table III.

In estimating the average rate of increase in the fourth ionization potential of the light actinides the rate taken to be somewhat greater than that observed in the light lanthanides (as indicated by the trend in values of the ionization potentials in the 3d and 4d elements). An estimate of 2.5 e.v. per unit increase in atomic number is used here.

Calculated hydration energies and estimated values of the fourth ionization potential are tabulated in Table III.

Table III

Hydration Energies and Fourth Ionization Potentials of the Light Actinides

Element	$M^{+3}(g)$ Hydration energy Kcal	$M^{+4}(g)$ Hydration energy Kcal	Fourth Ionization potential Kcal	ΔF reaction (1) Kcal	Stability in solution
Th	759	1420	661	121	Stable
Pa	771	1445	716	+75	Stable
U	786	1473	776	38	Stable
Np	789	1481	834	-21	Metastable
Pu	794	1500	891	-64	Unstable
Am	798	1510	949	-116	Unstable
Cm	803	1520	1006	-168	Unstable

The calculated stabilities do not entirely agree with observation. Whereas tetrapositive neptunium is calculated to be unstable with respect to reduction by water, it actually is stable. This also is true for plutonium IV. The tetrapositive ion of Am is the first in which instantaneous reduction

occurs in aqueous solution. The rate of increase used in estimating the fourth ionization potential in the light actinides may be a little too large.

An estimate of the effect of the half filled subshell on the fourth ionization potential cannot be made with any confidence. If it is taken to be the same as in the light lanthanides, then the tetrapositive ion of berkelium is calculated to possess sufficient stability to be obtained in solution. Tetrapositive ions of the succeeding elements are calculated to be unstable with respect to very rapid reduction by water.

To summarize briefly the extended range of stability of the tetrapositive ions of the light lanthanides appears to be a natural consequence of a smaller value of the fourth ionization potential (of a 5f as compared to a 4f electron), noted in the case of thorium.

The smaller value of the fourth ionization potential also accounts for an extended range of stability of the dioxides. The smaller value for the third ionization potential renders the dipositive state so unstable in aqueous solution that it is not likely to be observed in the actinide elements.

These factors account in a general way for the differences in stability of the di, tri and tetrapositive ions of the lanthanide and actinide elements.

The question of the stability of the higher oxidation states of the actinide elements in aqueous solution cannot be dealt with in any quantitative fashion.

We may note that if the ion $O\text{-}U\text{-}O^{+}$ is treated as an ionically bonded complex, the calculated coulombic energy per mole is 3096 Kcal. An additional two or three hundred kilocalories should probably be allowed for hydration energy. The ion would thus be stable with respect to spontaneous reduction to the tetrapositive ion by about 1600 Kcal, minus the (positive) energy of the fifth ionization of uranium. This would limit the value of the fifth ionization

potential to about 70 e.v. The actual value of the fifth ionization potential of uranium probably is considerably less than this.

The bonding in the UO_2^+ ion is, however, known to be covalent, and the charge on the central atom is less than +5. Until it is possible to obtain some measure of the actual bond energy it is impossible to correlate the stability with ionization potential data.

The oxidation-reduction behavior of the lanthanide and actinide elements already indicate the general trend in their thermodynamic properties. It is of interest, however, to compare accurate experimental values of some of these thermodynamic quantities.

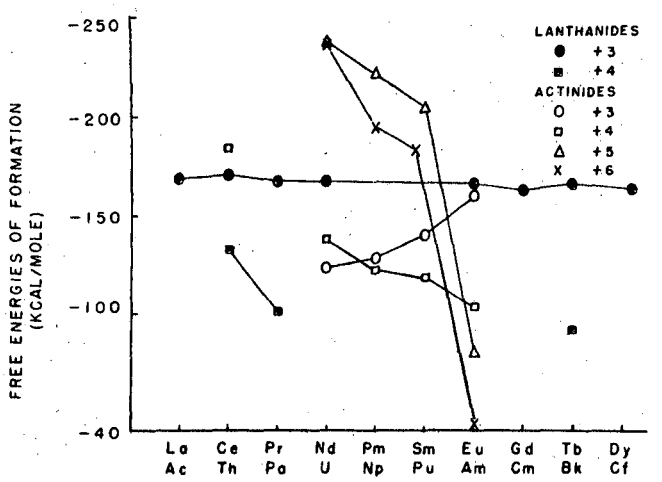
Slide No. 7 shows the free energies of formation of aqueous ions of the lanthanide and actinide elements, plotted as a function of atomic number. It will be recalled that these quantities are related not only to hydration energies and ionization potentials but also to the energies of sublimation of the metals.

The measured free energies of formation of the aqueous tripositive lanthanide ions are remarkably constant; those of the tetra and dipositive ions are strongly dependent on atomic number.

The free energies of formation of the actinide ions show a considerable variation with atomic number for all stages of oxidation, but there is a rapid stabilization of the tripositive state relative to higher states, as the atomic number increases.

In the actinides, differences in the free energies of formation of the various ions are of such magnitude as to produce a remarkable complexity in the solution chemistry of these elements. Intermediate oxidation states are unstable with respect to internal oxidation and reduction, and the equilibrium mixture may therefore consist of three or even four states of oxidation.

Slide 9



FREE ENERGIES OF FORMATION OF AQUEOUS LANTHANIDE AND ACTINIDE IONS

In the lanthanides, the potentials of the $M^{+2} = M^{+3} + e^-$ and $M^{+3} = M^{+4} + e^-$ couples are such as to prohibit disproportionation.

Potentials of the actinide and lanthanide couples are shown in Slide No. 10. The potentials of the actinide 3-4 couples fall on a smooth curve when plotted as a function of atomic number - exhibiting a decrease of about 1 e.v. per element.

The 4-5 couples are somewhat less regular but the 5-6 couples exhibit quite irregular behavior, that of plutonium being considerably less negative than would be expected. There is at present no adequate explanation for this behavior. Time precludes discussion of the free energies of formation of typical compounds, such as oxides and halides, but these free energies follow trends similar to those noted for the ions.

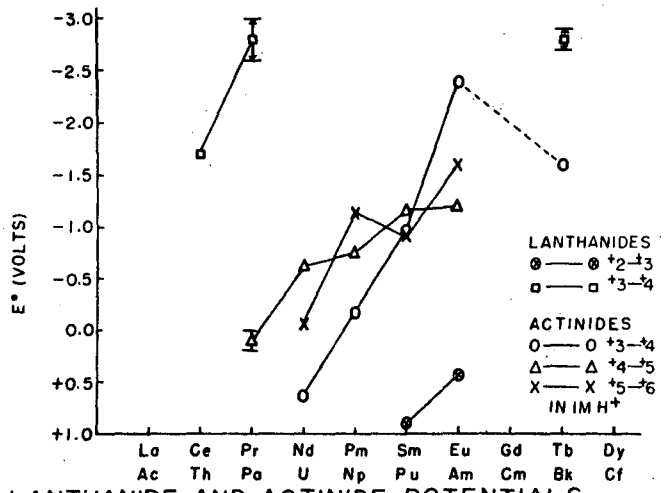
In such compounds, in corresponding oxidation states, the lanthanide and actinide elements have nearly the same ionic radii; for ions containing the same number of f electrons (Sm^{+3} and Pu^{+3} for example) the lanthanide ion is about 0.04 A smaller.

As a consequence of the similarity in radii and predominantly ionic nature of the bonding in these crystals there is a very close correspondence in the crystallography of the two series of elements. These correspondences have been the subject of a number of previous publications by Zachariasen and will not be elaborated on here.

Available data on the metals, on the otherhand, indicate substantial differences in some properties. Data on the crystal structures, atomic volumes, melting points and heats of vaporization of the lanthanide and actinide metals are presented in slide No. 11.

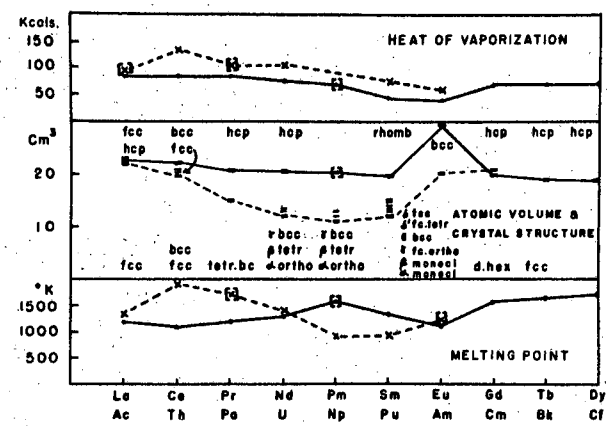
With the possible exception of thorium, melting points and boiling points of the elements of the two series lie within the same range of values.

Slide 10



LANTHANIDE AND ACTINIDE POTENTIALS

Slide 11



SOME PROPERTIES OF THE LANTHANIDE AND ACTINIDE METALS

The light actinides differ markedly from the light lanthanides in structure and atomic volume.

Throughout the lanthanide series no more than three (two in the cases of Eu and Yb) electrons are used in metallic bonding, whereas 4-5 electrons form metallic bonds in the elements thorium through plutonium. At americium the number of bonding electrons drops to three, and this actinide metal has a crystal structure and atomic volume which is of a typical lanthanide character. Metallic curium also exhibits a close packed structure, with a metallic radius expected for a three-electron-per atom type of bonding.

The use of more electrons for bonding in the light actinides is undoubtedly connected with their greater tendency to multiple ionization as compared with the lanthanides.

Stronger bonding accounts for the smaller atomic volumes and higher heats of vaporization observed for the metals from thorium through plutonium, as compared with americium and curium.

Protactinium, uranium, neptunium and plutonium crystallize in unique structures and the latter element is the most allotropic of any known metal.

Uranium, neptunium and plutonium exhibit anomalous magnetic, dilatometric and electrical resistivity behavior.

Similar anomalies are noted in such lanthanide elements are cerium, dysprosium and gadolinium, primarily at low temperatures where they appear to be associated with transitions of a ferromagnetic or antiferromagnetic character.

Whether similar transitions occur in the light actinide metals is not known at the present time. The magnetic susceptibility of plutonium is a complex function of temperature and strongly dependent on the purity of the sample.

Except for gadolinium, the magnetic susceptibilities of the lanthanide metals from cerium through ytterbium exhibit a simple Curie-Weiss type of

temperature dependence, with effective moments that are very close to the theoretical values for the field-free tripositive ions (dipositive ions, for europium and ytterbium.)

A Curie-Weiss type of temperature dependence of the susceptibility is not observed for any actinide metal lighter than americium. In the latter case the moment is that observed for the tripositive ion.

It is impossible at the present time to offer a satisfactory theoretical explanation of the anomalous properties of uranium, neptunium and plutonium metals.

The properties of elemental americium and curium suggest that the metals of the second half of the actinide series will be lanthanide-like, with normal close-packed structures and with more or less normal metallic behavior at ordinary temperatures.

In those properties of the lanthanide and actinide compounds related to the configuration in the f shell – notably spectroscopic and magnetic properties – greater similarities are evident.

Sharp line absorption and fluorescence spectra have been observed in solid compounds of both the lanthanide and actinide elements. The intensities of these lines as well as their sharpness leaves no doubt but that the majority of them are due to transitions between energy levels within the "f" configurational system. In the lighter actinides the transition probabilities are generally some 10 to 100 times as great as in the lanthanides, but at californium transition probabilities appear to be quite comparable.

The energy levels associated with these transitions have been almost completely identified for some of the lanthanides – praseodymium, thulium and europium, for example. Among the actinides considerable progress has been made in the analysis of the absorption spectrum of U^{+4} in calcium fluoride.

The spectroscopic properties of the actinides will be the subject of a paper to be presented later at this Congress and will not be considered further here.

Magnetic susceptibilities of the tripositive ions in condensed phases have been measured for all of the lanthanide elements, and for half of the actinides.

Effective magnetic moments of these ions are compared in Slide No. 12.

Among the lanthanides the experimentally measured moments are in close agreement with the theoretical values for the unperturbed ion, calculated on the assumption that Russel-Saunders coupling holds for the electronic system, and that the ground state is given by Hunds rules.

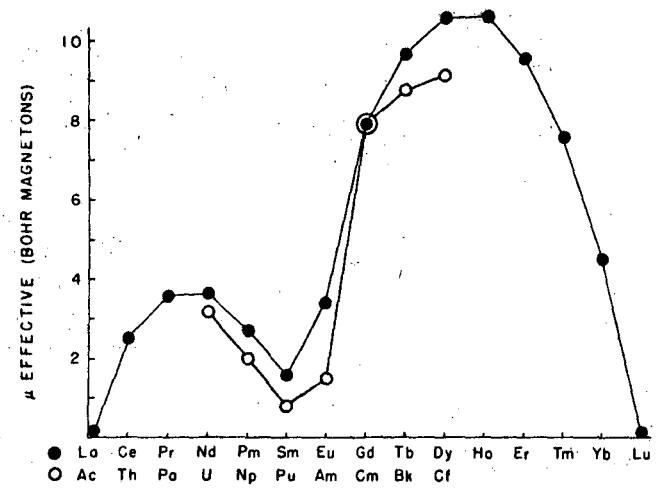
The moments of the actinide ions are not in such close agreement with theory, owing to stronger crystal field interactions and consequent greater depression of the orbital angular momentum. (Tripositive curium gives the theoretical value because it is in an S state in which there can be no interaction with the crystal field.)

It is clearly evident however that the variation of the moments with atomic number follows precisely the same pattern in the two series of elements, and that the electronic configurations of the ions have a one-to-one correspondence.

Since these and other data clearly establish the fact that the majority of the actinide elements are members of a 5f transition series, it is worth noting that 5f orbital wave functions differ from 4f functions in that they have substantially greater radial extension.

Overlapping of 5f orbitals with orbitals from bonding atoms therefore is possible and bond hybridization may occur. There is considerable evidence that 5f orbital bonding may account for some of the differences in chemical properties between lanthanide and actinide ions of the same charge. Street and Seaborg have correlated such bonding with ion exchange behavior of the actinide ions.

Slide 12



MAGNETIC MOMENTS OF THE f TRANSITION SERIES

It also may be noted that coulombic interaction of 5f electrons with the crystalline environment may be of substantially greater magnitude in the 5f as compared with the 4f elements. The net effect of such interaction is to lower the potential energy of the system and to stabilize the bonding.

Greater differences in complex ion stability between ions with an S ground state (Cm^{+3}) or Gd^{+3}, for which no crystal field interaction is possible, and those with a net orbital momentum (Am^{+3}), Eu^{+3}, Pu^{+3}, etc. may be noted in the 5f as compared with the 4f transition series.

No quantitative data on the relative magnitudes of crystal field interactions of the lanthanides as compared with the actinides is now available, but current work on the spectroscopy of solid compounds of these elements should provide such data in the near future. This information may well provide an explanation for some of the more subtle differences in the chemistry of the elements of these two series.

In summary, an attempt has been made here to show how the most obvious difference between the lanthanide and actinide elements — the greater range of oxidation states of the latter — can arise as a consequence of clearly discernible trends in the periodic system.

The treatment employed is undoubtedly too simple. It is unlikely that trends in ionization potentials in these two transition series are as regular as has been assumed. The assumption of purely coulombic binding and the treatment of hydration energies by the Born equation cannot be entirely accurate.

Nevertheless, this approximate treatment probably does indicate in a roughly quantitative way the origin of the differences in properties of the 4f and 5f elements.

Aside from this major difference in oxidation reduction behavior, the lanthanide and actinide elements are strikingly similar in many respects.

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