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Valencies of the lanthanides

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Abstract The valencies of the lanthanides vary more than was once thought. In addition to valencies associated with a half-full shell, there are valencies associated with a quarter- and three-quarter-full shell. This can be explained on the basis of Slater’s theory of many-electron atoms. The same theory explains the variation in complexing constants in the trivalent state (the “tetrad effect”). Valency in metallic and organometallic compounds is also discussed.

Keywords Lanthanide · Valency · f shell · Ionization energy · Hydration energy · Coulomb energy · Exchange energy · Nephelauxetic effect · Tetrad effect

Introduction

Fifty years ago, the lanthanides¹ were little more than a chemical curiosity. They were thought of as being very similar, and placed together in the same box of the Periodic Table. Since then, their chemistry has been studied in more detail, and found to vary more than was once thought. Also, some now have important applications, e.g. neodymium in lasers and magnets.

Discussions of lanthanide compounds and ions are often conducted using a classification by oxidation state. However, certain distinctions that we make in this paper are not well served by this concept. For example, some lanthanide monosulphides, LnS, are metallic and others are semiconductors, but in both types of compound, the formal oxidation state

¹ We take the lanthanides (Ln) to be the elements from lanthanum to lutetium inclusive. We take lutetium to be a transition element and lanthanum to ytterbium “inner” transition elements.

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of the lanthanide is +2. Here, therefore, we make the valency of the lanthanide element our classifying instrument and extend the classical definition of valency (Nelson 1997) to metals and metallic compounds by adding the number of electrons contributed to the metallic bonding. This gives sodium, for example, the same valency in the metal (Na^+e^-) as in its compounds (NaF, NaCl, etc.). An example more relevant to this paper is LaI_2 in which the lanthanum atom has an oxidation number of +2. The compound, however, is bronze in colour, has a high electrical conductivity, and is diamagnetic [$\text{La}^{2+}(\text{I}^-)_2$ would be paramagnetic]. It is accordingly formulated $\text{La}^{3+}(\text{I}^-)_2\text{e}^-$, in which the lanthanum has a valency of three. This definition of valency is essentially that adopted by Grimm and Sommerfeld (1926) and endorsed by Sidgwick (1927: 182): “it is numerically equal to the number of electrons of the atom ‘engaged’ (*beansprucht*) in attaching the other atoms”.

The variation in the valencies of the elements across the lanthanide series is of particular interest. Here we present a simple discussion of this problem based largely upon work which we have published elsewhere (Johnson 1969a, b, c, 1974, 1977, 1980, 1982a, b, 2006; Johnson and Corbett 1970).

Principal valency

The valencies of the lanthanides are shown in Table 1. Valencies that are stable enough to occur in aqueous solution are in bold type. A striking feature of the valencies is that they vary much less than they do for transition elements, and also for the actinides. Indeed, the most stable valency for all the elements is three.

Table 1 Valencies of the lanthanides

Valencies	
La	3
Ce	3 4
Pr	3 4 (5) ^b
Nd	2 3 4
Pm	(2) ^a 3
Sm	2 3
Eu	2 3
Gd	3
Tb	3 4
Dy	2 3 4
Ho	3
Er	3
Tm	2 3 (4?) ^c
Yb	2 3
Lu	3

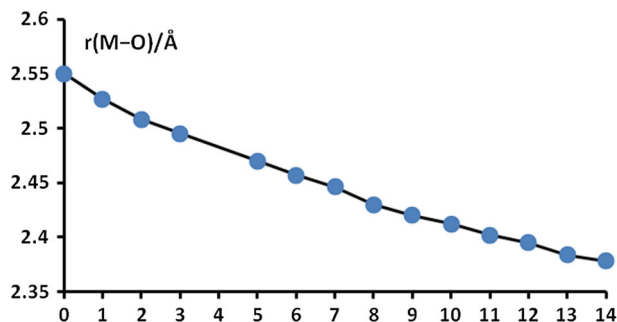
Bold numbers: valencies occurring in aqueous solution

^a Predicted (see text). Promethium, being very radioactive, has been little studied

^b In a personal communication dated 1980, Rudolf Hoppe told Meyer and Wickleder (2000: 55) that he had some evidence for the formation of CsPrF_6 . Zhang et al. (2016) detected PrO_2^+ ions in the mass spectrum of Pr/O₂ mixtures and isolated them in argon matrixes. They calculate that the Pr centre has the configuration f^0

^c See text

Fig. 1 Ln–O distances in $[\text{Ln}(\text{H}_2\text{O})_9](\text{C}_2\text{H}_5\text{OSO}_3)_3$ salts (Gerkin and Reppart 1984) plotted against number of f electrons



In this valency, the lanthanides live up to their reputation of being very similar. Their most commonly observed reactions are complexing or precipitation processes in which the valency retains its value of three. In reactions of this kind, differences between elements are small. Such differences as there are are mainly associated with a gradual reduction in size across the series (“the lanthanide contraction”). This is illustrated in Fig. 1 for $[\text{Ln}(\text{H}_2\text{O})_9](\text{C}_2\text{H}_5\text{OSO}_3)_3$ salts, all of which have the same structure (Gerkin and Reppart 1984; Persson et al. 2008). For some species, the reduction in size leads to a lowering of coordination number across the series. This is the case for $\text{Ln}^{3+}(\text{aq})$ ions, in which there is an increasing shift from nine- to eight-coordination beyond dysprosium (D’Angelo et al. 2010).

For the reactions we have just described, in which the valency of three is retained, there are other factors that can lead to small differences in chemistry. As in the transition series, these are ligand-field splitting, shell expansion (“the nephelauxetic effect”), and spin-orbit coupling. The net effect of these, however, is very much smaller than in the transition series (Johnson 2006). The most important is the second, whose prominence sometimes gives rise to the small irregularities in complexing constants illustrated in Fig. 2 (Peppard et al. 1969; Nugent 1970). There are four humps separated by three minima, first at the f^3/f^4 pair, secondly at f^7 and thirdly at the f^{10}/f^{11} pair. This is called the “tetrad effect”.

The tetrad effect can be explained by using Slater’s theory of many-electron atoms (Jørgensen 1970; Nugent 1970).² This gives the following equation for the energy of an f^n ion,

$$E = E_c + nE_f + E_r \quad (1)$$

where E_c is the energy of the core, E_f the energy of each f electron in the field of the core, and E_r is the repulsion energy between the f electrons. This energy is given in general by

$$E_r = c_0E^0 + c_1E^1 + c_2E^2 + c_3E^3 \quad (2)$$

where the E^k ’s are energy integrals³ and c_k ’s coefficients. From calculations using hydrogenic orbitals, E^3 is small, and E^2 very small, compared with E^0 and E^1 . For the ground state, the terms in E^2 disappear and Eq. (2) can then be written:

² Although Slater’s theory fails for some systems, it holds for electrons outside cores (Johnson and Nelson 2014).

³ This is one of several sets of integrals in the literature. It was proposed by Racah (1949). The superscripts are labels.

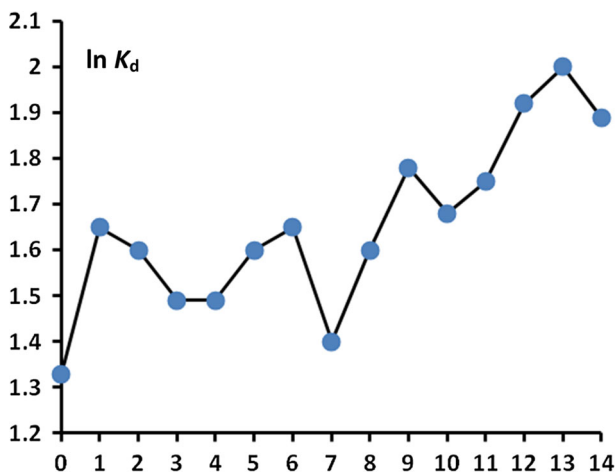


Fig. 2 Distribution constants (K_d) for lanthanide ions between an alkyl phosphonate [(CICH₂)PO(OC₈H₁₇)₂] in benzene and bromide ions in water plotted against the number of f electrons (Peppard et al. 1969; Fig. 1)

$$E_r = pE_p - qE_q + c_3E^3 \quad (3)$$

where $E_p = E^0 + (9E^1/7)$ and $E_q = (9E^1/7)$; p is the number of pairs of electrons [$1/2n(n-1)$] and q the number of pairs of electrons with parallel spins. The values of the coefficients are shown in Table 2.

The first term in Eq. (3) is approximately equal to the Coulomb energy between the electrons (J), and the second term to the exchange energy between electrons of the same spin (K).⁴ This arises because electrons can keep apart better if their spins are parallel rather than antiparallel. The third term is associated with the ability of electrons to keep apart better if they are travelling round a nucleus in the same direction rather than in opposite directions. This lowers the repulsion between electrons whose m_l values have the same sign compared with those whose m_l values have the opposite sign.⁵

From Eqs. (1) and (3), the equilibrium constant (K_{eq}) for a complexing reaction is given by⁶

$$\Delta G^\theta = L(n\Delta E_r + p\Delta E_p - q\Delta E_q + c_3\Delta E^3 + \Delta E') - T\Delta S^\theta = -RT \ln K_{eq} \quad (4)$$

where the first four terms arise from a change in the expansion of the f shell in the reaction, and the fifth term ($\Delta E'$) from a change in the energies of other electrons. L is the Avogadro constant; the other symbols have their usual meanings. The only terms in this equation that should vary irregularly with n are those in q and c_3 . Table 2 shows that the values of q have a cusp at f^7 . In the table, the values are compared with a base line drawn through the points for f^0 , f^7 , and f^{14} , i.e. $q_b = 3n$. The differences ($\delta q = q - q_b$) are then zero at f^0 , f^7 and f^{14} . They rise from f^4 to f^7 , and then fall, creating an upward cusp at f^7 . If, then, there is increased shell expansion ($\Delta E_q < 0$), this will lead to a downward cusp in $\ln K_{eq}$, which accounts for the minimum at f^7 in Fig. 2.

⁴ Details and a more exact treatment will be given in Johnson and Nelson (paper in preparation).

⁵ For an approximate treatment of this term, see Johnson (1982b).

⁶ Taking $\Delta H^\theta \approx \Delta E$.

Table 2 Values of the coefficients in Eqs. (3) and (4)

Ion (f^n)	p	q	δq	c_3
f^0	0	0	0	0
f^1	0	0	-3	0
f^2	1	1	-5	-9
f^3	3	3	-6	-21
f^4	6	6	-6	-21
f^5	10	10	-5	-9
f^6	15	15	-3	0
f^7	21	21	0	0
f^8	28	21	-3	0
f^9	36	22	-5	-9
f^{10}	45	24	-6	-21
f^{11}	55	27	-6	-21
f^{12}	66	31	-5	-9
f^{13}	78	36	-3	0
f^{14}	91	42	0	0

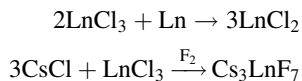
$\delta q = q - 3n$ (see text)

Table 2 also shows that δq and c_3 bottom out at f^3 and f^4 and at f^{10} and f^{11} . Since the terms in q and c_3 in Eq. (4) have opposite signs, the effect of this bottoming out will depend on the relative values of ΔE_q and ΔE^3 . Although $\Delta E^3/\Delta E_q$ is less than one, if it is sufficiently large, the variation in c_3 will predominate because of the large negative values at f^3 , f^4 , f^{10} , and f^{11} . In this case, when there is shell expansion ($\Delta E^3 < 0$), the values of $\ln K_{eq}$ will bottom out in the same way. This accords with Fig. 2, which can be reproduced with $\Delta E_q = -36 \text{ cm}^{-1}$ and $\Delta E^3 = -7 \text{ cm}^{-1}$, coupled with a linear increase. A more precise analysis takes account of changes in spin-orbit coupling and ligand-field stabilization.

A secondary effect, which is not brought out by Eq. (3), is the higher repulsion exercised between electrons in the same orbital as compared with different orbitals (Blake 1981). We discuss this elsewhere (see footnote 4).

Other valencies

The valencies other than three are two, four, and, for praseodymium, five. Some of these can be obtained in aqueous solution. Others are obtained by reactions like



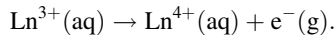
What is striking about these valencies is their distribution. As shown in Table 3, most correspond to ions whose f-electron configuration approaches or constitutes an empty (f^0), half-full (f^7), or full shell (f^{14}). The nearer the configuration approaches one of these types, the more stable the valency. For example, Nd^{4+} (f^2) can only form Cs_3NdF_7 , whereas Ce^{4+} (f^0) has an extensive chemistry. The remaining valencies (in blue in Table 3) correspond to a configuration approaching a three-quarter-full shell ($f^{10.5}$), i.e. f^{10} for valency two and f^{11} for valency four.

Table 3 Configurations of ions corresponding to the valencies in Table 1

	Configuration			
	M ²⁺	M ³⁺	M ⁴⁺	M ⁵⁺
La		f ⁰		
Ce		f ¹	f ⁰	
Pr		f ²	f ¹	(f ⁰)
Nd	f ⁴	f ³	f ²	
Pm	(f ⁵)	f ⁴		
Sm	f ⁶	f ⁵		
Eu	f ⁷	f ⁶		
Gd		f ⁷		
Tb		f ⁸	f ⁷	
Dy	f ¹⁰	f ⁹	f ⁸	
Ho		f ¹⁰		
Er		f ¹¹		
Tm	f ¹³	f ¹²	(f ¹¹ ?)	
Yb	f ¹⁴	f ¹³		
Lu		f ¹⁴		

^a High-lighted: f⁰, f⁷, and f¹⁴ ions. Red Ln²⁺, Ln⁴⁺, and Ln⁵⁺ ions with or approaching the configuration f⁰, f⁷, or f¹⁴. Blue see text

This distribution reveals very marked chemical differences between the lanthanide elements. The similarities associated with processes in which trivalency is retained are no longer apparent: we are now concerned with reactions in which the valency changes. The distribution can be explained by considering the energy factors behind the oxidation and reduction of trivalent compounds (variations in entropy are relatively small). Consider, for example, the process



The enthalpy of this can be analysed in terms of the following cycle (all standard molar enthalpy changes at 298.15 K):

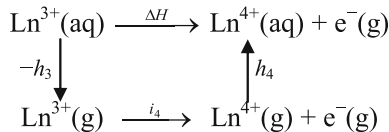


Figure 3 shows the variation in the hydration enthalpy, h_3 , with the number of f electrons.⁷ There is a detectable discontinuity between f⁰ and f¹ (Johnson and Nelson 2017a, b)

⁷ Values calculated from the standard enthalpies of formation of Ln³⁺(g) and of Ln³⁺(aq) relative to H⁺(aq) (Cordfunke and Konings 2001; Konings and Benes 2010; Konings et al. 2014; Kramida et al. 2016; Johnson and Nelson 2017a, b), and from the standard intrinsic enthalpy of formation of H⁺(aq). For the latter, we

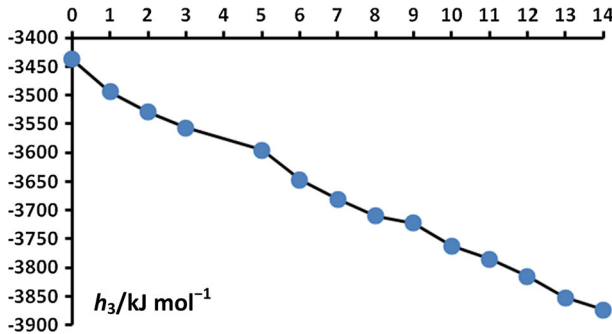
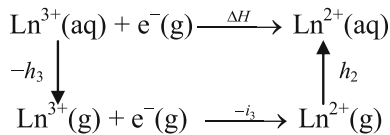


Fig. 3 Hydration enthalpies of Ln^{3+} ions (h_3) plotted against number of f electrons

arising from the break between two subshells, 5p ($4f^0$ being $5p^6$) and 4f. Nevertheless, despite this aberration, and the change in coordination number across the series, the variation is fairly smooth; the h_4 variation is expected to behave likewise. The ionization enthalpy i_4 , however, varies irregularly, as shown in Fig. 4.⁸ There is a general increase from f^1 to f^7 , followed by a big drop to f^8 , and then a general increase again. This explains why oxidation becomes increasingly difficult across the first half of the series, becomes easier at the half-full shell, and then becomes increasingly difficult again.

A similar analysis can be made of the corresponding reduction:



Apart from the sub-shell break between f^0 and f^1 , the variations in ΔH are mainly determined by those in $-i_3$, plotted in Fig. 5. In shape, this plot is the inverse of Fig. 4. There is a general decrease from f^1 to f^7 , followed by a big rise to f^8 , and then a general decrease again. This explains why reduction becomes easier towards the half-full shell, then becomes more difficult, then becomes easier again. There is also a definite irregularity around the three-quarter-full shell, making the f^{10} ion Dy^{2+} more stable than it would otherwise be. There is a similar irregularity around the quarter-full shell, but this is smaller. The plot suggests that Pm^{2+} (f^5) should be at least as stable as Nd^{2+} (f^4). Analysis of the reduction of solid trivalent compounds, including by the metals, leads to similar conclusions (Johnson 1982b: Sect. 6.8). The heightened stability of Dy^{2+} explains why, in agreement with Table 1, it has been possible to prepare solid dihalides of dysprosium, but not those of erbium.

The marked irregularity around the three-quarter shell is also apparent in Fig. 4. It suggests that compounds of tetravalent thulium, such as Cs_3TmF_7 , might be unexpectedly

Footnote 7 continued

took the value recommended by Hünenberger and Reif (2011: 460), made consistent with the standard states used by NBS/NIST (Wagman et al. 1982) and JANAF (Chase 1998). The uncertainty in this value is considerable (at least $\pm 30 \text{ kJ mol}^{-1}$), but this does not affect the precision of the relative values of h_3 , most of which have uncertainties less than $\pm 15 \text{ kJ mol}^{-1}$. We have used absolute values to simplify the equations.

⁸ Values calculated from ionization energies at 0 K (Johnson and Nelson 2017a, b) plus $(5/2)RT$.

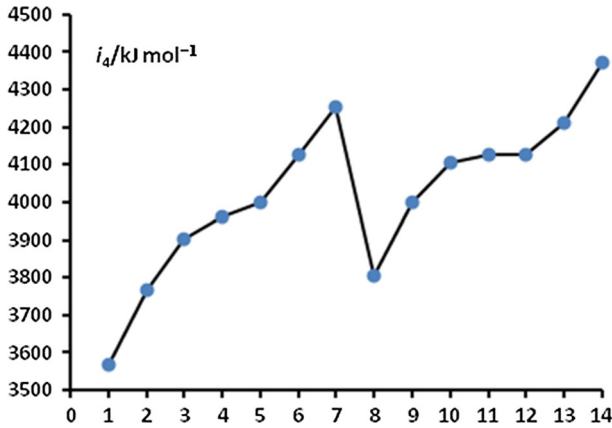


Fig. 4 Ionization enthalpies of Ln³⁺ ions (i_4) plotted against number of f electrons

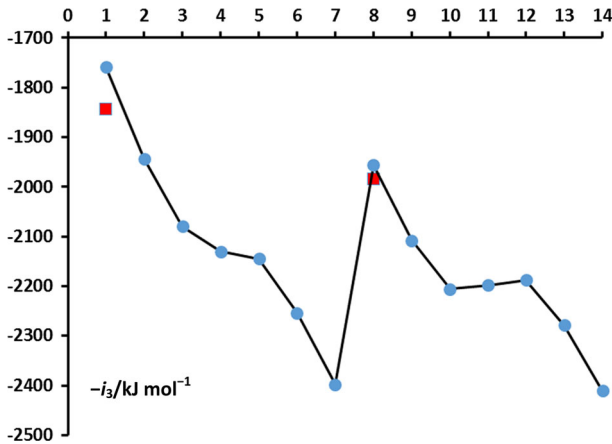


Fig. 5 Minus the ionization enthalpies of Ln²⁺ ions (enthalpies of Ln³⁺ + e⁻ → Ln²⁺) plotted against number of outer electrons. Blue points, fⁿ⁻¹ → fⁿ; red points, fⁿ⁻¹ → fⁿ⁻¹d¹ for ions having a fⁿ⁻¹d¹ ground state (La²⁺, d¹; Gd²⁺, f⁷d¹)

stable. Some workers claim to have prepared impure samples of this compound (Spitsin et al. 1982), but others have reported little or no oxidation [unpublished observations by the authors (1972), L. B. Asprey (1975) and R. Hoppe (1985)] and further confirmation is needed. This explains the question marks in Tables 1 and 3.

The reason for the big break in i_3 and i_4 is well known from the transition series. Repulsion energies between electrons are reduced by the exchange energy between electrons with the same spin. The latter builds up until a shell is half-full, then drops to zero as an electron is added with opposite spin. It then builds up again as more electrons are added with this spin.

This explanation is based on Eqs. (1) and (3) above. These give the following equation for the ionization enthalpy of an fⁿ ion

Table 4 Values of the coefficients in Eq. (6)

Process	$\Delta_i p$	$\Delta_i q$	$\Delta_i c_3$
$f^1 \rightarrow f^0$	0	0	0
$f^2 \rightarrow f^1$	1	1	-9
$f^3 \rightarrow f^2$	2	2	-12
$f^4 \rightarrow f^3$	3	3	0
$f^5 \rightarrow f^4$	4	4	+12
$f^6 \rightarrow f^5$	5	5	+9
$f^7 \rightarrow f^6$	6	6	0
$f^8 \rightarrow f^7$	7	0	0
$f^9 \rightarrow f^8$	8	1	-9
$f^{10} \rightarrow f^9$	9	2	-12
$f^{11} \rightarrow f^{10}$	10	3	0
$f^{12} \rightarrow f^{11}$	11	4	+12
$f^{13} \rightarrow f^{12}$	12	5	+9
$f^{14} \rightarrow f^{13}$	13	6	0

$$i = \Delta_i H = L[\Delta_i(nE_f) + \Delta_i(pE_p) - \Delta_i(qE_q) + \Delta_i(c_3E^3)] + (5/2)RT \quad (5)$$

If the energy integrals are approximated by the average values for the two ions involved (Ln^{z+} and $\text{Ln}^{(z+1)+}$),

$$i = L[\bar{E}_f + (\Delta_i p)\bar{E}_p + (\Delta_i q)\bar{E}_q + (\Delta_i c_3)\bar{E}^3] + (5/2)RT \quad (6)$$

The values of $\Delta_i p$, $\Delta_i q$, and $\Delta_i c_3$ are given in Table 4. The second of these determines the loss of exchange energy, and peaks at f^7 .

As with the tetrad effect, the irregularities in $\Delta_i c_3$ centred on the quarter- and the three-quarter-full shell are associated with the ability of electrons to keep apart better if their m_l values have the same sign rather than opposite. This eases the general increase in inter-electronic repulsion in the first quarter of the series, where electrons have m_l values of the same sign, relative to the second quarter, where they have both positive and negative values (Table 4); similarly in the third quarter over the fourth quarter.

Note that the pattern of variations exhibited by i_3 and i_4 holds for other processes involving the removal of an electron from an f shell (see below). Note also, with respect to the formation of 5-valent compounds by praseodymium, that this has the lowest fifth ionization energy of the lanthanides (Kramida et al. 2016).

Metallic compounds

In the reduction of trivalent compounds to metallic ones, there is no change in the number of f electrons. The ionization enthalpy $-i_3$ is accordingly no longer a factor. As a result, reductions are no longer restricted to bivalent elements. Thus, all of the elements form dihydrides (LnH_2), monosulfides (LnS), monoselenides (LnSe), monotellurides (LnTe) and monoacetylides (LnC_2), and most of them form diiodides (LnI_2). What varies, however, is the distribution of metallic and salt-like compounds in these series, as shown in Table 5.

Table 5 Nature of apparently bivalent compounds

	La	Ce	Pr	Nd	Pm ^b	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
LnI ₂	M	M	M	S	S	S	S	M	— ^c	S	— ^c	— ^c	S	S
LnTe	M	M	M	M	M	S	S	M	M	M	M	M	S	S
LnSe	M	M	M	M	M	S	S	M	M	M	M	M	X	S
LnS	M	M	M	M	M	S	S	M	M	M	M	M	M	S
LnH ₂	M	M	M	M	M	M	S	M	M	M	M	M	M	S
LnC ₂	M	M	M	M	M	M	S	M	M	M	M	M	M	X

S salt-like, *M* metallic, *X* mixed

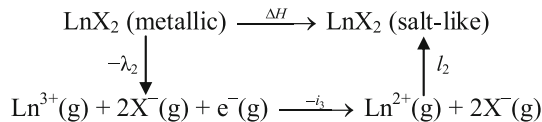
At room temperature and pressure

^a Predicted (from Fig. 6)

^b Attempts to prepare LnI₂ by the reaction of Ln with LnI₃, which were successful at dysprosium, were unsuccessful in these cases (Johnson and Corbett 1970)

Most compounds are metallic, but salt-like forms occur for some or all of the bivalent elements in Table 1.

This distribution can be explained by considering the following cycle (or the corresponding cycle for LnY):



This gives:

$$\Delta G = l_2 - i_3 - \lambda_2 - T\Delta S \quad (7)$$

The first and third terms do not involve a change in the number of f electrons, and so they, along with the entropy term, are expected to vary fairly smoothly with *n*. Assuming that this variation is approximately linear, we can write:

$$\Delta G = A + Bn - i_3 \quad (8)$$

The values of *A* and *B* for each series can be approximately determined by ensuring that $\Delta G < 0$ for salt-like compounds and $\Delta G > 0$ for metallic ones. The resulting values of ΔG are plotted against $(Bn - i_3)$ in Fig. 6, where we have used a common value of *B* (13 kJ mol⁻¹) and chosen the zero lines for each series to bring the graphs together. Comparison with Fig. 5 shows that the distribution of salt-like compounds is very largely determined by $-i_3$. Points lying below their specified zero line indicate salt-like character and an *fⁿ* configuration, points lying above, metallic character and an *fⁿ⁻¹* configuration. Where points lie close to a zero line, this is sometimes associated with states of mixed

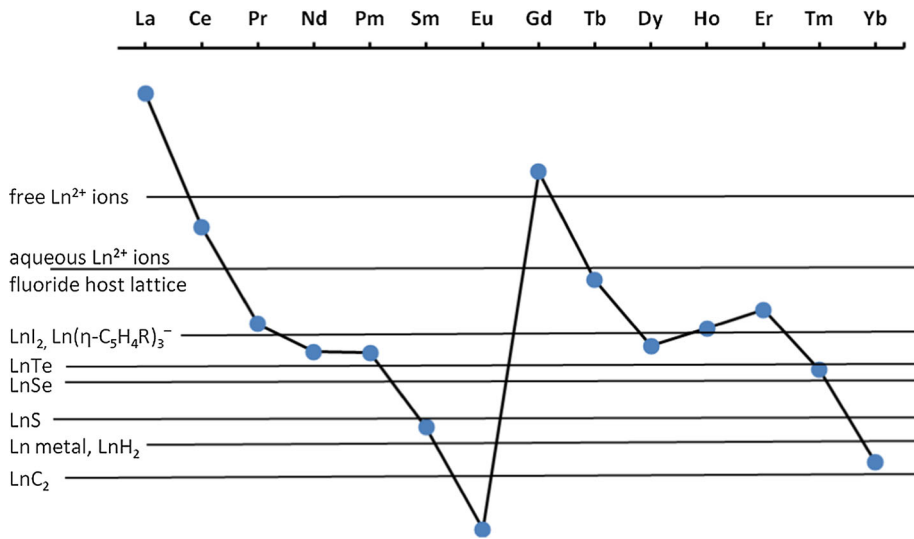


Fig. 6 Plots of ΔG for inter-valency conversion and other bi-f \rightarrow tri-f processes against $(Bn - i_3)$ showing approximate zero lines required to bring the graphs together (see text)

valency as for TmSe (Lebègue et al. 2005) and YbC₂ (Link et al. 2011) or with pressure-induced salt-like \rightarrow metallic transitions as in the case of SmS (Jayaraman et al. 1970; Johnson 1982a) and NdI₂ (Beck and Schuster 1992).

Other systems in figure 6

The scope of Fig. 6 can be enlarged beyond salt-like/metallic distributions by using a classification that focuses on the 4fⁿ configuration rather than on valency (Johnson 1977). Compounds or ions in which the lanthanide has the same 4f configuration as does the dipositive ion in an [Xe]4fⁿ state are described as bi-f; those with the same 4fⁿ configuration as the tripositive ion are called tri-f. Figure 6 then describes the distribution of systems between di-f and tri-f states. This allows us to include the free, gaseous dipositive ions which have either [Xe]4fⁿ or [Xe]4fⁿ⁻¹5d ground states, and the metals which may be (M²⁺2e⁻) or (M³⁺3e⁻). The bonding contribution of the outer 5d electron in the tri-f systems varies between zero in the gaseous ions to substantial in metallic compounds such as CeS where it populates a conduction band. Intermediate situations such as the dipositive ions in aqueous solution or fluoride host lattices also appear in Fig. 6. In the next section we encounter a case in which the d electron in tri-f compounds participates in π -bonding with ligands. This too has been included in Fig. 6.

Organometallic compounds

The lanthanides form a number of organometallic compounds (see, e.g. Cotton and Wilkinson 1988: 968–973). These are generally trivalent, e.g. the cyclopentadienyl compounds Ln(η -C₅H₅)₃. Compounds with other valencies are formed by elements for which

these valencies are most stable, e.g. Ce(η -C₅H₅)₄, Sm(η -C₅H₅)₂, Eu(η -C₅H₅)₂, and Yb(η -C₅H₅)₂.

Of interest are the ions [Ln(η -C₅H₄R)₃][−] [R = Si(CH₃)₃] (Hitchcock et al. 2008; Fieser et al. 2015; Evans 2016). These exhibit two valencies. Most have the same structure and size as Ln(η -C₅H₄R)₃, but those for samarium, europium, thulium and ytterbium are significantly larger. These are elements forming bivalent compounds (Table 1). Fieser et al. (2015) and Evans (2016) suggest that the lanthanide atoms in the latter ions are bivalent and have the configuration f^n ($M^{3+} = f^{n-1}$) while those in the former have the configuration $f^{n-1}d^1$ and are trivalent, the d electron being involved in the bonding. This pattern of valencies can be explained in a similar way to the pattern in metallic compounds; we have accordingly included these ions in Fig. 6.

Also of interest are the arene complexes [Ln(η -C₆H₃Bu¹)₂]. Anderson et al. (1989) account for the relative stabilities and magnetic moments of these by proposing an $f^{n-1}d^1s^2$ valence state for the lanthanide atoms. Promotion energies from $f^n s^2$ into this state vary in a similar way to i_3 and i_4 (above).

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