Relative Stabilities of Dipositive and Tripositive Lanthanoid Ions in Aqueous Solution

By **D. A. Johnson**, Department of Chemistry, The Open University, Milton Keynes MK7 6AA

Values of $E°[M^{3+}/M^{2+}]$ for the lanthanoid elements are estimated by using a simple ionic model and auxiliary thermodynamic data. The results correlate closely with the ionization potentials of the M^{2+} ions and are in good agreement with both chemical observations and other estimates obtained by spectroscopic correlations. This suggests that the method used here provides a quite general way of estimating thermodynamic data for those divalent lanthanoid compounds to which ionic models are commonly applied. Values of $E°[M^{3+}/M]$, calculated from recent thermodynamic data, are also tabulated.

Two methods have been used to estimate thermodynamic data for redox reactions in the lanthanoid series. The first exploits the fact that, if a particular type of spectroscopic transition involves the same change in the number of $4f$ electrons as does the redox process, then the energies of the transition and of the redox process will vary in a similar way across the lanthanoid series. Thus Nugent, Baybarz, Burnett, and Ryan [1] used the theory of atomic spectra to deduce the form of an expression for the energy difference between the lowest levels of the $4f^n5d^16s^2$ and $4f^{n+1}6s^2$ configurations of the neutral lanthanoid atoms. Their expression contained several unknown parameters, but these could be obtained empirically by a fitting procedure which used the ten experimentally known values for the energy difference. They then demonstrated that the expression successfully reproduced the experimental values of $-FE°[M^{3+}/M^{2+}]$ for samarium, europium, and ytterbium when a simple linear function of n was added. Such a relationship exists because, in these three cases, the redox process is of the type $[Xe]4f^{n+1} \longrightarrow [Xe]4f^n$ and, as one moves across the lanthanoid series, the *discontinuities* in the energy of a particular process which involves a decrease of one in the number of $4f$ electrons, depends almost entirely upon the change in repulsion between the $4f$ electrons, and is virtually unaffected by the outer electron population. The relationship was used by Nugent, Baybarz, Burnett, and Ryan to estimate $E°[M^{3+}/M^{2+}]$ for those lanthanoid elements for which no experimental value exists, corrections being made in those cases where the dipositive ion is thought to have an $[Xe]4f^n5d^1$ ground state, and the redox process is of the type $[Xe]4f^n5d^1 \longrightarrow [Xe]4f^n$.

The second method of estimation is based upon the quite different assumption that the lattice energies or hydration energies of a particular set of lanthanoid compounds or ions vary almost smoothly across the series, provided that there is no change in the number of $4f$ electrons during the condensation process. In the only case where this has so far been applied,[2] the lattice energies of $BaCl_2$, $NdCl_2$, $SmCl_2$, $EuCl_2$, and $YbCl_2$ were calculated from experimental standard enthalpies of formation and other auxiliary data, and fitted to a nearly smoothly varying function of ionic radius across the lanthanoid series. The lattice energies of other dichlorides were then obtained from the curve, and used, with the heats of sublimation, and first and second ionization energies of the metals, to obtain estimates of $\Delta H_f°(MCl_2,s)$ for all the lanthanoids. Experimental values of $\Delta H_f°(MCl_3,s)$ and estimated entropies then allowed calculation of $\Delta G°$ for the reactions

$$MCl_2(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow MCl_3(s)$$

$$3MCl_2(s) \longrightarrow M(s) + 2MCl_3(s)$$

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[1] L. J. Nugent, R. D. Baybarz, J. L. Burnett, and J. L. Ryan, *J. Phys. Chem.*, 1973, **77**, 1528.

[2] D. A. Johnson, *J. Chem. Soc.* (*A*), 1969, 2578.

The second method of estimation has a more restricted range of application than the first because it requires thermodynamic data which are at present unavailable for many elements. The first method, for example, has been used to estimate values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ and $E_f[\mathrm{M}^{\mathrm{IV}}/\mathrm{M}^{\mathrm{III}}]$ for all the lanthanoid and actinoid elements [1,3] whereas the second is restricted by a shortage of thermodynamic data to the lanthanoid series. However, only a single assumption, that of a smooth variation in the lattice energies or hydration energies of divalent compounds or ions is required in the second method, and this is founded upon familiar ionic models,[4,5] the almost smooth nature of the lanthanoid contraction,[6] and the well established absence of significant ligand field stabilization energies in the lanthanoid series.[7] By contrast, a number of less familiar assumptions are involved in the method of spectroscopic correlation. During the fitting procedure, values for certain Racah parameters are taken to be the same in both oxidation states [3] and Jørgensen [8] has cited more general suppositions which are inherent in the correlation of spectroscopic transition energies and redox stabilities.

In this paper, values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ for the lanthanoid elements are calculated by the second method. The purpose of this calculation is first, to demonstrate that the method of ref. 2 is quite general for M^{II}–$\mathrm{M}^{\mathrm{III}}$ processes in the lanthanoid series, and second, to make a direct comparison with the values obtained by spectroscopic correlation. A by-product of the calculations in this paper is a set of values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}]$ for the lanthanoid elements which is more accurate than that published by Latimer [9] some 20 years ago.

CALCULATIONS

Unless otherwise stated, auxiliary thermodynamic data have been taken from ref. 10 and all calculations refer to a temperature of 298·15 K. The unit of enthalpy is the calorie where 1 cal = 4·184 J. As in ref. 10, values of ΔH_f° and ΔG_f° for aqueous ions refer to the reaction of the metals with $\mathrm{H}^+(\mathrm{aq})$ to give the aqueous metal ion and hydrogen gas, and are based upon a convention $S^\circ(\mathrm{H}^+,\mathrm{aq}) = 0$.

The calculations may be divided into three parts. In the first part, values of $\Delta G_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$ for all the lanthanoid elements are obtained from what are almost entirely experimental data. Values of $\Delta H_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$ are obtained from the standard enthalpies of formation of the trichlorides and their heats of solution; these are then combined with the standard entropies of the metals and of their aqueous tripositive ions to give $\Delta G_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$. The latter are readily converted into values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}]$. These calculations are described more fully in Table 1.

In the second part, values of $\Delta G_f^\circ(\mathrm{M}^{2+},\mathrm{aq})$ for samarium, europium, and ytterbium are calculated from experimental figures for the electrode potentials $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ and the values of $\Delta G_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$ given in Table 1. Standard Gibbs energies of hydration of the gaseous dipositive ions, $\Delta G_h^\circ(\mathrm{M}^{2+},\mathrm{g})$ are then obtained for samarium, europium, ytterbium, calcium, strontium, and barium by using equation (1) where both $\Delta H_f^\circ(\mathrm{M}^{2+},\mathrm{g})$ and $\Delta S_f^\circ(\mathrm{M}^{2+},\mathrm{g})$ refer

$$\Delta G_h^\circ(\mathrm{M}^{2+},\mathrm{g}) = \Delta G_f^\circ(\mathrm{M}^{2+},\mathrm{aq}) - \Delta H_f^\circ(\mathrm{M}^{2+},\mathrm{g}) + T\Delta S_f^\circ(\mathrm{M}^{2+},\mathrm{g}) + 2\Delta G_{\mathrm{H}}^\circ \quad (1)$$

to the reaction

$$\mathrm{M(s)} \longrightarrow \mathrm{M}^{2+}(\mathrm{g}) + 2\mathrm{e}^-(\mathrm{g})$$

the molar entropy of the gaseous electron in its standard state is taken to be zero by convention,[11] and $\Delta G_{\mathrm{H}}^\circ$, the standard Gibbs energy for the reaction

$$\tfrac{1}{2}\mathrm{H}_2(\mathrm{g}) \longrightarrow \mathrm{H}^+(\mathrm{aq}) + \mathrm{e}^-(\mathrm{g})$$

has an estimated value [11] of 104·8 kcal mol⁻¹.

The six values of $\Delta G_h^\circ(\mathrm{M}^{2+},\mathrm{g})$ were a smooth function of cation radius. Values of 1·00, 1·16, 1·35, 1·16, 1·15, and 1·01 Å were used for the ionic radii of Ca^{2+}, Sr^{2+}, Ba^{2+}, Sm^{2+}, Eu^{2+}, and Yb^{2+}; these were obtained from the internuclear distances in the monoxides and monosulphides

TABLE 1

Thermodynamic properties of the lanthanoids

	$\Delta H_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$ [a] kcal mol⁻¹	$S^\circ(\mathrm{M}^{3+},\mathrm{aq})$ [b] cal K⁻¹ mol⁻¹	$\Delta G_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$ [c] kcal mol⁻¹	$E^\circ[\mathrm{M}^{3+}/\mathrm{M}]$ [d] V
La	−169·4 ± 0·6	−52 ± 3	−163·8 ± 1·2	−2·37 ± 0·02
Ce	−166·8 ± 1	−49 ± 4	−160·7 ± 2	−2·32 ± 0·03
Pr	−168·0 ± 1	−49 ± 3	−161·9 ± 2	−2·34 ± 0·03
Nd	−166·8 ± 0·6	−49 ± 3	−160·8 ± 1·2	−2·32 ± 0·02
Pm	−166 ± 4	−51 ± 7	−160 ± 5	−2·31 ± 0·07
Sm	−164·3 ± 2	−52 ± 4	−158 ± 3	−2·28 ± 0·04
Eu	−144·6 ± 2	−53 ± 4	−137 ± 3	−1·98 ± 0·04
Gd	−164 ± 3	−53 ± 3	−157 ± 3	−2·27 ± 0·04
Tb	−164·5 ± 2	−55 ± 4	−157 ± 3	−2·27 ± 0·04
Dy	−168 ± 4	−55 ± 3	−160 ± 4	−2·32 ± 0·06
Ho	−171·5 ± 2	−54 ± 3	−164 ± 3	−2·37 ± 0·04
Er	−169·5 ± 2	−58 ± 3	−160·9 ± 2	−2·33 ± 0·03
Tm	−167·6 ± 2	−58 ± 7	−159 ± 4	−2·30 ± 0·06
Yb	−161·2 ± 2	−57 ± 4	−154 ± 3	−2·23 ± 0·04

[a] Calculated from the values of $\Delta H_f^\circ(\mathrm{MCl}_3,\mathrm{s})$ given in ref. 2, except for the value of EuCl_3 which is from L. R. Morss and H. O. Haug, *J. Chem. Thermodynamics*, 1973, **5**, 513. Heats of solution are reviewed by L. R. Morss, *J. Phys. Chem.*, 1971, **75**, 392 and the value of $\Delta H_f^\circ(\mathrm{Cl}^-,\mathrm{aq})$ is from the CODATA task group, *J. Chem. Thermodynamics*, 1971, **3**, 1. [b] R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, 1970, **9**, 917. [c] Calculated from the data in columns 2 and 3 using the values of $S^\circ(\mathrm{M},\mathrm{s})$ given by E. J. Huber, C. E. Holley, and F. B. Baker, 'Progress in the Science and Technology of the Rare Earths,' ed. L. Eyring, Pergamon, Oxford, 1968, vol. 3, p. 343, except for promethium where an estimate of 17·2 cal K⁻¹ mol⁻¹ was taken from D. R. Stull and G. C. Sinke, 'Thermodynamic Properties of the Elements,' American Chemical Society, Washington D.C., 1956. [d] Calculated from figures in the preceding column using the relationship 1 eV = 23·061 kcal mol⁻¹.

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[3] L. J. Nugent, R. D. Baybarz, J. L. Burnett, and J. L. Ryan, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2503.

[4] A. F. Kapustinskii, *Quart. Rev.*, 1956, 283.

[5] W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, 1939, **7**, 108.

[6] D. H. Templeton and C. H. Dauben, *J. Amer. Chem. Soc.*, 1954, **76**, 5237.

[7] C. K. Jørgensen, 'Orbitals in Atoms and Molecules,' Academic Press, London, 1962, p. 150.

[8] C. K. Jørgensen, 'Halogen Chemistry,' ed. V. Gutmann, vol. 1, Academic Press, New York, 1967, pp. 329—330.

[9] W. M. Latimer, 'Oxidation Potentials,' 2nd edn., Prentice-Hall, New York, 1952, p. 291.

[10] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, U.S. National Bureau of Standards Technical Note 270-3, Washington D.C., 1968.

[11] R. M. Noyes, *J. Amer. Chem. Soc.*, 1962, **84**, 513.

of calcium, strontium, barium, and europium,[12-14] and in the monosulphides of samarium and ytterbium,[13] by using values [15a] of 1·42 and 1·84 Å for the radii of the oxide and sulphide ions.

It was found that the six values of $\Delta G_h^\circ(\mathrm{M}^{z+},\mathrm{g})$ could be fitted to the Born equation in the modified form proposed by Latimer, Pitzer, and Slansky: [5]

$$\Delta G_h^\circ(\mathrm{M}^{z+},\mathrm{g}) = -\frac{z^2e^2}{2(r+c)}\left(1-\frac{1}{\varepsilon}\right) \qquad (2)$$

where r is the crystal radius of the cation, c is a constant, and ε is the dielectric constant of water. Substitution of fundamental constants [16] and the value [17] of the static dielectric constant at 25° gives

$$\Delta G_h^\circ(\mathrm{M}^{2+},\mathrm{g}) = -\frac{655{\cdot}6}{r+c} \qquad (3)$$

when $\Delta G_h^\circ(\mathrm{M}^{2+},\mathrm{g})$ is expressed in kcal mol^{-1} and $(r + c)$ in Å. For the six values of $\Delta G_h^\circ(\mathrm{M}^{2+},\mathrm{g})$, the value of c was 0·741 ± 0·002 Å, the small standard deviation indicating the closeness of fit.

TABLE 2

Thermodynamic properties of the lanthanoids and alkaline earth metals

	$\Delta H_f^\circ(\mathrm{M,g})$ kcal mol^{-1}	$\Delta H_f^\circ(\mathrm{M}^{2+},\mathrm{g}')$ kcal mol^{-1}	$\Delta S_f^\circ(\mathrm{M}^{2+},\mathrm{g}')$ [f] cal K^{-1} mol^{-1}
Ba		396·0 ± 0·3 [d]	25·6 ± 0·8
La	103·0 ± 2 [a]	510 ± 3 [e]	30·8 ± 0·4
Ce	100·2 ± 1 [b]	479 ± 3 [e]	27·0 ± 0·4
Pr	85·0 ± 1 [a]	456 ± 3 [e]	27·9 ± 0·4
Nd	78·3 ± 2 [a]	455 ± 3 [e]	27·7 ± 0·4
Pm	72 ± 8 [c]	454 ± 8 [e]	27·2 ± 2
Sm	49·4 ± 1 [a]	438 ± 3 [e]	24·4 ± 0·3
Eu	42·4 ± 0·4 [a]	435·8 ± 1 [e]	26·2 ± 0·4
Gd	95·0 ± 1 [a]	525 ± 3 [e]	29·8 ± 0·3
Tb	92·9 ± 1 [a]	497 ± 3 [e]	29·1 ± 0·3
Dy	69·4 ± 1 [a]	478 ± 3 [e]	28·8 ± 0·3
Ho	71·9 ± 0·6 [a]	484·3 ± 2 [e]	28·6 ± 0·3
Er	75·8 ± 2 [a]	495 ± 3 [e]	28·8 ± 0·4
Tm	55·5 ± 2 [a]	479 ± 3 [e]	27·6 ± 0·3
Yb	36·4 ± 0·4 [a]	464·3 ± 2 [e]	27·0 ± 0·3
Ca		460·3 ± 0·3 [d]	27·1 ± 0·3
Sr		428·0 ± 0·5 [d]	26·8 ± 0·8

[a] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, 'Selected Values for Thermodynamic Properties of Metals and Alloys,' Wiley, New York, 1963 and subsequent supplements issued at irregular intervals. [b] Mean of value from ref. *a* and R. J. Ackermann, M. Kojima, E. G. Rauh, and R. R. Walters, *J. Chem. Thermodynamics*, 1969, **1**, 527. [c] Estimated by linear extrapolation of the praseodymium–neodymium interval, a procedure justified by the theoretical interpretation of ref. 23. [d] V. B. Parker, D. D. Wagman, and W. H. Evans, U.S. National Bureau of Standards Technical Note 270-6, Washington D.C., 1971. [e] Calculated from the expression $\Delta H_f^\circ(\mathrm{M,g}) + I_1 + I_2' + 5RT$ thus ignoring the effect of any population of excited states. The values of I_1 and I_2' are those recommended by J. Sugar and J. Reader, *J. Chem. Phys.*, 1973, **59**, 2083. I_2' is the same as I_2 except for the elements lanthanum and gadolinium where it is 7194 and 2381 cm^{-1} greater respectively. [f] Calculated by using values of $S^\circ(\mathrm{M}^{2+},\mathrm{g}')$ obtained from the Sackur–Tetrode expression $\frac{3}{2}R\ln M + 26{\cdot}0 + R\ln(2J + 1)$ where M is the atomic weight and J is the ground state quantum number, population of excited states being ignored. Values of $S^\circ(\mathrm{M,s})$ were those given in footnote *c* of Table 1. As described in the text, the standard molar entropy of the gaseous electron is zero by convention.

Now the aqueous ions Ba^{2+}, Sm^{2+}, Eu^{2+}, and Yb^{2+} have configurations of the type $[\mathrm{Xe}]4f^{n+1}$ where n is the number of $4f$ electrons possessed by the corresponding M^{3+} ion.[18] It follows that the values of ΔG_h° for other lanthanoid elements which are obtained by interpolation of these four values will be those appropriate to $[\mathrm{Xe}]4f^{n+1}$ configurations. In Tables 2 and 3, this is emphasized by denoting species of this kind by a single prime placed against the symbol specifying their physical state, *e.g.* $\mathrm{M}^{2+},\mathrm{g}'$. Interpolation was carried out as follows: estimates of the radii of ions of this kind were obtained by plotting the values for Ba^{2+}, Sm^{2+}, Eu^{2+}, and Yb^{2+} against those of the isoelectronic tripositive ions [6] when a good straight line was obtained. This procedure ensures that the estimated radii of the dipositive ions vary with atomic number like the radii of the tripositive ions in an almost, but not perfectly smooth fashion. The estimated radii were used to derive unknown values of $\Delta G_f^\circ(\mathrm{M}^{2+},\mathrm{g}')$ from equation (3), and these were substituted into equation (1) to give the estimated figures for $\Delta G_f^\circ(\mathrm{M}^{2+},\mathrm{aq}')$ which appear in column 2 of Table 3.

TABLE 3

Thermodynamic properties of the lanthanoid and alkaline earth elements

	$\Delta G_f^\circ(\mathrm{M}^{2+},\mathrm{aq}')$ [a] kcal mol^{-1}	$\Delta G_h^\circ(\mathrm{M}^{2+},\mathrm{g}')$ [a] kcal mol^{-1}	$E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]'$ [a] V
Ba	−134·0 ± 0·6 [b]	−313·7 [d]	
La	−29	−321	−5·8
Ce	−64	−326	−4·2
Pr	−92	−330	−3·0
Nd	−97	−335	−2·8
Pm	−102	−339	−2·5
Sm	−123 ± 6 [c]	−344 [d]	−1·50 ± 0·2 [e]
Eu	−129 ± 3 [c]	−348 [d]	−0·35 ± 0·03 [f]
Gd	−44	−351	−4·9
Tb	−77	−355	−3·5
Dy	−100	−360	−2·6
Ho	−97	−364	−2·9
Er	−91	−368	−3·0
Tm	−110	−371	−2·1
Yb	−129 ± 4 [c]	−375 [d]	−1·10 ± 0·1 [g]
Ca	−132·3 ± 0·4 [b]	−374·9 [d]	
Sr	−133·7 ± 0·8 [b]	−344·1 [d]	

[a] Unless otherwise stated, values were estimated by methods described in the text. [b] Footnote *d* of Table 2. [c] Calculated from the figures in column 4, and the values of $\Delta G_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$ in Table 1. [d] Calculated from equation (1). [e] The value obtained from the polarographic results of A. Timnick and G. Glockler, *J. Amer. Chem. Soc.*, 1948, **70**, 1347, adjusted positively by 0·05 V to allow for halide complexing. [f] L. R. Morss and H. O. Haug, *J. Chem. Thermodynamics*, 1973, **5**, 513. [g] Value of H. A. Laitinen, *J. Amer. Chem. Soc.*, 1942, **64**, 1133 corrected as in footnote *e* for chloride complexing.

Figures for $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]'$ could then be obtained from the relation

$$FE^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]' = \Delta G_f^\circ(\mathrm{M}^{3+},\mathrm{aq}) - \Delta G_f^\circ(\mathrm{M}^{2+},\mathrm{aq}') \qquad (4)$$

where the prime against the E° term indicates, as with $\Delta G_f^\circ(\mathrm{M}^{2+},\mathrm{aq}')$, that the aqueous dipositive ion has a configuration of the type $[\mathrm{Xe}]4f^{n+1}$. These values are in the fourth column of Table 3.

In the final part of the calculation, we correct the values

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[12] 'Crystal Data Determinative Tables,' eds. J. D. H. Donnay and G. Donnay, American Crystallographic Association, 2nd edn., 1963.

[13] J. Flahaut and P. Laruelle, 'Progress in the Science and Technology of the Rare Earths,' ed. L. Eyring, Pergamon, Oxford, 1968, vol. 3, p. 149.

[14] H. A. Eick, N. C. Baenziger, and L. Eyring, *J. Amer. Chem. Soc.*, 1956, **78**, 5147.

[15] D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge University Press, Cambridge, 1968, (*a*) p. 37, (*b*) p. 126.

[16] F. D. Rossini, *Pure and Appl. Chem.*, 1964, **8**, 95.

[17] Landolt–Bornstein Tables, vol. 2, part 6, Springer, Berlin, 1959, p. 743.

[18] L. B. Asprey and B. B. Cunningham, *Progr. Inorg. Chem.*, 1960, **2**, 267.

of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]'$ in those cases where the ground state configuration of the ion M^{2+}(aq) is not [Xe]$4f^{n+1}$. As footnote *e* of Table 2 implies, for the gaseous ions, lanthanum and gadolinium represent the sum total of such cases, but in condensed phases, the number will be increased because the $5d$ orbitals are stabilized by ligand field effects. To estimate stabilizations that might be achieved by the adoption of $4f^n5d^1$ configurations, we follow the procedure used for fluoride host crystals by McClure and Kiss:[19] we assume that the ligand field stabilization energy is *ca.* $\frac{3}{5}\Delta$ for [Xe]$4f^n5d^1$ configurations of the divalent aqueous ions, and that Δ decreases linearly from 15 000 to 11 000 cm^{-1} across the lanthanoid series. For La^{2+}(aq) and Gd^{2+}(aq), the stabilization achieved by adoption of the $4f^n5d^1$ configuration is estimated by adding $\frac{3}{5}\Delta$ to 7194 and 2381 cm^{-1} which, as in footnote *e* of Table 2, are the respective separations between the ground states, and the lowest levels of the [Xe]$4f^1$ and [Xe]$4f^7$ configurations, in La^{2+}(g) and Gd^{2+}(g). This raises $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ by 2·0 and 1·3 V respectively. With this procedure, the only other ion to be affected is Ce^{2+}(aq). In the case of Ce^{2+}(g), the lowest level of the $4f^15d^1$ configuration lies 3277 cm^{-1} above the $4f^n$ ground state,[20] a figure which is less than $\frac{3}{5}\Delta$, so we take the stabilization of the $4f^15d^1$ state of the Ce^{2+}(aq) ion with respect to the $4f^2$ state to be $(\frac{3}{5}\Delta - 3277)$ cm^{-1}, or 0·7 V. The only other aqueous ions that might conceivably have $5d^1$ ground states are Tb^{2+}(aq) and Pr^{2+}(aq). Calculations of the type just described, based upon gaseous ion data cited in ref. 21, suggest that in the aqueous ions, the lowest levels of the [Xe]$4f^85d^1$ and [Xe]$4f^25d^1$ configurations lie *ca.* 1000 and 2000 cm^{-1} respectively above the [Xe]$4f^n$ ground states, and that Δ values *ca.* 15 000 and 18 000 cm^{-1} would be needed to interchange the ground and excited states. We note here also that the ligand field stabilization of the $5d$ shell could not possibly be enough to create $5d^2$ ground states because the energy of promotion of the second electron is much too high. Thus for Ce^{2+}(g), the energy of the second promotion[20] $(4f^2\ {}^3H_4 \longrightarrow 5d^2\ {}^3F_2)$ is 40 440 compared with 3277 cm^{-1} for the first. To summarize, the method described above suggests that the values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ for lanthanum, cerium, and gadolinium are greater than the values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]'$ by 2·0, 0·7, and 1·3 V respectively, but that in all other cases the two quantities are the same. A very similar correction procedure was followed by Nugent, Baybarz, Burnett, and Ryan.[1] The final estimates of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ are given in Table 4.

TABLE 4

Values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ for the lanthanoid elements

	$E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]/\mathrm{V}$			$E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]/\mathrm{V}$	
	This work	Ref. 1		This work	Ref. 1
La	−3·8	−3·1	Gd	−3·6	−3·9
Ce	−3·5	−3·2	Tb	−3·5	−3·7
Pr	−3·0	−2·7	Dy	−2·6	−2·6
Nd	−2·8	−2·6	Ho	−2·9	−2·9
Pm	−2·5	−2·6	Er	−3·0	−3·1
Sm	−1·5	−1·6	Tm	−2·1	−2·3
Eu	−0·35	−0·35	Yb	−1·1	−1·1

DISCUSSION

Unlike the figures given by Latimer[9] the values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}]$ given in Table 1 show appreciable departures from a smooth variation across the series. However, if the europium and ytterbium values are excluded a nearly regular variation with atomic number results and the values lie in the narrow range −2·32 ± 0·05 V. The displacement of the europium and ytterbium towards more positive values is a general phenomenon for the energies of formation of trivalent lanthanoid compounds, and it is caused by the adoption of divalency, as opposed to the normal trivalency of other lanthanoids, in the metallic state.[22,23] Such displacements are perceptible, for instance, in the values of $\Delta H_f^\circ(\mathrm{MCl_3},\mathrm{s})$ and $\Delta H_f^\circ(\mathrm{M_2O_3},\mathrm{s})$.

The estimated values $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]$ are shown in Table 4. They are in good agreement with qualitative chemical observations in that the estimates for neodymium, dysprosium, and thulium suggest that the dipositive ions are thermodynamically very unstable with respect to the reduction of water; the dichlorides of these elements are salt-like but dissolve in water with evolution of hydrogen to form trivalent aqueous ions or hydroxides.[24-26]

Table 4 also shows that the agreement with the spectroscopic estimates from ref. 1 is, for the most part, excellent; indeed, in the cases of neodymium, promethium, dysprosium, holmium, erbium, and thulium, any disagreement is of the same order as the uncertainties in the experimental values of $\Delta G_f^\circ(\mathrm{M}^{3+},\mathrm{aq})$. For elements such as lanthanum, cerium, and gadolinium which are most remote from the empirically fitted experimental values, the disagreement is larger, and inspection of Figure 12 in ref. 1 suggests that it arises from different values of $E^\circ[\mathrm{M}^{3+}/\mathrm{M}^{2+}]'$ rather than from differences in corrections made for the occurrence of [Xe]$4f^n5d^1$ ground states in the ions La^{2+}(aq), Ce^{2+}(aq), and Gd^{2+}(aq). This may be an indication of uncertainties in the spectroscopic procedure which is essentially a theoretically based extrapolation from the experimentally fitted points at samarium, europium, and ytterbium. When the extrapolation is long, as at lanthanum and cerium, the uncertainty is greater. In the method used in this paper, the empirically fitted point at barium which is adjacent to lanthanum and cerium should help to reduce such errors. The important feature, however, is that it is those elements which are at, or adjacent to, the empirically fitted points that are likely to occur in divalent compounds, and for those elements the agreement is excellent.

Another encouraging feature of the calculations is the fact that it was possible to include data for strontium and calcium without significantly altering the value of c in equation (3). This suggests that the method not only provides a general way of estimating the thermodynamic stabilities of divalent lanthanoid compounds in

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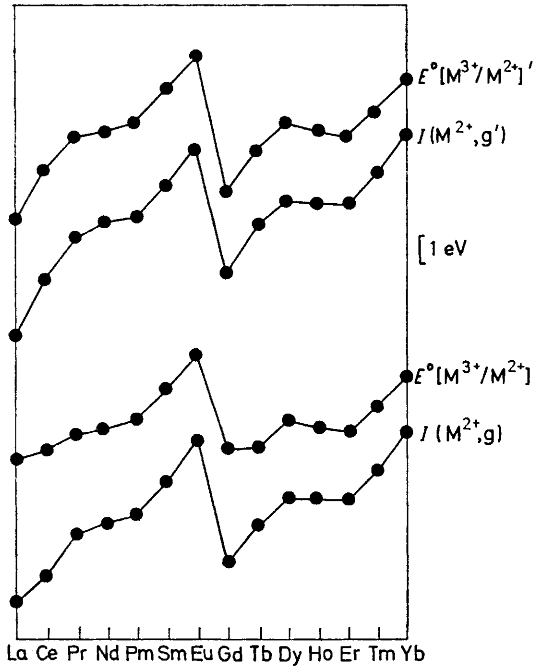
those systems where the ionic model is commonly applied, but that estimates can be obtained even when no *experimental* energies of formation for such lanthanoid compounds exist. In such cases, *rough* estimates could be obtained from values for the barium, strontium, and calcium compounds and the data in Table 2 alone.



Thermodynamic properties of the lanthanoid elements

Finally, we note that, as with the values of $\Delta G°$ for the process[2]

$$MCl_2(s') + \tfrac{1}{2}Cl_2(g) \longrightarrow MCl_3(s)$$

the values of $\Delta G°$ for the reaction

$$M^{2+}(aq') + H^+(aq) \longrightarrow M^{3+}(aq) + \tfrac{1}{2}H_2(g) \quad (5)$$

correlate very closely with $I(M^{2+},g')$, the ionization potentials of the dipositive ions in the $[Xe]4f^{n+1}$ configuration. This is apparent from the very close parallelism between the two upper plots in the Figure which show the variations in $E°[M^{3+}/M^{2+}]'$ and in $I(M^{2+},g')$. The two lower plots show the correlation between the variations in $E°[M^{3+}/M^{2+}]$ and in $I(M^{2+},g)$, the ionization energies of the dipositive ions in their ground state configuration. Here, the parallelism is reduced relative to the two upper plots because of the ligand field stabilization energies of the $[Xe]4f^n5d^1$ configurations of the aqueous La^{2+}, Ce^{2+}, and Gd^{2+} ions but it is still close.

These good correlations exist because when the problem of the variations in $\Delta G°$ for reaction (5) is restated by means of the equation

$$\Delta G° = -\Delta H_h°(M^{2+},g') + \Delta H_h°(M^{3+},g) + I(M^{2+},g') - T\Delta S° + \tfrac{5}{2}RT \quad (6)$$

the variations in $\Delta G°$ show the full impact of those in $I(M^{2+},g')$ because the other terms on the right-hand side of equation (5) vary nearly smoothly with atomic number. The smooth variation in the enthalpies of hydration of the ions is particularly notable, and arises, as noted earlier, because the $4f$ orbitals are not greatly exposed to the ligands, so ligand field effects are small. This is in distinct contrast to the case of the reactions

$$M^{2+}(aq) + H^+(aq) \longrightarrow M^{3+}(aq) + \tfrac{1}{2}H_2(g)$$

$$MX_2(s) + \tfrac{1}{2}X_2 \longrightarrow MX_3$$

in the first transition series.[15b,27] Here the variations in $\Delta G°$ only show the influence of the third ionization potential of the metal in a much attenuated form, because the hydration enthalpies of the ions and the lattice energies of the halides show the familiar cusp-shaped variation [28,29] which is attributed to the effects of ligand field stabilization energies.

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