Thermochemical Properties of Yttrium, Lanthanum, and the Lanthanide Elements and Ions

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I. Introduction

A. Background

Elements 57 (lanthanum) through 71 (lutetium) form an unique series within the Periodic Table. When considered together with scandium and yttrium, these metals display a predominantly trivalent chemistry which would be expected for "representative" (inert-gas electron configuration) cations. But when considered as transition metals, these elements display structural, electronic, and energetic characteristics which are reflected in subtle differences in their chemistry. Only within the past decade have these characteristics become fully understood.

The earliest attempts at precise characterization of lanthanide elements and their compounds were frustrated by the difficulties of separating the elements from each other and of preparing pure substances. For example, the careful work of Bommer and Hohmann[1,2] succeeded in preparing anhydrous trichlorides but yielded metal samples which must have been heavily contaminated with the reductant metal (potassium). Results based on measurements before 1940 (and a few published estimates) are summarized in NBS Circular 500.[3]

During World War II, ion-exchange methods of separating the rare earths, modern methods of metal preparation, and precise analytical standards for the metals were developed, principally under the leadership of Professor F. H. Spedding at (then) Iowa State College. Beginning at about the time of publication of NBS Circular 500 (1952), several American laboratories began extended series of investigations of lanthanide thermochemistry using much purer materials and more efficient instruments. Spedding and many co-workers began definitive studies on lanthanide metals, aqueous species, and compounds; these measurements are still continuing. Holley and Huber at Los Alamos Scientific Laboratory conducted heats of combustion, and later heats of solution, which are still in progress. B. B. Cunningham and L. Eyring and their students performed many measurements as parallels to their work on actinide species. In 1959 researchers at the U.S. Bureau of Mines began a series of careful determinations of enthalpies of formation of rare-earth compounds. In that year Montgomery published a comprehensive review and evaluation, "Thermodynamics of Rare-Earth Compounds".[4]

Although a few studies had been made by 1960 of unusual oxidation states of the lanthanides,[5] it was generally believed that the stability of $4f^0$, $4f^7$, and $4f^{14}$ subshells of the 2+, 3+, and 4+ *ions* were responsible for the presence of divalent or tetravalent species. Evidence began to accumulate after 1960 that the energetics of lanthanide species were dependent on electron configurations and structures of the (crystalline) metals and of the gaseous atoms:

1. Enthalpies of sublimation of the metals were found to decrease regularly from La to Eu, then again from Gd to Yb.[6]
2. The relative energy levels of various configurations were shown to vary systematically.[7,8]
3. Several new saline (ionic) dihalides were found to be stable.[9]
4. $Eu^{3+}(aq)$ was found to be remarkably less stable (with respect to the metal) than its neighbors.[10]

During the last decade, a number of significant theoretical and experimental advances in interpretation and characterization of lanthanide species have been made. Some of these were achieved to aid in the study of the actinide elements, but the 4f (lanthanide) and 5f (actinide) elements are sufficiently different that it has been worthwhile to focus attention solely on the lanthanides themselves. Most of these recent advances will be discussed in succeeding sections of this review.

B. Scope

This review is limited to those species of the elements yttrium and lanthanum through lutetium, and the energetics of transitions between them, which are components of useful Born–Haber cycles. For this reason, thorough evaluation of the thermochemistry of lanthanide sesquioxides and trichlorides has been included. Where experimental results of doubtful precision are presented, or where two or more pieces of data conflict, a "best-value" judgment has been made. Where meaningful estimates have been arrived at, these estimates have been included in this review.

C. Previous Systematic Reviews

A comprehensive and recent revision to Series I of NBS Circular 500[3] is NBS Technical Note 270-7,[11] which presents essential thermochemical properties for species involving La through Lu. The related element yttrium was included in NBS Technical Note 270-5.[12] Unfortunately, entries in the Technical Note 270 series do not quote precision indices (other than as implied by the number of significant figures shown), and there are no references to any entries.

The standard reference work on properties of lanthanide metals (solid, liquid, and gaseous enthalpies, entropies, and free energies) is the Hultgren compilation.[13] It presents literature data, critical evaluations, and up-to-date lists of references.

A very useful (well-evaluated and current) compilation is "Thermochemistry of the Rare Earths" by Gschneidner et al.[14] For this review, Gschneidner's oxide data have been used; in general, they agree with the data of NBS Technical Note 270-7.

There are two excellent sources of data on oxidation–reduction potentials. One, of course, is Latimer;[15] another is the contemporary, critical, and speculative review by Nugent.[16]

There are other recently published monographs on the lanthanide elements which are somewhat useful as thermochemical references. Among these are Brown's text on the lanthanide halides,[17] Topp's monograph,[18] and Moeller's recent chapter in "Comprehensive Inorganic Chemistry".[19] One compendium which is not very useful is Krestov's extensive survey;[20] for the most part, entries are taken from other Russian surveys and are not always representative of most recent research.

The Gmelin Handbuch is in the process of issuing new volumes on the "rare earth elements" (Sc, Y, La, and lanthanides, system 39). New volumes are Section B3 (physical properties of metals), Section C1 (hydrides, oxides), and Section C2 (compounds with H + O, alkali metals + O, N, etc.).[21-23]

D. Literature Searched

This review begins essentially with the review by Montgomery.[4] Primary literature has been searched, with the assistance of the Bulletin of Thermodynamics and Thermochemistry through Volume 18,[24] through June 1975. As mentioned above (section I.B, Scope), only data for metals, monatomic ions (gaseous, hydrated, and in ionic crystals), oxides, and chlorides are reviewed.

II. Recent Advances

A. Preparation and Characterization of Pure Metals, Dihalides, and Monoxides

The standards of quality of samples of lanthanide metals have been set and improved upon by many years of research at the Institute for Atomic Research at Iowa State University.[25-27] Sublimed metals, analyzed for many nonmetallic impurities, are now available from commercial suppliers. For all of the metals except Pm, high-temperature vapor-pressure measurements have yielded accurate "second-law" enthalpies of sublimation. For most metals, low- and moderate-temperature heat-capacity measurements have yielded entropies which permit "third-law" confirmation of the extrapolated enthalpy of sublimation at 298 K. Hultgren et al. have evaluated and tabulated these data.[13]

Using pure metals as reductants for the trihalides, Corbett[9] and Novikov and Polyachenok[28] have investigated the phase diagrams of the metal–trihalide systems and have prepared many reduced halides. Thermochemical properties are now known not only for the easily reduced chlorides of Sm, Eu, and Yb[29-31] but also for the less stable $NdCl_2$ and $TmCl_2$.[32,33] Vaporization processes for the dihalides have been studied by Eick and coworkers.[34,35] Johnson[36] utilized experimental data and thermochemical cycles to estimate the enthalpies of formation of all the lanthanide dichlorides. Since the most powerful method of preparation of a lanthanide dichloride is the reduction of a trichloride by its metal,

$$2MCl_3(c) + M(c) \rightarrow 3MCl_2(c) \qquad (1)$$

the reverse (disproportionation) reaction must not be thermodynamically favorable if the dichloride is to be stable. Johnson[36] and Corbett[9] showed that the important Born–Haber terms in the disproportionation reaction are twice the third ionization energy of the metal and the negative of its enthalpy of sublimation. In fact, since a plot of the third ionization energy mirrors the enthalpy of sublimation as a function of atomic number,[9] either a *high* third ionization energy or a *low* enthalpy of sublimation favors the stability of the dichloride. It is now evident that the energetics of formation of lanthanide dichlorides are valuable tools for interpreting these elements' divalent behavior.

Although preparations of many solid monoxides have been attempted, only EuO is a well-characterized compound.[10,22,37] Thorough studies of the thermochemistry of EuO have been made,[10,37-39] but there are conflicting reports on the existence of SmO and YbO.[22,40-42] The difficulty in preparing pure crystalline monoxides has precluded their use in interpreting the elements' divalent behavior. Peterson[43] has reviewed the compounds of divalent lanthanides and has compared their behavior to that of divalent actinide compounds.

B. Experimental Entropies and Entropy Estimates

For many years the entropies of aqueous rare-earth ions were based upon a very few, inherently suspicious measurements.[15] In 1970 Hinchey and Cobble[44] published the results of new experiments and extensive calculations, which permitted the calculation or estimation of standard-state aqueous-ion entropies. More recently, Spedding et al.[45] have carefully remeasured the heat capacities of several lanthanide trichloride hydrates, so that now even better entropies are available.

Two decades ago, numerous semiempirical correlations of the partial molal entropies of monatomic aqueous ions were presented; these have been reviewed by Rosseinsky.[46] Many more such entropies, particularly for transition-metal ions,[11,12,44,47] have been calculated from experimental data. The physical parameters which are recognized as significant in determining the ordering of water molecules about an ion, and therefore in determining the partial molal entropy of the ion, are the formal charge (oxidation number for a monatomic ion) and the size of the ion. Ionic sizes are best measured from crystallographic internuclear distances, and a comprehensive set of crystallographic radii in oxides and fluorides has been published by Shannon and Prewitt.[48] Using these experimental entropies and ionic radii, many functions have been considered (each having some relationship to theoretical, absolute entropies of hydration of ions) and fitted to the known entropies, charges, and ionic radii.[49]

The best equation found[49] for 62 monatomic aqueous ions,[47,50] ranging in charge from +4 to −2, is

$$\bar{S}^\circ(M^z,\text{aq}) = \frac{3}{2}R\ln(\text{at. wt}) + R\ln(2J+1) + 256.8 - 32.84\frac{(|z|+3)^2}{r+c} \qquad (I)$$

TABLE I. Standard-State Thermodynamic Properties at 25 °C

	S°(M,c)[a]	ΔH_f°(M,g)[a]	ΔH_f°(M^{2+},aq)[b]	$\bar{S}^\circ$(M^{2+},aq)[c]	ΔH_f°(M^{3+},aq)[d]	$\bar{S}^\circ$(M^{3+},aq)[a]	ΔH_f°(M^{4+},aq)[b]	$\bar{S}^\circ$(M^{4+},aq)[c]
M	J mol^{-1} K^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
Y	44.4	421.3			−715	−251		
La	57.0	431.0	(−302)	(3)	−709.4	−218		
Ce	72.0	420.1[e,f]	(−294)	(6)	−700.4	−205	−576[86]	−419[86]
Pr	73.2	356.9[f]	(−370)	(3)	−706.2	−209	(−372)	(−412)
Nd	71.5	326.9[f]	(−402)[33]	(−2)	−696.6	−207	(−263)	(−413)
Pm	(71)[g]	(318)[57,h]	(−390)	(−8)	(−688)[b]	(−209)[c]	(−211)	(−417)
Sm	69.6	206.7	(−504)[i]	(−26)	−691.1	−212	(−236)	(−423)
Eu	77.8	177.4[f]	−527.8[31]	−10[31]	−605.6	−222	(−53)	(−432)
Gd	68.1	397.5	(−282)	(−18)	−687.0	−206	(−24)	(−450)
Tb	73.2	388.7	(−319)	(−12)	−698.	−226	(−443)[j]	(−436)
Dy	74.8[k]	290.4	(−418)[l]	(−15)	−696.5	−231	(−307)	(−435)
Ho	75.3	300.6[f]	(−394)	(−18)	−707.	−227	(−202)	(−436)
Er	73.2	316.4[m]	(−373)	(−23)	−705.	−244	(−192)	(−438)
Tm	74.0	232.2	(−442)[33]	(−28)	−705.2	(−243)[n]	(−202)	(−442)
Yb	59.9	155.6[o]	(−537)[33]	(−47)	−674.5	−238	(−57)	(−446)
Lu	51.0	427.6			−702.6	−264	(41)	(−452)

[a] Reference 11 or 12 except where noted. [b] Estimated from Born–Haber cycles (section VI) in this review, except where noted. [c] From text, section II.B and eq I except where noted. Ionic radii used in eq I are listed in Table X. [d] From "best value" of Table III except where noted. [e] Including vapor pressure data of R. J. Ackermann, M. Kojima, E. G. Rauh, and R. R. Walters, *J. Chem. Thermodyn*, **1**, 527 (1969). [f] Recalculated by 3rd law method from vapor pressure data and gaseous free-energy functions of ref 13, using entropy of ref 11 to derive new condensed free-energy functions. [g] Estimated by comparison with isostructural metals. [h] Corrected from Table I of ref 57 by use of ΔE(Pm) = 7000 cm^{-1} (ref 52) instead of 6000 cm^{-1} (ref 51). [i] Estimated by method of ref 33 but using ΔH_f° ($SmCl_2$,c) = −802.5 kJ mol^{-1} (ref 82). [j] From E° and ΔS° for reduction of Tb^{4+} to Tb^{3+} (see section V). [k] Correction to ref 11 (R. H. Schumm, personal communication). [l] Estimated by method of ref 33 but using ΔH_f° ($DyCl_2$, c) = −693 kJ mol^{-1} (ref 82). [m] Using vapor pressure data of J. M. McCormack, P. R. Platt, and R. K. Saxer, *J. Chem. Eng. Data*, **16**, 167 (1971), thermal functions from ref 13, and 3rd law method. [n] Tabulated in ref 11, but an estimate (R. H. Schumm, personal communication). [o] A. Desideri, V. Piacente, and S. Nobili, *J. Chem. Eng. Data*, **18**, 140 (1973).

where $\bar{S}^\circ$ represents the partial molal entropy of the ion in J mol^{-1} K^{-1}, based upon the convention $\bar{S}^\circ(H^+,aq) = 0$. For this equation, $R = 8.314$ J mol^{-1} K^{-1}, J is the total angular momentum quantum number of the ion, z is the ionic charge, and r is the ionic radius for coordination number 6 as tabulated by Shannon and Prewitt in Å (except that coordination number 8 was used for M^{4+}).[48] The term c is an additive correction to ionic radii: 1.20 Å for cations and 0.40 Å for anions.

This equation was selected because it fits the functional form of the Born equation for the entropy of solvation of an ion:

$$\Delta S = \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{z^2e^2}{2rD^2}\left(\frac{\partial D}{\partial T}\right)_P$$

The additive corrections to z and r, as well as the constants 256.8 and 32.84, were chosen to provide the best least-squares fit to the observed entropies of the 62 monatomic aqueous ions. The additive corrections to z and to r were inserted to compensate for the solvent polarization, particularly by highly charged ions, so as to *reduce* their effective charges and to increase their effective radii.

The above equation has been used to estimate aquo-ion entropies for many ions so that enthalpies and free energies of these ions may be calculated and compared. Entropies thus estimated are shown in Table I in parentheses.

C. Energy Differences of Electron Configurations

It has been recognized for several years that the only lanthanide gaseous atoms which have the "normal" trivalent ground-state configuration f^qds^2 are La, Ce, Gd, and Lu. As improved spectroscopic interpretations of atomic energy levels became available, it was also recognized that the energy difference between the f^qds^2 and the $f^{q+1}s^2$ configurations (the latter being the ground-state configuration of all other lanthanides) fit a regular pattern.[8] Nugent and Vander Sluis showed how these energy differences were explained by application of Jorgensen's refined electron-spin pairing correlation theory,[51] and they later refined their treatment of these energy differences.[52] The same theory has been applied to other low-lying electron configurations,[53] to lanthanide and actinide aquo ion (IV)–(III) and (III)–(II) reduction potentials,[54–57] to vaporization properties of the lanthanide and actinide metals,[57] and to third and fourth ionization energies of the lanthanides.[58]

Brewer[59,60] and Martin[61] also independently correlated the energy differences between several configurations in the gaseous neutral atoms, and in the +1, +2, and +3 ions. These correlations were used to systematize vaporization behavior and to estimate the energy levels of many unassigned configurations.

D. Correlation of f–d and Electron Transfer Spectra with Aqueous Electrode Potentials

Nugent, Baybarz, Burnett, and Ryan have shown in two major papers[55,56] that the known lanthanide and actinide (IV)–(III) and (III)–(II) reduction potentials in aqueous solution may be correlated with linear and unit-slope behavior with appropriate f–d bands observed in crystals, aqueous solution, and nonaqueous complexed solutions. Similarly, they showed a linear, unit-slope correlation between the reduction potentials and the electron-transfer bands of hexahalo-coordinated M(IV) and M(III) ions in acetonitrile solution. Using the electron-spin correlation "linearization energies", they have linearized these directly or indirectly determined reduction potentials and then used the straight-line plots to predict "linearized" M(IV)–(III) and M(III)–(II) reduction potentials. The linearization energies were then applied to generate predicted reduction potentials. (To predict trivalent–divalent reduction potentials for elements whose divalent aquo ions are in the f^qd configuration instead of in the f^{q+1} configuration, appropriate f–d spectra were used.) It should be noted that these authors present "best values" for both (IV)–(III) and (III)–(II) potentials in the latter paper,[56] as well as in a more recent review.[16]

E. Enthalpies of Vaporization of Metals

Corbett[62] stated that the enthalpies of vaporization of the lanthanide metals correlate with ease of reduction of trivalent species; i.e., reaction 1 will proceed further to the right when the metal is unstable (easily vaporized). (More recently, Johnson[36] showed that the third ionization energies are also responsible for the ease of reduction of the trihalides: reaction 1 proceeds further to the right when the M^{2+} ion has a higher ionization energy.) Brewer[59] clearly showed why the enthalpies of vaporization of the lanthanide metals vary as they do. Even though the crystal structures of most of the metals, excepting Sm, Eu, and Yb, are similar, and even though the metallic bonding is trivalent and the cohesive energy, represented by melting point, of these trivalent metals increases steadily with atomic number, the enthalpies of sublimation *decrease* steadily and sharply from La through Eu and again decrease (though not steadily) from Gd through Yb. This anomalous behavior of the sublimation enthalpies "is not to be attributed to the metallic phase, but is due to the abnormality of the gas. The vapor consists predominantly of atoms of different valence character than in the metal".[59]

By correcting the sublimation enthalpies of those metals whose gaseous atoms are divalent ($f^{n+1}s^2$) to a uniformly trivalent (f^nds^2) atomic configuration (using spectroscopically derived electron configuration energy differences), Brewer[59] and later Nugent et al.[57] showed that the effective bonding energy, or effective sublimation enthalpy, from trivalent metal to trivalent gas, follows a systematic trend as a function of atomic number. Brewer then utilized this trend to predict the energies of unknown electron configurations; Nugent et al. used electron-spin-correlation energy differences to predict the energies of unknown configurations and thus were able to use the sublimation-enthalpy trend to predict sublimation enthalpies (from actual metal to ground-state gaseous atom) for several elements.

Renewed interest in these sublimation enthalpies and their systematic interpretation has been partly responsible for new (and more consistent) determinations of the sublimation enthalpies of Am, Np, and Pu[63,64] and for better preparative methods of the rather volatile heavy actinide metal californium.[65]

F. Ionization Energies

In 1965 Sugar and Reader[66] showed how the smooth change (with number of f electrons) in energy differences ΔT between baricenters of $4f^n6s$ and $4f^n7s$ configurations in the singly ionized elements Ba through Yb could be used to derive ionization energies I_2 for the process $M^+ \rightarrow M^{2+}$. (Hereafter, the ionization energy for $M^{(n-1)+} \rightarrow M^{n+}$ will be referred to as I_n.) They have since extended their treatment to first ionization energies, I_1,[67,68] and to I_3 and I_4.[69] Hertel has presented surface-ionization I_1 values and a tabulation of other determinations published by 1968.[70]

The recent summaries of ionization energies by Moore[71] and by Martin et al.[72] accept the values of Sugar and Reader for I_1 and I_2. Recent experimental values for I_1 of Tb and Tm[69,73] confirm that Hertel's values deviate slightly but systematically from those derived from optical spectra. This review accepts Moore's and Martin's compilations of Sugar and Reader's values for I_1 and I_2.

Vander Sluis and Nugent[53] have extended their electron-spin correlation method to several low-lying configurations of the lanthanide and actinide gaseous atoms and ions; in particular, they related the energy differences of f^qd and f^{q+1} configurations for the ions Ln^{2+} and Ln^{3+} (spectroscopic notation Ln III and Ln IV, respectively). Since the $4f^q$ subshell is relatively unaffected by chemical changes such as the oxidation state of the ion, they successfully applied these energy differences to "linearize" the ionization energies (transitions from f^{q+1} to f^q).[58] They point out that the difference between the I_3 and I_4 values calculated by them and the values calculated by Sugar and Reader[69] may be attributed to the latter authors' interpolation of ΔT (energy differences between $4f^n6s$ and $4f^n7s$). Where differences between the two sets of I_3 and I_4 values exist, the differences are usually less than the sum of the authors' error limits.

Later in this review, a careful comparison of "spectroscopic" ionization energy sums with ionization-energy sums derived from Born–Haber cycles will be made.

G. Hydration Enthalpies and Entropies

Two fundamental calculations of thermodynamic functions of hydration have appeared recently.[74,75] Thetreatment by Goldman and Bates included calculations for several dipositive and tripositive cations. Goldman and Morss have recently extended this treatment to the tripositive lanthanide and actinide ions.[76]

III. Standard-State Experimental Thermodynamic Properties

In this section are reviewed those properties for which definitive measurements have been made. In some cases (such as entropies and ionization energies) the "measurement" may represent enthalpy and free energy, or a self-consistent treatment of some measured energy levels with other reliably estimated terms.

A. Enthalpies of Formation

1. Gaseous Metal Atoms

In Table I are reported the standard-state enthalpies of sublimation at 298.15 K of Y, La, and the lanthanides. Entries are taken from Hultgren et al.,[13] who discuss sources of data and error estimates. (In this review, the policy of NBS Technical Note 270 is followed by tabulating entries so that the error is estimated to be between 2 and 20 times the order of magnitude of the least significant figure.[47]) In the cases of all elements except Ce, the values agree with NBS Technical Notes 270-5 and 270-7.[11,12] Ce exists in two allotropes below room temperature with sluggish and poorly characterized transition properties. The "standard-state" γ form is not stable below about 350 K but it is accepted as the reference state.[11,13] Impurities and uncertainties in phases present are responsible for the poor consistency of reported values of $S°$ for Ce(γ).

2. Trivalent Aquo Ions

The standard state of an aqueous ion is its "hypothetical one-molal" solution which, in the case of enthalpy, corresponds to the infinitely dilute state. It is conventional to tabulate single-ion properties by defining the corresponding property for the hydrogen aquo ion as equal to zero. For the lanthanides, the commonly encountered tripositive ions are only slightly hydrolyzed in neutral solution, and it is experimentally meaningful to describe standard-state enthalpies.

The most precise way of determining a standard-state aquo-ion enthalpy is to proceed experimentally in three steps:

a. React the metal with hydrogen-saturated acid HX as dilute as possible while maintaining a moderate reaction time (eq 2).

b. Dissolve the anhydrous metal halide MX_3 in the same acid, or more precisely, in HX of a molality such that the final concentrations are identical in steps a and b (eq 3).

c. Dissolve the metal halide MX_3 in pure water at high dilution and extrapolate the enthalpy of solution to infinite dilution by an extended Debye–Hückel calculation[77-79] (eq 5). These measurements may be combined with appropriate literature thermodynamic data (eq 4).

$$M(c) + 3HCl(m) \rightarrow MCl_3(\text{in } m\text{ HCl}) + \tfrac{3}{2}H_2(g) \qquad (2)$$

$$MCl_3(c) \rightarrow MCl_3(\text{in } m\text{ HCl}) \qquad (3)$$

$$\tfrac{3}{2}H_2(g) + \tfrac{3}{2}Cl_2(g) \rightarrow 3HCl(m) \qquad (4)$$

$$MCl_3(c) \rightarrow MCl_3(\text{in } \infty\ H_2O) \qquad (5)$$

(In the following calculations and in Tables I and III, it is assumed that solutions of MCl_3 *are infinitely dilute in* MCl_3*, i.e., that corrections have been made to infinite dilution when* MCl_3 *is dissolved in pure water and that no corrections are necessary when M or* MCl_3 *is dissolved in high dilution in HCl.)* From the above equations, $\Delta H_f°(MCl_3,c) = \Delta H_2 - \Delta H_3 + \Delta H_4$, and $\Delta H_f°(M^{3+},aq) = \Delta H_2 - \Delta H_3 + \Delta H_4 + \Delta H_5 - 3(\Delta H_f°(Cl^-,aq))$.

Another possible sequence of reactions begins with the heat of combustion of the metal to its sesquioxide:

$$M(c) + \tfrac{3}{4}O_2(g) \rightarrow MO_{1.5}(c) \qquad (6)$$

$$MO_{1.5}(c) + 3HCl(m) \rightarrow MCl_3(\text{in } m\ HCl) + \tfrac{3}{2}H_2O(\text{in } m\ HCl) \qquad (7)$$

$$\tfrac{3}{2}H_2(g) + \tfrac{3}{2}Cl_2(g) \rightarrow 3HCl(m) \qquad (4)$$

$$\tfrac{3}{2}H_2(g) + \tfrac{3}{4}O_2(g) \rightarrow \tfrac{3}{2}H_2O(\text{in } m\ HCl) \qquad (8)$$

$$MCl_3(c) \rightarrow MCl_3(\text{in } m\ HCl) \qquad (3)$$

$$MCl_3(c) \rightarrow MCl_3(\text{in } \infty\ H_2O) \qquad (5)$$

For this reaction sequence, $\Delta H_f°(MCl_3,c) = \Delta H_6 + \Delta H_7 + \Delta H_4 - \Delta H_8 - \Delta H_3$, and $\Delta H_f°(M^{3+},aq) = \Delta H_6 + \Delta H_7 + \Delta H_4 - \Delta H_8 - \Delta H_3 + \Delta H_5 - 3(\Delta H_f°(Cl^-,aq))$.

Calorimetric determinations of the heats of reactions 2, 3, 5, 6, and 7 have been made by numerous investigators. Reactions 4 and 8 represent the partial molal enthalpies of formation of HCl and H_2O into solutions of the indicated HCl molality *m*. These partial molal enthalpies, $\bar{H}$, were calculated from apparent molal enthalpies[47] by the method of Young and Vogel.[80] The values used are shown in Table II. The NBS value[47] of $\Delta H_f°(Cl^-,aq) = -167.16$ kJ mol^{-1} has been used, in preference to the CODATA value,[81] *in order to maintain self-consistency with Table II.*

In Table III are shown the values of ΔH_1 through ΔH_7 and the resulting $\Delta H_f°(MCl_3,c)$, with a "best value" chosen for each $\Delta H_f°(MCl_3,c)$. Then the "best value" of $\Delta H_f°(MCl_3,c)$ was combined with $\Delta H_5 - 3(\Delta H_f°(Cl^-,aq))$ and a "best value" for $\Delta H_f°(M^{3+},aq)$ was estimated from the relative quality of the experimental entries. The "best values" of $\Delta H_f°(M^{3+},aq)$ were then entered into Table I; these values are generally in good agreement with those of the National Bureau of Standards.[11] Error limits represent the author's estimate of 95% confidence and are based where possible on errors quoted for the individual measurements.

3. Divalent Aquo Ions

Experimental measurements have been completed only for the enthalpy of formation and of solution of $EuCl_2$, since Eu(II) is the only lanthanide(II) ion which can exist in water for an appreciable period of time.[30,31] Although the compounds $NdCl_2$, $SmCl_2$, $DyCl_2$, $TmCl_2$, and $YbCl_2$ reduce water rapidly, enthalpies of formation of all these compounds have been determined. From estimates of their heats of solution, the enthalpies of formation of these $Ln^{2+}(aq)$ ions have been calculated.[33,82] These estimates are shown in Table I. The only other lanthanide(II) chloride which has been prepared is $HoCl_{2.14}$, and its enthalpy of formation is not yet known.[83]

TABLE II. Thermal Properties of HCl(aq) (25 °C)[a]

Molarity	Molality	Mol of H_2O / Mol of HCl	$\bar{H}(HCl)$, kJ mol^{-1}	$\bar{H}(H_2O)$, kJ mol^{-1}
6.00	6.83	8.12	−153.5	−286.65
4.00	4.36	12.72	−158.5	−286.14
2.00	2.08	26.7	−162.6	−285.89
1.50	1.55	35.8	−163.5	−285.87
1.00	1.02	54.4	−164.4	−285.85
0.50	0.50	111.0	−165.4	−285.83
0.25	0.25	222.0	−166.0	−285.83
0.10	0.10	555.1	−166.4	−285.83
0	0	∞	−167.2	−285.83

[a] Calculated from the apparent molal properties in ref 47 by the method of ref 80.

4. Tetravalent Aquo Ions

The only tetravalent aquo ion of the lanthanides is that of cerium, although there is an unconfirmed claim of preparation of complexed aquo ions of Pr(IV).[84] Although the heat of reduction of Ce(IV) by Fe(II) has recently been determined in aqueous sulfuric acid, the resultant conventional $\Delta H = -134.3$ kJ mol^{-1} for the reaction

$$Ce^{4+}(aq) + \tfrac{1}{2}H_2(g) \rightarrow Ce^{3+}(aq) + H^+(aq) \qquad (9)$$

cannot be corrected for the effects of sulfate complexing.[85] Conley conducted a careful potentiometric study of the emf of the Ce(IV)-Ce(III) couple in 1.0 *m* $HClO_4$ at temperatures between 8 and 45 °C and at cerium ion concentrations between 0.0005 and 0.07 *m*.[86] By extrapolating to zero concentrations of cerium species, and by correcting for the extensive hydrolysis

$$Ce^{4+} + H_2O \rightarrow Ce(OH)^{3+} + H^+ \qquad (10)$$

for which $K_{eq} \approx 5.2$ at 25 °C,[87,88] Conley used emf temperature coefficient data to calculate $\Delta H = -n[\partial(E/T).\partial(1/T)]$ for reaction 9 as -121 ± 3 kJ mol^{-1} and ΔH *for the reaction*

$$Ce(OH)^{3+}(aq) + \tfrac{1}{2}H_2(g) \rightarrow Ce^{3+}(aq) + H_2O(l) \qquad (11)$$

as -171.5 ± 1.7 *kJ mol*$^{-1}$*. The* ΔH *measured by many* researchers and reported by NBS Technical Note 270-7 as −696.2 − (−537.2) = −160.0 kJ mol^{-1} is believed to correspond mostly to reaction 11. The $\Delta H_f°(Ce^{4+},aq)$ entry in Table I was calculated from the entry for Ce^{3+},aq and ΔH for reaction 9 calculated from Conley's data as follows:

$$\Delta G°(9) = -nFE° = -(96487)(1.7431) = -168.2 \text{ kJ mol}^{-1}$$

$$\Delta S°(9) = nF\frac{dE°}{dT} = -(96487)\left(\frac{0.00154\ V}{K}\right) = 148.6 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta H°(9) = \Delta G°(9) + T\Delta S°(9) = -123.9 \text{ kJ mol}^{-1}$$

Everett and Skoog[88] derived $K_{eq} = 6.4 \pm 0.4$ and $\Delta H = 67 \pm 5$ kJ mol^{-1} for the hydrolysis reaction, eq 10, measuring concentrations of Ce(IV) species spectroscopically in the near-ultraviolet. If their data are combined with the calorimetric ΔH for reaction 11, then $\Delta H(9)$ becomes −104 kJ mol^{-1}, a value in fair agreement with that derived above from potentiometry.

B. Entropies

1. Metals

Low-temperature heat capacities are available for all of the lanthanide metals (excepting Pm), most determinations having been made at the Ames Laboratory of Iowa State University. Entropies derived from these measurements have been evaluated by Hultgren et al.[13] Hultgren's "selected values" are in good agreement with the recently evaluated "selected values" of the National Bureau of Standards,[11] and the latter values are listed in Table I. Promethium metal is isostructural with Pr and Nd metals; its entropy was estimated.[15,89]

TABLE III. Experimental Data Used to Derive $\Delta H_f^\circ(MCl_3, c)$ and $\Delta H_f^\circ(M^{3+}, aq)$ (all entries in kJ mol^{-1})

M	m(HCl)	ΔH_2	Ref	ΔH_3	Ref	ΔH_6	Ref	ΔH_7	Ref	$\Delta H_f^\circ(MCl_3, c)$	ΔH_5	Ref	$\Delta H_f^\circ(M^{3+}, aq)$
Y	1.47	−678.1	*a*	−195.0	*a*					−973.9			
	0.50			−215.4	*b*	−952.8	14	−195.3	*b*	−1000.2			
									Best value:	−996 ± 10	−203.7	*c*	−698
											−224.6	*b*	−719
											−194.6	*d*	−689
												Best value:	−715 ± 15
La	0.26	−705.7	*a*	−130.3	*a*					−1073.4			
	1.02	−705.0	*e*	(−125.5)	*f*					−1072.7			
	1.02	−705.5	*g*	(−125.5)	*f*					−1073.2			
	1.55	−701.0	*h*	(−121.8)	*f*					−1069.7			
	0.52			−130.0	*i*	−897.1	14	−237.2	*i*	−1071.8			
	1.02	−707.9	*j*	(−125.5)	*f*					−1075.6			
	1.02			(−125.5)	*f*	−897.1	14	−237.1	*g*	−1073.1			
	1.02			(−125.5)	*f*	−897.1	14	−237.7	*j*	−1073.7			
									Best value:	−1073.2 ± 1.5	−137.8	*c,i*	−709.4
											−134.9	*k*	−706.5
												Best value:	−709.4 ± 1.6
Ce	0.24	−699.1	78	−137.1	78					−1060.0			
	1.5	−695.5	*l*	−129.4	*l*					−1056.6			
									Best value:	−1058.0 ± 2.0	−144.0	77	−700.4 ± 2.1
Pr	0.25	−704.1	*a*	−142.2	*a*					−1059.9			
	1.47	−692.8	*a*	−125.5	*a*					−1058.1			
	1.02	−687.8	*m*	(−128.)	*f*					−1053.			
	1.55	−694.3	*h*	(−125.5)	*f*					−1059.3			
									Best value:	−1059.0 ± 1.5	−149.3	*c*	−706.7
											−148.4	*k*	−705.8
												Best value:	−706.2 ± 1.6
Nd	0.20	−685.8	32	−154.8	32					−1029.3			
	0.24	−680.3	78	−148.7	78					−1029.6			
	1.02			(−146.)	*f*	−904.0	14	−217.4	*n*	−1040.			
	4.36	−693.6	*o*	−127.3	*o*					−1041.8			
	4.36	−693.6	*p*	−127.3	*o*					−1041.8			
	4.36			−127.3	*o*	−904.0	14	−219.2	*p*	−1042.2			
									Best value:	−1041.8 ± 1.5	−156.9	77	−697.1
											−155.2	*k*	−695.4
												Best value:	−696.6 ± 1.7
Sm	0.48			−158.5	*q*	−911.8	14	−204.4	*q*	−1025.2			
	1.02	−682.8	*j*	(−155.)	*f*					−1021.			
	2.08			−151.9	82	−911.8	14	−208.6	*r*	−1027.5			
	2.08	−690.1	*r*	−151.9	82					−1026.0			
	1.02			(−155.)	*f*	−911.8	14	−195.6	*j*	−1017.			
									Best value:	−1026.0 ± 1.5	−167.1	*c*	−691.5
											−166.9	*k*	−691.3
											−166.1	82	−690.5
												Best value:	−691.1 ± 1.7
Eu	4.36	−582.4	*s*	−143.6	*s*					−914.3			
	4.36	−605.2	*t*	−143.6	*s*					−937.1			
	4.36			−143.6	*s*	−825.7	*t*	−207.2	*t*	−935.6			
	4.36			−143.6	*s*	−831.4	*t*	−202.8	*s*	−936.9			
	1.02	−632.6	*n*	(−159.)	*f*					−967.			
	6.83	−589.1	30	−129.3	29					−920.3			
	1.02			(−159.)	*f*	−825.7	*t*	−198.7	*n*	−930.			
									Best value:	−936.5 ± 2.0	−170.7	29	−605.6 ± 2.3
Gd	0.25	−683.6	*a*	−174.1	*a*					−1007.5			
	6.83	−694.6	*n*	(−142.)	*f*					−1013.1			
	6.83			(−142.)	*f*	−907.8	14	−211.3	*n*	−1007.6			
									Best value:	−1007.6 ± 2.0	−179.9	*c*	−685.9
											−181.8	79	−687.8
												Best value:	−687.0 ± 2.1
Tb	0.89	−696.2	*u*	−181.5	*u*					−1008.5			
	1.02	−701.7	*v*	(−180.)	*f*					−1014.			
	4.36	−689.9	*w*	−167.9	*w*					−997.5			
									Best value:	−1007 ± 6	−187.0	*d*	−692
											−192.4	*u*	−698
												Best value:	−698 ± 6
Dy	4.36	−695.3	*x*	−180.4	*y*					−990.4			
	4.36	−692.4	*y*	−180.4	*y*					−987.5			
	4.36			−180.4	*y*	−931.6	*x*	−192.6	*x*	−990.1			
									Best value:	−990.1 ± 2.5	−207.4	*y*	−695.9 ± 2.8

TABLE III (Continued)

M	m(HCl)	ΔH_2	Ref	ΔH_3	Ref	ΔH_4	Ref	ΔH_7	Ref	$\Delta H_f°(\mathrm{MCl_3}, c)$	ΔH_5	Ref	$\Delta H_f°(\mathrm{M^{3+}}, aq)$
Ho	0.89	−698.3	*u*	−202.3	*u*					−989.8			
	4.36	−710.5	*w*	−180.5	*w*					−1005.5			
									Best value:	−995 ± 8	−213.4	*u*	−707 ± 8
Er	1.44	−661.4	*a*	−193.3	*a*					−959.2			
	1.43	−661.4	*a*	−201.9	*y*					−950.6			
	1.43			−201.9	*y*	−948.9	14	−188.	*y*	−997.			
									Best value:	−995 ± 10	−215.1	*y*	−708
											−208.3	*c*	−702
											−210.7	*d*	−704
												Best value:	−705 ± 10
Tm	0.91	−705.7	*u*	−205.8	*u*					−993.7			
	4.36	−698.0	*z*	−186.6	*z*					−986.9			
									Best value:	−991.0 ± 3.0	−215.8	*u*	−705.2 ± 3.0
Yb	4.36	−671.7	*z*	−187.2	*z*					−960.0 ± 3.0	−216.1	*c*	−674.5 ± 3.0
Lu	0.91	−700.0	*u*	−208.1	*u*					−985.7 ± 2.6	−218.5	*u*	−702.6 ± 2.6

[a] F. H. Spedding and J. P. Flynn, *J. Am. Chem. Soc.*, **76**, 1474 (1954). [b] R. L. Montgomery and T. D. Hubert, *U.S. Bur. Mines, Rep. Invest.*, No. 5659 (1960) (ΔH_5 corrected to infinite dilution). [c] F. H. Spedding and J. P. Flynn, *J. Am. Chem. Soc.*, **76**, 1477 (1954). [d] G. A. Krestov, V. A. Kobenin, and S. V. Semenovskii, *Russ. J. Inorg. Chem.*, **18**, 1 (1973). [e] L. R. Morss, Ph.D. Thesis, University of California, Berkeley, 1969 (Lawrence Radiation Laboratory Report UCRL-18951). [f] Estimated from functional dependence of ΔH(soln, $\mathrm{MCl_3}$) on m(HCl). [g] G. C. Fitzgibbon, C. E. Holley, Jr., and I. Wadsö, *J. Phys. Chem.*, **69**, 2464 (1965). [h] H. R. Lohr and B. B. Cunningham, *J. Am. Chem. Soc.*, **73**, 2025 (1951), omitting runs La-1, La-2, and Pr-3. [i] R. L. Montgomery, *U.S. Bur. Mines, Rep. Invest.*, No. 5445 (1959). [j] G. G. Gvelesiani and T. S. Yashvili, *Zh. Neorg. Khim.*, **12**, 3233 (1967). [k] G. A. Krestov, V. A. Kobenin, and S. V. Semenovskii, *Russ. J. Inorg. Chem.*, **17**, 421 (1972). [l] R. L. Montgomery, *U.S. Bur. Mines, Rep. Invest.*, No. 6146 (1962). [m] C. T. Stubblefield, *Rev. Sci. Instrum.*, **40**, 456 (1969). [n] T. S. Yashvili and G. G. Gvelesiani, *Russ. J. Phys. Chem.*, **45**, 551 (1971) (values refer to monoclinic oxides). [o] J. M. Stuve, *U.S. Bur. Mines, Rep. Invest.*, No. 6697 (1965). [p] G. C. Fitzgibbon, D. Pavone, and C. E. Holley, Jr., *J. Chem. Eng. Data*, **13**, 547 (1968). [q] R. L. Montgomery and T. D. Hubert, *U.S. Bur. Mines, Rep. Invest.*, No. 5525 (1959). [r] F. B. Baker, G. C. Fitzgibbon, D. Pavone, C. E. Holley, Jr., L. D. Hansen, and E. A. Lewis, *J. Chem. Thermodyn.*, **4**, 621 (1972). [s] J. M. Stuve, *U.S. Bur. Mines, Rep. Invest.* No. 6640 (1965) (values for cubic $\mathrm{EuO_{1.5}}$ were used). [t] G. C. Fitzgibbon, E. J. Huber, Jr., and C. E. Holley, Jr., *J. Chem. Thermodyn.*, **4**, 349 (1972) (values for cubic or monoclinic $\mathrm{EuO_{1.5}}$ were used as appropriate). [u] F. H. Spedding and W. R. Bisbee, private communication (heats of solution of metals corrected for presence of impurities). [v] G. C. Fitzgibbon and C. E. Holley, Jr., *J. Chem. Eng. Data*, **13**, 63 (1968). [w] J. M. Stuve, *U.S. Bur. Mines, Rep. Invest.*, No. 7046 (1967). [x] E. J. Huber, Jr., G. C. Fitzgibbon, and C. E. Holley, Jr., *J. Chem. Thermodyn.*, **3**, 643 (1971). [y] R. L. Montgomery and J. M. Stuve, *U.S. Bur. Mines, Rep. Invest.*, No. 5892 (1961) (ΔH_5 corrected to infinite dilution). [z] J. M. Stuve, *U.S. Bur. Mines, Rep. Invest.*, No. 6902 (1967).

2. *Aqueous Ions*

The careful measurements and calculations for $\bar{S}°(\mathrm{Ln^{3+}},aq)$ of Hinchey and Cobble[44] have been refined by Schumm.[11,90] Recently, a set of careful measurements of heat capacities of hydrated lanthanide trichlorides has been begun by Spedding et al.[45] Their measurements have not yet been reported for the entire series, but agree with earlier values with the exception of Gd. Schumm has recalculated $S(\mathrm{GdCl_3{\cdot}6H_2O})$ = 408.2 J mol^{-1} K^{-1} from the data of Hellwege et al.,[91] whereas Spedding et al. find 400.8 J mol^{-1} K^{-1}. The National Bureau of Standards values[11] have been accepted in Table I. The values for $\mathrm{Pm^{3+}}$(aq) and $\mathrm{Tm^{3+}}$(aq) are estimates based upon eq 1. (The entry for $\mathrm{Tm^{3+}}$(aq) in NBS Technical Note 270-7 is also an estimate.[90])

The only nontrivalent ions for which experimental data are available are $\mathrm{Eu^{2+}}$(aq) and $\mathrm{Ce^{4+}}$(aq). The NBS Technical Note 270-7 entry[11] $\bar{S}°(\mathrm{Eu^{2+}},aq)$ = 4 J mol^{-1} K^{-1} has been calculated from the entries for $\Delta H_f°$ and $\Delta G_f°$. The self-consistent set of data selected by Morss and Haug[31] yields a more reliable value for this datum, and their value is quoted in Table I. Likewise, the NBS Technical Note 270-7 entry $S°(\mathrm{Ce^{4+}},aq)$ = −301 J mol^{-1} K^{-1} has been calculated from the corresponding entries for $\Delta H_f°$ and $\Delta G_f°$. However, Conley's emf study[86] of the Ce(IV)–Ce(III) couple in 1.0 m $\mathrm{HClO_4}$ yielded $E°$ = +1.7431 ± 0.0002 V and $\mathrm{d}E°/\mathrm{d}T$ = +1.54 mV/K for reaction 9, and $E°$ = +1.6966 ± 0.0002 V and $\mathrm{d}E°/\mathrm{d}T$ = −0.28 mV/K for reaction 11. The calculated $\Delta S = n(\mathrm{d}E°/\mathrm{d}T)$ for these two reactions, combined with entropies of other species, yields $\bar{S}°(\mathrm{Ce^{4+}},aq)$ = −419 J mol^{-1} K^{-1}.

C. Reduction Potentials

In this section, only direct experimentally derived potentials will be considered: equilibrium emf measurements, polarographic values, and spectroscopic electron-transfer spectra. All potentials are reduction potentials, as defined by IUPAC, referenced to the standard hydrogen electrode.[92]

1. *M(IV)–(III)*

The only couple for which equilibrium emf data may be obtained in aqueous solution is the Ce(IV)–(III) couple. The value of −1.74 V has been derived by Conley[86] and has been accepted by Nugent et al.[55] and by NBS.[11] It is in substantial agreement with the earlier review of Wadsworth et al.[93]

From spectroscopic evidence (f-d absorption band energies of M(III) species and electron transfer spectra of complexes of M(IV) species), Nugent et al.[55,56] estimated M(IV)–(III) potentials for Pr, Nd, Tb, and Dy. Their estimates agree reasonably well with earlier estimates based upon the stability of Pr(IV) and Tb(IV) compounds,[5] and with similar systematic correlations for the actinide(IV) aquo ions, for which more emf data are available. The spectroscopic values are quoted in Table IV in the far right-hand column.

2. *M(III)–(II)*

The only couple for which equilibrium M(III)–(II) emf data are measurable is that for europium. It is well recognized that the early datum of McCoy,[94] $E°$ = −0.43 V, is too negative because of the preferential complexing of $\mathrm{Eu^{3+}}$(aq) in the 0.1 M formate medium. Three independent measurements,[31,95,96] confirm this conclusion; $E°$ = −0.35 ± 0.03 V. Entries for $\Delta G_f°(\mathrm{Eu^{2+}},aq)$ and $\Delta G_f°(\mathrm{Eu^{3+}},aq)$ in NBS Technical Note 270-7 also yield $E°$ = −0.35 V.[11]

Unfortunately, agreement is not so good for the other two classical M(II) ions. The definitive electrochemical studies are the polarographic determinations of Timnick and Glockler[97] for Sm and of Laitinen[98] for Yb. These determinations were performed in supporting electrolytes consisting principally of 0.1 M $\mathrm{I^-}$ and $\mathrm{Cl^-}$ respectively; Johnson[99] has corrected the reported $E°$ estimates (−1.55 and −1.15 V respectively) to −1.50 and −1.10 V to correct for complexing and ionic strength (in the solutions used for polarographic measurements) so as to be consistent with $E°(\mathrm{Eu^{3+}}–\mathrm{Eu^{2+}})$. For example, Laitinen and Taebel[100] found $E°(\mathrm{Yb^{3+}}–\mathrm{Yb^{2+}})$ and $E°(\mathrm{Eu^{3+}}–\mathrm{Eu^{2+}})$ to be

TABLE IV. Standard Reduction Potentials and Free Energies of Formation at 25 °C

M	ΔG_f° (M^{2+},aq)/ kJ mol^{-1} [a]	$E^\circ(M^{3+} \rightarrow M^{2+})$/V				ΔG_f° (M^{3+},aq)/ kJ mol^{-1} [c]	$E^\circ(M^{3+} \rightarrow M)$/V [d]	ΔG_f° (M^{4+},aq)/ kJ mol^{-1} [a]	$E^\circ(M^{4+} \rightarrow M^{3+})$/V		
		Elec	Therm[b]	Therm[99]	Spect[56]				Elec	Therm[e]	Spect[56]
Y						−685	−2.37				
La	−325		−3.74	−3.8	−3.1	−686	−2.37				
Ce	−313		−3.76	−3.5	−3.2	−676	−2.34	−506	1.74[86]	1.76	1.8
Pr	−388		−3.03	−3.0	−2.7	−680	−2.35	−304		3.9	3.2
Nd	−419		−2.62	−2.8	−2.6	−672	−2.32	−197		4.9	5.0
Pm	−405		−2.67	−2.5	−2.6	−663	−2.29	−143		5.4	4.9
Sm	−514	−1.55[97]	−1.57	−1.5	−1.6	−665	−2.30	−167		5.2	5.2
Eu	−541	−0.35[31]	−0.35	−0.35	−0.3	−574	−1.99	21		6.2	6.4
Gd	−295		−3.82	−3.6	−3.9	−664	−2.29	52		7.4	7.9
Tb	−332		−3.47	−3.5	−3.7	−667	−2.30	−369		*f*	3.1
Dy	−430		−2.42	−2.6	−2.6	−664	−2.29	−233		4.5	5.2
Ho	−405		−2.80	−2.9	−2.9	−675	−2.33	−128		5.7	6.2
Er	−383		−2.96	−3.0	−3.1	−669	−2.31	−117		5.7	6.1
Tm	−450		−2.27	−2.1	−2.3	−669	−2.31	−125		5.6	6.1
Yb	−544	−1.15[98]	−1.04	−1.1	−1.1	−644	−2.22	16		6.8	7.1
Lu						−667	−2.30	113		8.1	8.5

[a] From appropriate enthalpies and entropies in Table I; see text, section VI. [b] Using $\Delta G_f^\circ(M^{2+},aq)$ and $\Delta G_f^\circ(M^{3+},aq)$ in this table. [c] From ΔH and appropriate entropies in Table I. [d] Using $\Delta G_f^\circ(M^{3+},aq)$ in this table. [e] Using $\Delta G_f^\circ(M^{4+},aq)$ and $\Delta G_f^\circ(M^{3+},aq)$ in this table. [f] E° used to calculate $\Delta H_f^\circ(Tb^{4+},aq)$, so that there is no independent "thermal" E°. See section V, final paragraph.

TABLE V. First Ionization Potentials (eV)

M	Electron impact[a]	Surface ionization[70]	Optical spectra[72, b]
La		5.55 (5)	5.5770 (6)
Ce		5.54 (6)	5.466 (20)
Pr		5.40 (5)	5.422 (20)
Nd		5.49 (5)	5.489 (20)
Pm			5.554 (20)
Sm	5.56 (10)	5.61 (5)	5.631 (20)
Eu	5.61 (10)	5.64 (5)	5.666 (7)
Gd	5.98 (10)	6.16 (5)	6.141 (20)
Tb		5.89 (4)	5.852 (20)
Dy	5.80 (10)	5.82 (3)	5.927 (8)
Ho	5.85 (10)	5.89 (3)	6.018 (20)
Er	6.11 (10)	5.95 (3)	6.101 (20)
Tm	5.87 (10)	6.03 (4)	6.18436 (6)
Yb	5.90 (10)	6.04 (4)	6.25394 (2)
Lu		5.32 (5)	5.42589 (2)

[a] K. F. Zmbov and J. L. Margrave, *J. Phys. Chem.*, **70**, 3014 (1966). [b] The entries with error limits of 0.02 eV are interpolations from energy differences.

−1.173 and −0.429 V, respectively. Since $E^\circ(Eu^{3+}\text{-}Eu^{2+})$ is generally agreed to be nearer to −0.35 V, a similar correction is reasonable for $E^\circ(Yb^{3+}\text{-}Yb^{2+})$. The polarographic medium for Sm[97] was somewhat different, but a similar correction was applied.[101] Poor agreement is indicated by the derived E° values, from ΔG_f° entries in NBS Technical Note 270-7, of −1.75 and −1.21 V for these two reduction potentials.[11]

Again, spectroscopically estimated M(III)–(II) potentials by Nugent et al.[56] are also quoted in Table IV.

IV. Ionization Potentials

A. Measurements

1. First Ionization Potentials (I_1)

There are three methods of determining first ionization potentials from experimental measurements: analyses of optical spectra, surface ionization, and electron impact. The three most recent determinations of I_1 for the lanthanides are quoted in Table V. There is general agreement that spectroscopic ionization potentials are the most accurate whenever they are available. Unfortunately, the most recent compilation of lanthanide ionization potentials[72] is based solely on spectroscopic interpretations; despite the small error limits on these values, it must be remembered that some entries are based in part upon estimates and interpolations. Nevertheless, they are the best available ionization potentials and the spectroscopic values have been used in all calculations in this review.

2. Second Ionization Potentials ($M^+ \rightarrow M^{2+}$) (I_2)

Accurate (±0.01 eV or better) values have been derived from optical spectra for La, Eu, and Yb. Other values have been estimated from interpolations of energy differences, with an estimated uncertainty of ±0.08 eV. The one exception is Lu, for which the uncertainty in the second ionization potential is ±0.4 eV. Best values are tabulated by Martin et al.[72]

3. Third and Fourth Ionization Potentials (I_3, I_4)

For these transitions, the number of independently derived spectroscopic ionization potentials is quite small; the best experimental values are those of Sugar et al.[68,102] There are two independent sets of semiempirical correlations for the remaining members of each series.[58,69]

B. Calculations

In recent years, three independent sets of lanthanide ionization-potential sums were calculated from thermochemical cycles.[103-105] Even though spectroscopic correlations are now available, thermochemical calculations are still important: Sugar and Reader[69] compared their spectroscopic results with the thermochemical ones of Faktor and Hanks;[103] and there is no a priori way of choosing between the methodology of Sugar and Reader and that of Vander Sluis and Nugent.[58] Because excellent enthalpies of formation of oxides and chlorides are now available, a careful Born–Haber cycle calculation of ionization-potential sums is given here for comparison with the spectroscopic values.

There are two series of isostructural lanthanide compounds for which accurate structural and thermodynamic data are known, and for which it is reasonable to assume that the compounds are nearly ionic: the cubic sesquioxides and the compounds Cs_2NaMCl_6. The C-form (bccub) sesquioxides of Sm through Lu are the stable modifications at room temperature; it is also possible to prepare pure Pr_2O_3 and Nd_2O_3 in the bccub C modification.[106-108] Enthalpies of formation have been reviewed by Gschneidner et al.[14] Crystallographic unit-cell di-

TABLE VI. Born–Haber Cycle for Cubic Sesquioxides

M	a_0/Å	U_{calcd}/kJ mol^{-1}	ΔH_f°/kJ mol^{-1}	U_{BH}/kJ mol^{-1}	$(I_1 + I_2 + I_3)$/kJ mol^{-1}
Y	10.6021[108]	−13428	−1864[14]	−13466[a]	3776[71]
La	11.36[b]	−12687	−1799[c]	−12780[a]	3456[72]
Ce	11.172[d]	−12901	−1799[c]	−12897[a]	3523[72]
Pr	11.140[e]	−12938	−1828[107]	−13002[a]	3628[72]
Nd	11.080[108]	−13008	−1812[c]	−13057[h]	3691[a]
Pm	10.99[f]	−13114		−13148[h]	
Sm	10.934[108]	−13181	−1828[14]	−13200[h]	3876[a]
Eu	10.860[108]	−13271	−1663[14]	−13275[h]	4027[a]
Gd	10.8122[108]	−13330	−1827[14]	−13320[h]	3746[a]
Tb	10.7281[g]	−13434	−1865[14]	−13409[h]	3780[a]
Dy	10.6647[108]	−13514	−1863[14]	−13475[h]	3912[a]
Ho	10.6065[108]	−13588	−1881[14]	−13534[h]	3922[a]
Er	10.5473[108]	−13665	−1898[14]	−13596[h]	3928[a]
Tm	10.4866[108]	−13744	−1889[14]	−13660[h]	4050[a]
Yb	10.4334[108]	−13814	−1815[14]	−13715[a]	4194[72]
Lu	10.3907[108]	−13871	−1878[14]	−13757[h]	3908[a]

[a] Calculated from Born–Haber cycle (see text). [b] V. B. Glushkova and E. K. Keler, *Dokl. Akad. Nauk SSSR*, **152**, 611 (1963); *Chem. Abstr.*, **60**, 68g (1964). [c] Estimated by assuming $\Delta H_f^\circ(M_2O_3,c) = \Delta H_f^\circ(M_2O_3, \text{hex}) - 4$ kJ/mol. $\Delta H_f^\circ(M_2O_3, \text{hex})$ from ref 14. [d] H. Bommer, *Z. Anorg. Allg. Chem.*, **241**, 273 (1939). [e] L. Eyring and N. Baenzinger, *J. Appl. Phys.*, **33**, 428 (1962). [f] F. Weigel, *Radiochim. Acta*, **4**, 197 (1965). [g] L. Eyring and B. Holmberg in "Nonstoichiometric Compounds", Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D.C., 1963, Chapter 4. [h] U_{calcd} + correction term (to agree with U_{BH} for Pr and Yb).

mensions have been reviewed by Roth and Schneider.[108] The chloro complex compounds Cs_2NaMCl_6 are all face-centered cubic and their enthalpies of formation are known.[105,109-111] For both of these sets of compounds, Born–Haber cycles have been used to calculate ionization-potential sums.[103-105] These calculations are updated in the following section.

1. Oxides

The Born–Haber enthalpy cycle for M_2O_3 is shown in Scheme I. The sublimation term, $\Delta H_f^\circ(M,g)$, is given for each metal in Table I. The common terms are $3\Delta H_f^\circ(O,g) + 3(EA) - 5RT = 3(249.17) + 3(824) - 12.4 = 3207$ kJ.[81,112] Enthalpies of formation of $M_2O_3(c)$ are given in Table VI. The lattice energy U was calculated for each oxide from the equation

$$U = -1389.3\frac{A}{R}\left(1 - \frac{1}{n}\right)\text{ kJ/mol} \qquad (12)$$

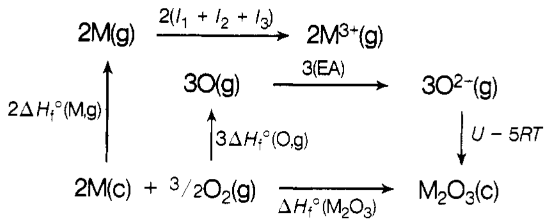
where A is the Madelung constant, R is the average nearest-neighbor Ln–O distance, and n is the exponent in the repulsive term $1/r^n$, estimated from Pauling's rules.[113] Johnson and Templeton calculated the Madelung constant for Y_2O_3, based upon an X-ray powder unit-cell parameter and estimated atomic positions, as $A(R_0) = 24.844$, using the estimated *shortest* internuclear distance $R_0 = 2.2532$ Å.[114] A more precise unit-cell parameter has since been determined by X-ray powder diffraction.[108] Single crystals of Y_2O_3 have since been studied by X-ray and neutron diffraction.[115,116] Converting the Madelung constant from that for the *shortest* internuclear distance R_0 to that for Johnson and Templeton's[114] *mean* internuclear distance $\langle R\rangle$, 2.2781 Å, we obtain $A(\langle R\rangle) = 25.118$. It has also been shown by Gashurov and Sovers[117] that the repulsive parameter $n = 9$ is most consistent with the Ln_2O_3 lattice energies and that the relative atomic positions are nearly the same for the entire series of cubic oxides. From Gashurov and Sovers' calculations, one may calculate the *mean* Ln–O distance $\langle R\rangle$ to be $0.21523a_0$ for the cubic oxides Pr_2O_3 through Lu_2O_3. Using $A(\langle R\rangle) = 25.118$ for the lanthanide oxides is justified because Gashurov and Sovers[117] showed that there is little variation between lattice energy and relative atomic positions, and because this value was used in calculating the lattice energies U_{calcd} shown in Table VI. An accurate cubic lattice parameter a_0 is known for most lanthanide sesquioxides; even for La_2O_3 and Ce_2O_3 there are reported values, the best of which are shown in Table VI.

For those elements with accurate spectroscopic ionization-potential sums (La, Ce, Pr, Yb, and Y), we have calculated Born–Haber lattice energies $U(M_2O_3)_{\text{BH}} = \Delta H_f^\circ(M_2O_3,c) - 2\Delta H_f^\circ(M,g) - 2(I_1 + I_2 + I_3) - 3207$ kJ. Because La_2O_3 and Ce_2O_3 have poorly characterized cubic oxides, and because yttrium is not a 4f element, the differences between U_{calcd} and U_{BH} for Pr_2O_3 and Yb_2O_3 have been interpolated and extrapolated to generate U_{BH} for the other oxides; the lattice-energy corrections take into account systematic errors such as the constant uncertainty in the heat of formation of O^{2-} and the differing covalent contributions to the lattice energy through the 4f series. Then, for the elements Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Lu,

$$I_1 + I_2 + I_3 = \frac{\Delta H_f^\circ(M_2O_3,c) - 2\Delta H_f^\circ(M,g) - 3207 - U_{\text{BH}}}{2} \qquad (13)$$

with results shown in Table VI. The relative error (ignoring any errors in the "experimental" ΣI for Pr and Yb) of other $(I_1 + I_2 + I_3)$ values is estimated as ±5 kJ mol^{-1}.

SCHEME I



2. Cs_2NaMCl_6

Enthalpies of solution of compounds of this face-centered-cubic series were measured by Morss,[105] and the cubic lattice parameters a_0 were reported by Morss et al.[109] Because of recent improvements in such auxiliary thermochemical data as $\Delta H_f^\circ(MCl_3,c)$, $\Delta H_f^\circ(CsCl,c)$, and the ionization potentials of Ce, Pr, and Yb, the Born–Haber cycle calculations of Morss[105] are updated here. First, better $\Delta H_f^\circ(Cs_2NaMCl_6,c)$ are reported in Table VII from the thermochemical cycle

$$\begin{aligned}\Delta H_f^\circ(Cs_2NaMCl_6,c) &= 2\Delta H_f^\circ(Cs^+,aq) + \Delta H_f^\circ(Na^+,aq)\\ &\quad + \Delta H_f^\circ(M^{3+},aq)\\ &\quad + 6\Delta H_f^\circ(Cl^-,aq) - \Delta H^\circ(\text{soln},Cs_2NaMCl_6)\\ &= -1758.9 + \Delta H_f^\circ(M^{3+},aq) - \Delta H^\circ(\text{soln},Cs_2NaMCl_6) \qquad (14)\end{aligned}$$

TABLE VII. Born–Haber Cycle for Cs_2NaMCl_6

M	U_{calcd}/ kJ mol^{-1} [105]	$\Delta H_f°$/kJ mol^{-1}[a]	U_{BH}/kJ mol^{-1}	$(I_1 + I_2 + I_3)$/ kJ mol^{-1}
Y	−6316	−2396	−6655[c]	3776[71]
La	−6009	−2385	−6334[c]	3456[72]
Ce	−6066	−2386	−6391[c]	3523[72]
Pr	−6108	−2393	−6438[c]	3628[72]
Nd	−6136	−2384	−6468[b]	3694[c]
Pm	−6171			
Sm	−6206	−2380	−6542[b]	3893[c]
Eu	−6237	−2294	−6576[b]	4043[c]
Gd	−6259	−2376	−6599[b]	3763[c]
Tb	−6292	−2387	−6635[b]	3797[c]
Dy	−6322	−2385	−6667[b]	3930[c]
Ho	−6350	−2395	−6697[b]	3939[c]
Er	−6371	−2392	−6720[b]	3950[c]
Tm	−6395	−2392	−6746[b]	4060[c]
Yb	−6416	−2361	−6769[c]	4194[72]
Lu	−6436	−2389	−6791[b]	3912[c]

[a] Using eq 14 (see text); $\Delta H_f°(M^{3+}, aq)$ from Table I and $\Delta H°$ (soln, Cs_2NaMCl_6) from ref 105. [b] U_{calcd} + correction term (to agree with U_{BH} for La, Ce, Pr, and Lu compounds). [c] Calculated from Born–Haber cycle, eq 15.

TABLE VIII. Comparison of Lanthanide Third Ionization Potentials (kJ/mol)

	Spectroscopic		Thermal	
M	Sugar–Reader[69]	Vander Sluis–Nugent[56]	Ln_2O_3[a]	$Cs_2NaLnCl_6$[b]
Nd	2132	2108	2129	2126
Pm	2152	2127		
Sm	2258	2238	2265	2282
Eu	2405	2379	2396	2412
Gd	1991	1976	1987	2004
Tb	2114	2095	2104	2121
Dy	2200	2200	2214	2232
Ho	2204	2200	2203	2220
Er	2194	2194	2188	2210
Tm	2285	2285	2291	2301
Lu[c]	1341[c]	· · ·	1362[c]	1366[c]

[a] Table VI $(I_1 + I_2 + I_3)$ less I_1 and I_2 from ref 72. [b] Table VII $(I_1 + I_2 + I_3)$ less I_1 and I_2 from ref 72. [c] For Lu, *second* ionization potentials are compared here because the spectroscopic value for I_2 (ref 72) has error limits of ±0.4 eV (39 kJ) whereas the spectroscopic I_3 is much more accurately known.

All constant terms are taken from CODATA Bulletin 10.[81] Second, Born–Haber cycle lattice energies were calculated for the La, Ce, Pr, Yb, and Y compounds using the accurate spectroscopic ionization-potential sums, using eq 4 of ref 105:

$$\begin{aligned} U(Cs_2NaMCl_6)_{BH} &= \Delta H_f°(Cs_2NaMCl_6,c) - (I_1 + I_2 + I_3) \\ &\quad - \Delta H_f°(M,g) - 2\Delta H_f°(Cs,g) - \Delta H_f°(Na,g) \\ &\quad - 6\Delta H_f°(Cl,g) - 2I(Cs) - I(Na) - 6(EA) + 10RT \\ &= \Delta H_f°(Cs_2NaMCl_6,c) - (I_1 + I_2 + I_3) - \Delta H_f°(M,g) \\ &\quad - 2(76.1) - 107.1 - 6(121.29) - 2(375.3) - 495.4 \\ &\quad - 6(-357.7) + 24.9 = \Delta H_f°(Cs_2NaMCl_6,c) \\ &\quad - (I_1 + I_2 + I_3) - \Delta H_f°(M,g) - 61.9 \end{aligned} \quad (15)$$

The differences between U_{calcd} and U_{BH} vary slightly and monotonically with ionic radius of M^{3+}, so U_{BH} was calculated for other chlorides by interpolating or extrapolating this correction to U_{calcd}. Then, for the elements Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Lu,

$$I_1 + I_2 + I_3 = \Delta H_f°(Cs_2NaMCl_6,c) - \Delta H_f°(M,g) - 62 - U_{BH} \quad (16)$$

TABLE IX. Ionization-Potential Sums (kJ mol^{-1})[72]

M	$I_1 + I_2$	$I_1 + I_2 + I_3$	$I_1 + I_2 + I_3 + I_4$
La	1605	3456	8275
Ce	1574	3523	7070
Pr	1541	3628	7389
Nd	1565	3697	7596
Pm	1587	3739	7705
Sm	1611	3869	7864
Eu	1631	4036	8146
Gd	1759	3750	7995
Tb	1676	3790	7629
Dy	1698	3898	7899
Ho	1719	3923	8024
Er	1740	3934	8049
Tm	1759	4044	8163
Yb	1779	4194	8414
Lu	1888[a]	3910[a]	8270[a]

[a] Includes averaged thermal I_2 (1364 kJ) from Table VIII.

The relative error (ignoring any errors in the "experimental" ΣI for La, Ce, Pr, and Yb) of other $(I_1 + I_2 + I_3)$ values is estimated as ±8 kJ mol^{-1}.

C. Comparisons

The ionization-potential sums from Born–Haber cycles for M_2O_3 (Table VI) and for Cs_2NaMCl_6 (Table VII) are in remarkably good agreement; the average absolute deviation between the two sets for all calculated values is 13.1 kJ/mol, or 0.14 eV. The agreement between the Born–Haber (thermal) values for I_3, calculated by subtracting the spectroscopic $I_1 + I_2$[72] from the ionization-potential sums, is shown in Table VIII to be significantly in better agreement with the Sugar–Reader I_3 values[69] than with those of Vander Sluis and Nugent.[58] Since it is believed that spectroscopic ionization potentials, even if derived from semiempirical correlations, are better than thermal ionization potentials, the spectroscopic values reported by Martin et al.[72] are accepted as "best values" and are summed in Table IX.

V. Hydration Enthalpies

Although it is possible to utilize hydration enthalpies as intermediates in a thermochemical cycle by referencing them to some arbitrary, relative, reference value (such as $\Delta H(hyd,H^+) = 0$), it is preferable for most purposes to have as nearly as possible an absolute reference point. A convenient and often-discussed reference point is the absolute enthalpy of hydration of the proton, $\Delta H(hyd,H^+)$.

In Figure 1 are shown Born–Haber enthalpy cycles, on a rough "energy-level" scale, for hydrogen and for a multivalent cation, La^{3+}. The numerical entries in Figure 1 for H(g) and H^+(g) are those of National Bureau of Standards Technical Note 270-3,[47] and we follow the convention[47,118] that $\Delta H_f°$ of a gaseous ion includes the enthalpy associated with an ideal-gas mole of electrons, thereby assuming $\Delta H_f°(e^-,g,0\ K) = 0$. We have used the absolute enthalpy of hydration of the proton recommended by Halliwell and Nyburg,[119] −1091 ± 10 kJ mol^{-1}. (Other values might equally well have been selected, such as −1102 ± 13 kJ mol^{-1} recommended by Morris.[120] The actual value chosen for this datum will have no effect on any other calculated thermodynamic properties. One reason for preferring Halliwell and Nyburg's datum to that of Morris is that the former authors used a table of ionic radii nearly consistent with the ionic radii of Shannon and Prewitt;[48] Morris used ionic radii from electron-density distribution minima in crystals.)

The hydration cycle for La^{3+} in Figure 1 uses standard-state data from other tables in this review. It may readily be seen that, for all cations,

TABLE X. Hydration Enthalpies

	Divalent ions		Trivalent ions			Tetravalent ions	
M	I R[m] Å	$-\Delta H$(hyd) kJ mol^{-1}	I R[48] Å	$-\Delta H$(hyd) kJ mol^{-1}	$-\Delta H$(hyd)[76] kJ mol^{-1}	I R Å	$-\Delta H$(hyd) kJ mol^{-1}
Ba	1.36[48]	1307[a]					
La	1.31[b]	1460[c,d]	1.045	3278[a]	3293		
Ce	1.28[e]	1410[c,d]	1.010	3326[a]	3302	0.97[48]	6309[a]
Pr	1.25[e]	1390[d]	0.997	3373[a]	3336	0.96[e]	6360[d]
Nd	1.22[f]	1416[33]	0.983	3403[a]	3371	0.945[e]	6430[d]
Pm	1.20[e]	1430[d]	0.97[g]	3427[d]	3407	0.93[e]	6490[d]
Sm	1.18[h]	1444[33,82]	0.958	3449[a]	3441	0.915[e]	6550[d]
Eu	1.17[48]	1458[33]	0.947	3501[a]	3479	0.90[e]	6620[d]
Gd	1.14[b]	1560[c,d]	0.938	3517[a]	3520	0.89[e]	6660[d]
Tb	1.11[e]	1505[d]	0.923	3559[a]	3548	0.88[48]	6704[i]
Dy	1.09[j]	1528[33,82]	0.912	3567[a]	3584	0.872[e]	6740[d]
Ho	1.07[e]	1535[d]	0.901	3613[a]	3623	0.865[e]	6770[d]
Er	1.05[e]	1550[d]	0.890	3637[a]	3656	0.857[e]	6800[d]
Tm	1.04[k]	1555[33]	0.880	3664[a]	3693	0.849[e]	6840[d]
Yb	1.03[l]	1594[33]	0.868	3706[a]	3724	0.841[e]	6870[d]
Lu			0.861	3722[a]	3768	0.835[e]	6900[d]
Hf						0.83[48]	6920[d]

[a] From Born–Haber cycle eq 17. [b] Radius if electron configuration were f^n; actual configuration is $f^{n-1}d$. [c] Corrected for ground-state configuration of $f^{q-1}d$: ref 53 (gas) and 56 (aq). [d] Estimated from plot of ionic radius vs. ΔH(hyd). [e] Estimated (see text). [f] From crystal structure of $NdCl_2$: L. F. Druding and J. D. Corbett, *J. Am. Chem. Soc.*, **83**, 2462 (1961). See text for method of derivation. [g] From crystal structure of Pm_2O_3: F. Weigel and V. Scherer, *Radiochim. Acta*, **4**, 197 (1967). [h] From crystal structure of $SmCl_2$: W. Doll and W. Klemm, *Z. Anorg. Chem.*, **241**, 239 (1939). [i] Calculated from Born–Haber cycle, using estimated $\Delta H_f^\circ(Tb^{4+},aq)$ as described in text. [j] From crystal structure of $DyCl_2$: J. D. Corbett and B. C. McCollum, *Inorg. Chem.*, **5**, 938 (1966). [k] From crystal structure of $TmCl_2$: P. E. Caro and J. D. Corbett, *J. Less-Common Metals*, **18**, 1 (1969). [l] From crystal structure of $YbCl_2$: H. P. Beck and H. Barnighausen, *Z. Anorg. Allg. Chem.*, **386**, 221 (1971).

$$\begin{aligned}\Delta H^\circ(\text{hyd},M^{n+}, 298\text{ K}) &= \Delta H_f^\circ(M^{n+},\text{aq}) + n\Delta H_f^\circ(H^+,\text{aq,absolute}) - \Delta H_f^\circ(M,g) \\ &- \sum_n I_n - 5nRT/2 = [\Delta H_f^\circ(M^{n+},\text{aq}) - \Delta H_f^\circ(M,g) \\ &- \sum_n I_n + 439.2n]\text{ kJ mol}^{-1} \quad (17)\end{aligned}$$

Enthalpies of hydration of all lanthanide ions, for which the necessary data are independently available, have been calculated from eq 17 and are entered into Table X.

Many hydration enthalpies could not be calculated from thermochemical data when the essential $\Delta H_f^\circ(M^{n+},aq)$ are not available. In some cases (Nd^{2+}, Sm^{2+}, Dy^{2+}, Tm^{2+}, and Yb^{2+}) a more detailed thermochemical cycle was used.[33] In other cases, a graphical plot of ionic radii vs. hydration enthalpies was used to estimate necessary values. In table X, a reference for each entry is given to explain how the entry was derived.

For enthalpies of hydration of trivalent ions, the independent calculations of Goldman and Morss are shown for comparison in Table X.[76]

Some entries in Table X require further comment. Some ionic radii of divalent and tetravalent ions were estimated by comparing the radii of principal maxima of the outer electronic orbitals of neighboring ions;[121] or by plotting the ratio of radii of isoelectronic ions, such as $r_{Ba^{2+}}/r_{La^{3+}}$, as a function of the number of f electrons, and then deriving missing ionic radii from the smoothly varying radius-ratio plot. The ionic radii of Nd^{2+}, Sm^{2+}, Dy^{2+}, Tm^{2+}, and Yb^{2+} were calculated by determining the *difference* between M(II)-Cl distance in MCl_2 and the corresponding distance in $BaCl_2$ or $EuCl_2$; this *difference* was then applied to the $r_{Ba^{2+}}$ or $r_{Eu^{2+}}$ to obtain self-consistent divalent radii for those ions which exist in binary compounds. The ΔH(hyd) for La^{2+} and Gd^{2+} were first estimated from the ionic radii for the nonground state configurations 4f and $4f^8$; these ΔH(hyd) were then corrected for the estimated f-d energy differences from atomic spectra[53] and CaF_2-doped f-d spectra.[56] For Ce^{2+}, the configuration of the gaseous ion is $4f^2$, but that of the aquo ion is believed to be 4f5d, and again a correction was applied which represents the increased stability of the 4f5d configuration from the CaF_2-doped f-d band. The ΔH(hyd) for Tb^{4+} was calculated by estimating $\Delta H_f^\circ(Tb^{4+},aq)$ as follows.

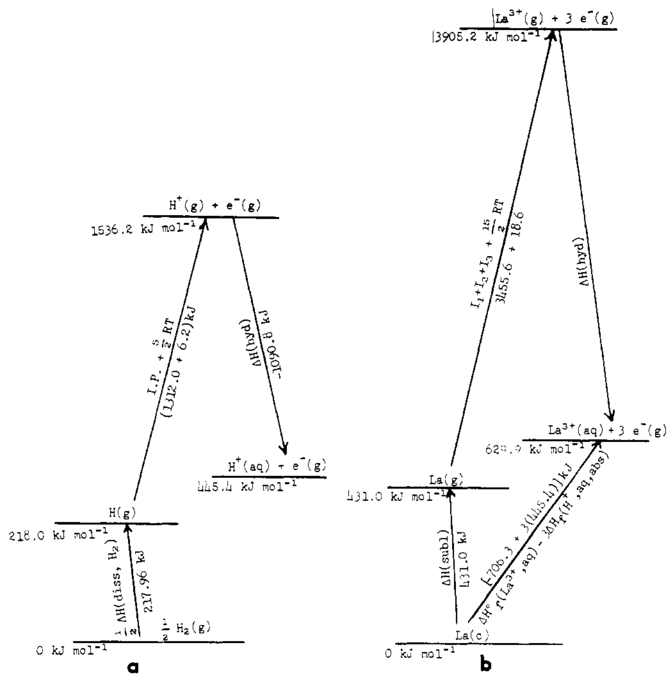


Figure 1. Born–Haber enthalpy hydration cycle (25 °C).

For the reaction $Tb^{4+}(aq) + \frac{1}{2}H_2(g) \rightarrow Tb^{3+}(aq) + H^+(aq)$, $\Delta G^\circ = -nFE^\circ = -299$ kJ mol^{-1}; $\Delta S^\circ = -226 - (-438) - \frac{1}{2}(130.6) = 147$ J mol^{-1} K^{-1}. Thus $\Delta H^\circ = -299 + .298(147) = -255$ kJ mol^{-1}, whence $\Delta H_f^\circ(Tb^{4+},aq) = -698 + 255 = -443$ kJ mol^{-1}.

VI. Predicted Standard-State Properties

Given the complete sets of self-consistent ionization-potential sums and hydration enthalpies of Tables IX and X, it is worthwhile

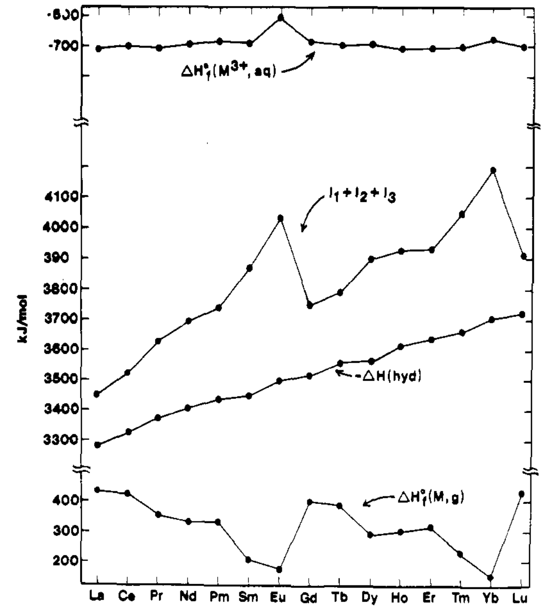


Figure 2. Stability terms for M → M^{3+}.

SCHEME II

$$M(c) + 3H^+(aq) \longrightarrow M^{3+}(aq) + {}^3\!/_2H_2(g)$$

$$\begin{tikzcd}
M(g) \arrow[rrr, "I_1 + I_2 + I_3"] \arrow[dd, "\Delta H(\mathrm{subl})"'] & & & M^{3+}(g) \arrow[dd, "\Delta H(\mathrm{hyd})"] \\
& 3H^+(g) \arrow[r, "-I"] \arrow[d, "-3\Delta H(\mathrm{hyd})"] & 3H(g) \arrow[d, "-3\Delta H_f^\circ(H,g)"] & \\
M(c) & + 3H^+(aq) \arrow[r] & {}^3\!/_2H_2(g) & + M^{3+}(aq)
\end{tikzcd}$$

to calculate enthalpies of formation of aquo ions using eq 17. The results are shown in Table I (footnote *b* to that Table).

Using the enthalpies of formation and the entropies of Table I, free energies of formation were calculated and are reported in Table IV. From these free energies, of course, the reduction potentials for $M^{n+}(aq) + me^- \rightarrow M^{(n-m)+}(aq)$ were calculated directly. Because of the paucity of experimental data on M^{4+} ions, the (III)-(II) reduction potential estimates are much better (ca. ±0.1 V) than are the (IV)-(III) estimates (ca. ±0.4 V) in Table IV.

There are two recent and independent sources of calculated stability parameters for lanthanide aquo ions. The spectroscopic correlations of Nugent et al.[55,56] have already been mentioned; their calculated reduction potentials are shown in Table IV for comparison. The agreement is excellent in most cases, with La(III)-(II) and Pr(IV)-(III) being notable exceptions.

Johnson[99] has already calculated values of $\Delta G_f^\circ(M^{3+},aq)$ which are in good agreement with NBS Technical Note 270-7 and with Table IV. He then estimated $\Delta G_f^\circ(M^{2+},aq)$ from calculated values of the Gibbs energy of hydration of the divalent ions. His resulting $E^\circ(M^{3+} \rightarrow M^{2+})$, shown in Table IV, are also in good agreement with those derived here.

VII. Interpretations

A. Stability of the Trivalent Lanthanide Aquo Ions: $E^\circ(M^{3+} \rightarrow M)$

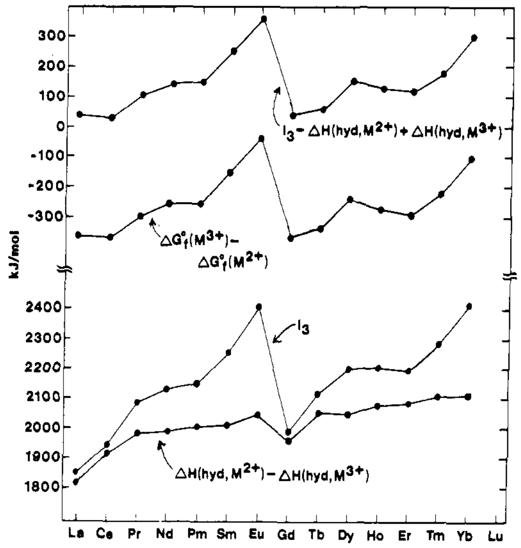


Figure 3. Stability terms for $M^{3+} \rightarrow M^{2+}$.

SCHEME III

$$\begin{tikzcd}
M^{2+}(g) \arrow[rrr, "I_3"] \arrow[dd, "-\Delta H(\mathrm{hyd})"'] & & & M^{3+}(g) \arrow[dd, "\Delta H(\mathrm{hyd})"] \\
& H^+(g) \arrow[r] \arrow[d] & H(g) \arrow[d] & \\
M^{2+}(aq) & + H^+(aq) \arrow[r] & {}^1\!/_2H_2(g) & + M^{3+}(aq)
\end{tikzcd}$$

It had been assumed, until Burnett's work[10,37] showed otherwise, that the Gibbs energies of the trivalent lanthanide aquo ions were a smoothly varying function of atomic number. It is now known that the enthalpies and Gibbs energies of formation of $Eu^{3+}(aq)$ and of $Yb^{3+}(aq)$ are significantly less stable than are those of other lanthanides (cf. Figure 2, top curve). An examination of this phenomenon can be made by considering the terms in the thermochemical cycle for the reaction given in Scheme II. The three steps which involve changes in M are displayed in Figure 2 (from data in Tables I, IX, and X). The plot of $\Delta H_f^\circ(M,g)$, the sublimation enthalpy, reflects the decreasing stability of the trivalent metallic state in the sequence La-Eu and again in the sequence Gd-Yb.[59] The ionization-potential sums are dominated by I_3, where again the ions $Eu^{2+}(g)$ and $Yb^{2+}(g)$ are the most divalent; i.e., their configurations f^7 and f^{14} most strongly resist ionization because of the maximization of electron-spin pairing.[104] The steady trend of hydration enthalpies reflects the lanthanide contraction and neatly balances the increase in ionization-potential sums for the spherically symmetric ions La^{3+}, Gd^{3+}, and Lu^{3+}. As a result, all of the lanthanides have nearly the same $\Delta H_f^\circ(M^{3+},aq)$: elements such as La and Gd with stable trivalent metals also have the most stable trivalent ions; elements such as Sm with barely stable trivalent metals also have less stable trivalent ions; and the lanthanide contraction balances increasingly endoergic ionization potentials with increasingly exoergic hydration enthalpies. Only for the elements Eu and Yb, which have stable divalent metals, is the pattern of energetic balance upset. From Figure 2 one may estimate that trivalent metallic Eu and Yb are 85 and 25 kJ mol^{-1} less stable than the known divalent metals. Nugent et al. estimated these differences to be 79 and 29 kJ mol^{-1}, respectively, by similar reasoning.[57]

B. Trends in Reduction Potentials $E^\circ(M^{3+} \rightarrow M^{2+})$

For the thermochemical reaction $M^{2+}(aq) + H^+(aq) \rightarrow M^{3+}(aq) + {}^1\!/_2H_2(g)$ the thermochemical cycle is given in Scheme III, and the relevant steps are shown in Figure 3. If the three anomalous f^nd ions La^{2+}, Ce^{2+}, and Gd^{2+} are ignored, the ΔH(hyd) difference shows only an unexpected dip at Dy; it is likely that this dip is due to an error in $\Delta H_f^\circ(Dy^{2+},aq)$. This property has only been roughly estimated by a hydration-solution cycle.[33] As Johnson has pointed out,[99] I_3 is of overwhelming importance in explaining the trends in $E^\circ(M^{3+} \rightarrow M^{2+})$. Since the

SCHEME IV

$$\begin{tikzcd}
M^{4+}(g) \arrow[rrr, "-I_4"] \arrow[dd, "-\Delta H(\text{hyd})"'] & & & M^{3+}(g) \arrow[dd, "\Delta H(\text{hyd})"] \\
& H(g) \arrow[r, "I(H)"] \arrow[d, "\Delta H_f^\circ(H,g)"] & H^+(g) \arrow[d, "\Delta H(\text{hyd})"] & \\
M^{4+}(aq)\,{}^1\!/_2H_2(g) \arrow[rr] & & H^+(aq) & M^{3+}(aq)
\end{tikzcd}$$

hydrogen terms in the above cycle sum to -445.4 kJ(mol H)$^{-1}$, I_3 is never unfavorable enough to prevent the oxidation of M^{2+} in aqueous solution, although $Eu^{2+}(aq)$, and, fleetingly, $Yb^{2+}(aq)$ and $Sm^{2+}(aq)$ are metastable. As expected, the sum of terms in M precisely parallels the free-energy difference between the two aquo ions (Figure 3, top two plots).

C. Trends in Reduction Potentials $E^\circ(M^{4+} \rightarrow M^{3+})$

For the reaction $M^{4+}(aq) + {}^1\!/_2H_2(g) \rightarrow M^{3+}(aq) + H^+(aq)$, the cycle is given in Scheme IV with relevant steps shown in Figure 4. Here, as expected, the differences in ΔH(hyd) show a smooth trend, since there are no ions of anomalous electron configuration. Clearly, variation in I_4 is the only significant feature and I_4 is always unfavorable enough to cause reduction of $M^{4+}(aq)$, although $Ce^{4+}(aq)$ does not oxidize water at an appreciable rate. Figure 4 (top two plots) compares the terms in M with the free-energy differences and, again, the two effects are parallel.

D. Areas for Future Study

1. Thermodynamic measurements should be undertaken on complex compounds, especially those involving unusual +2 or +4 lanthanide oxidation states. The enthalpies of formation of $CsLnCl_3$ are being determined.[122]

2. Careful thermochemical measurements on nonstoichiometric lanthanide compounds will lead to better understanding of their stability relationships and to better estimates of $\Delta H_f^\circ(M^{2+},aq)$.

3. Since other strongly reducing cations, such as U^{3+} and Ho^{2+}, have been found[123] or claimed[124] to persist in oxygen-free aqueous solution, it is quite likely that Yb^{2+} and even Sm^{2+} can be so prepared. Because appreciable $Sm^{2+}(aq)$ persists in water for at least 1 h,[125] it should be possible to measure the enthalpies of oxidation of $Sm^{2+}(aq)$ and $Yb^{2+}(aq)$ directly. In this way, thermal information may be obtained to complement the limited E° values already available.

4. Recent preparation of $HoCl_{2.14}$[83] and the partial reduction of Ho_2O_3 by γ irradiation[124] are consistent with the reduction potential calculated for $Ho^{3+}(aq)$ (Table IV). However, the claims[124] that Ho^{2+} persists in aqueous solution, that its polarographic and chronopotentiometric reduction potentials are observable, and that the Ho^{3+}–Ho^{2+} reduction potential is about -2.0 V should be independently substantiated or refuted.

5. There have been two challenges[126,127] to Pajakoff's claim[84] that aqueous solutions of Pr(IV) can be prepared. This ion is clearly such a strong oxidant that it should not exist, even when complexed, in the presence of water or chloride ion. Unfortunately, the strong evidence[126,127] that Pr(IV) cannot exist in strongly complexing aqueous solutions does not rule out the possibility of preparations of solid chlorides or sulfates containing Pr(IV). This author concurs with Nugent's prediction[16] that no chloride or complex chloride can be prepared for any tetravalent ion whose M(IV)–(III) reduction potential is more negative than -2.0 V; this prediction should be tested by repetition of Pajakoff's studies.

6. It is noteworthy that Pm(II) is expected to be only a slightly stronger reductant than is Nd(II). Preparation of $PmCl_2$, $PmBr_2$, and PmI_2 should be possible.

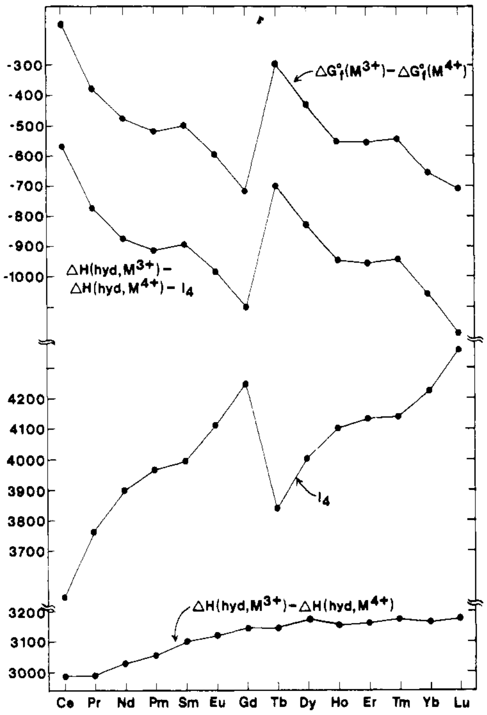


Figure 4. Stability terms for $M^{4+} \rightarrow M^{3+}$.

7. The predicted oxidizing power of Sm(IV) is barely greater than that of Nd(IV) and Dy(IV). Preparation of the double salt Cs_3SmF_7 should be attempted.

8. The third ionization potential of at least one of the elements Nd–Tm should be determined spectroscopically, so that the differences between the systematic treatments of Sugar and Reader[69] and of Vander Sluis and Nugent[58] may be resolved.

VIII. Addendum

Several thermodynamic studies involving lanthanide chlorides and ions have been reported recently. Spedding and coworkers[128–131] have reported the heat capacities, densities, partial molal volumes, thermal expansion coefficients, and activity coefficients of the aqueous rare-earth chlorides. Sommers and Westrum[132] have measured the low-temperature heat capacities of several anhydrous lanthanide trichlorides; these measurements are interesting because they have been interpreted in terms of various theoretical lattice contributions as a function of temperature. Recent vapor-pressure measurements on the $LaCl_3 \cdot nH_2O$ equilibria[133] may be used to yield thermodynamic properties for all of the hydrates of $LaCl_3$.

Fitzgibbon et al.[134] reported titration calorimetric enthalpies of reactions of excess Ce(IV) in 0.5 M $HClO_4$ with H_2O_2 (-71.5 ± 1.2 kJ mol^{-1}), with Fe(II) (-126.2 ± 0.4 kJ mol^{-1}), and with U(IV) (-96.8 ± 0.6 kJ mol^{-1}). Their measurements lead to $\Delta H = -167.3 \pm 0.6$ kJ mol^{-1} for reaction 11; see section III.A.4 for earlier enthalpies for this reaction.

Myasoedov et al.[135] studied the electrochemical reduction of water–acetonitrile solutions of perchlorates of trivalent Sm, Eu, Er, and Tm at mercury cathodes. They interpret the formation of precipitates of basic erbium(III) and thulium(III) perchlorates in terms of two parallel processes: reduction of water and reduction of M(III) to M(II) followed by its oxidation by water. Formation of metal amalgam at the mercury cathode is usually interpreted as evidence of a two-step reduction,[136] but Myasoedov et al. found amalgam formation only with Sm and Eu; therefore, their half-wave potentials for Er and Tm were probably caused by reduction of water, as had been the case in the early studies of Noddack and Brukl.[137,138] Nugent's recent correlation[139] (see below) supports this interpretation.

Myers has suggested the bonding of gaseous lanthanide trihalide molecules in terms of a covalent model involving d^2s hybridization at the lanthanide atom,[140] and in terms of a "polarized ion model".[141]

Two papers discussing hydration numbers have appeared recently. Novikov and Vasilev[142] used heat capacities of aqueous solutions of the trichlorides at infinite dilution to estimate hydration numbers of 7.8 (La^{3+}), 8.2 (Pr^{3+}), and 7.3 (Yb^{3+}). Smith and Wertz[143] have examined concentrated aqueous solutions of $LaCl_3$ by x-ray diffraction. They conclude that each La^{3+} ion is coordinated only to H_2O, even in 10 M HCl, with an average of eight nearest oxygen neighbors at 2.48 Å; the average La^{3+}–Cl^- ion-pair distance is 4.7 Å.

Several reviews and correlations have appeared recently. Nugent[139] summarized the behavior of the amalgamation half-wave potentials observed by David[144] and earlier workers in terms of two mechanisms: fast amalgamation (for Sm, Eu, and Yb) because M(II) ions are produced, and "regular" amalgamation (for all other lanthanides, with $E°$(III)–(II) less than -1.8 V) from direct reduction of M^{3+}(aq) to M/Hg. He used lanthanide values to estimate corresponding actinide (II)–(0) potentials; from these and estimated actinide (III)–(II) potentials, he then estimated values for actinide $\Delta H_f°(M^{3+},aq)$. A thorough and critically evaluated review of thermodynamic properties and equilibria for lanthanum has been published by Hepler et al.;[145] this paper was preceded by an equally thorough review for scandium.[146] Hepler[145] notes two additional sources of data on heats of solution of anhydrous lanthanide trichlorides.[147,148] Ward and Hill[149] have presented a correlation of the entropies of the lanthanide and actinide metals in terms of their structures, magnetic properties, and vaporization behavior; they estimate $S°$(Pm,c) = 71.5 kJ mol^{-1}.

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