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LANTHANUM: THERMODYNAMIC PROPERTIES, CHEMICAL EQUILIBRIA, AND STANDARD POTENTIALS

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ABSTRACT

We have gathered, critically evaluated, calculated, and tabulated thermodynamic properties and related equilibrium constants and standard potentials for inorganic compounds and aqueous species of lanthanum. We have been explicit about sources of data and our calculations so that interested readers can check the steps leading to tabulated thermodynamic quantities and thus form their own opinions about reliability and accuracy.

INTRODUCTION

In this paper we are concerned with the thermodynamic properties of lanthanum, its compounds, and various aqueous species derived from lanthanum. Thermodynamic data for all of these are useful in several areas of chemistry and also for applications of chemical principles to other disciplines such as metallurgy. Because many of these thermodynamic data are most useful when presented in the form of equilibrium constants or standard potentials, we have listed some of these quantities that are related to our tabulated free energies.

We have been critical in our evaluations and have recalculated many of the published results cited here. When data from several sources are in poor agreement, we have attempted to justify our choices. We have been explicit about the sources and treatment of data so that interested readers can check the steps leading to tabulated thermodynamic properties (also related equilibrium constants and standard potentials) and form their own opinions about reliability and accuracy.

In several cases we have combined experimental data from a cited source with an estimate of some thermodynamic property. *Numerical values of estimates are given in parentheses.* Except where explicitly stated otherwise, we have used auxiliary data [such as ΔH_f° for Cl^- (aq)] from the National Bureau of Standards Technical Notes[1] 270-3 and 270-4.

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In spite of considerable discussion, general agreement is still lacking on "sign conventions" for potentials. Confusion arises because "sign" can be either electrical or algebraic. All potentials listed here are reduction potentials with algebraic signs, and may also be taken to be electrode potentials with electrical signs relative to the standard hydrogen electrode.

The symbols E° and K are ordinarily used for potentials and equilibrium constants that have been determined in very dilute solutions or in such ways that activity coefficients could be considered in treating the experimental data. Similarly, we use ΔG°, ΔH°, and S° to indicate quantities that refer to the usual standard states[1]. Other useful investigations have been carried out with solutions maintained at some constant ionic strength by means of an "inert" supporting electrolyte. In some such cases, it has been possible to make reasonable adjustments to obtain values that refer to the usual standard states. In other cases, we refer to properties based on "uncorrected" data and call attention to the fact that the cited properties refer to solutions having some stated composition.

Except where explicitly stated otherwise, all thermodynamic properties cited here refer to 298.15 K (25°C).

GENERAL CHEMISTRY OF LANTHANUM

Only the 3+ oxidation state $(\ldots 5s^2 5p^6)$ is of general importance in the chemistry of lanthanum, although there is some evidence for lower oxidation states. The La^{3+} ion ($r = 1.1$ Å) is larger than the Y^{3+} ion ($r = 0.9$ Å) and many of the differences in their chemical properties can be accounted for on this basis. The $La^{3+}(aq)$ ion is less hydrolyzed in weakly acidic solution than most $M^{3+}(aq)$ ions, which makes it a convenient choice for some kinds of investigations of solutions.

Some slightly soluble (in water) compounds of lanthanum include the hydroxide, phosphate, carbonate, fluoride, and various double salts such as $La[Ag(CN)_2]_3 \cdot 3H_2O(c)$.

Because of widespread use of organic complexing agents in separation of the rare earths, and also because of theoretical interests, there have been many investigations of the association of $La^{3+}(aq)$ with various organic ligands. In this paper we limit our attention to the inorganic compounds and complexes of lanthanum.

THERMODYNAMIC DATA

Our best general source of thermodynamic data for elemental lanthanum, its compounds, and its aqueous species is the National Bureau of Standards Technical Note 270-7[2], to which we frequently refer as NBS 270-7. Because references have not been included in NBS 270-7, we are unable to compare their sources of data with our sources.

We follow NBS 270-7 in adopting $\Delta H_f^\circ \equiv 0$, $\Delta G_f^\circ \equiv 0$, and $S^\circ = 13.6$ cal K^{-1} mol^{-1} for La(c) at 298 K. This entropy is in agreement with heat capacity results cited by Kelley and King[3]. High temperature calorimetric measurements have been made by Stretz and Bautista[3a].

On the basis of two investigations[4,5] of the vapor pressure at high temperature, we adopt $\Delta H_f^\circ = 103.0$ kcal mol^{-1} for La(g), as listed in NBS 270-7. Combination of this quantity with $S^\circ = 43.563$ cal K^{-1} mol^{-1} for La(g) as listed in NBS 270-7 (good agreement with value calculated by Kelley and King[3]) leads to the tabulated ΔG_f°.

Our adopted properties for La_2(g) are consistent with the results that have been reviewed by Drowart[6] and also with properties listed in NBS 270-7.

Our adopted properties (Table 1) for LaO(g) are consistent with the results of a variety of high temperature measurements reported by Drowart et al.[7,8] and Ackermann and Rauh[9], and are in agreement with properties listed in 270-7. Our ΔH_f° values for La_2O(g) and La_2O_2(g) are based on the results reported by Smoes et al.[8].

TABLE 1

THERMODYNAMIC PROPERTIES OF LANTHANUM AT 298 K[a]

Substance	ΔH_f° (*kcal mol*$^{-1}$)	ΔG_f° (*kcal mol*$^{-1}$)	S° (*cal K*$^{-1}$ *mol*$^{-1}$)
La(c)	0	0	13.6^{3}
La(g)	$103.0^{4,5}$	94.1	43.563^{3}
La^+(g)	233.1		
La^{2+}(g)	490		
La^{3+}(g)	933.2		
La^{3+}(aq)	$-169.0^{16,17}$	-163.4	$-52._0{}^{23}$
La_2(g)	147^{6}	135	66
LaO(g)	-29.0^{7-9}	-34.7	57.27
La_2O(g)	-2^{8}		
La_2O_2(g)	-146^{8}		
La_2O_3(c)	$-428.7^{10,11}$	-407.7	30.43^{15}
LaH_2(c)	$-48._3{}^{34-36}$	$-38._5$	~12
LaD_2(c)	$-45._2$		
$La(OH)^{2+}$(aq)		$-208._2{}^{28}$	
$La(OH)_3$(aged ppt)	-337.0^{32}	$-307._1{}^{31}$	34
$La(OH)_2Cl$(fresh ppt)		$-291._1{}^{31}$	
$La(OH)_2Cl$(aged ppt)		$-292._7{}^{31}$	
$La_2(OH)_5Cl$(aged ppt)		$-594._0{}^{31}$	
LaF(g)			56.9^{48}
LaF^{2+}(aq)		$-234.1^{53,54}$	
LaF_2(g)			$70._1{}^{48}$
LaF_3(g)			78.7
$LaF_3 \cdot \frac{1}{2}H_2O$(ppt)	-441	-417	(32)
$LaCl_3$(c)	$-256.0^{16,17}$	-238	(32)
$LaCl_3$(g)	$-173^{56,57}$	-172	(90)
$LaCl_3 \cdot 7H_2O$(c)	-759.7^{16}	-648.5	110.6^{23}
LaOCl(c)	-243^{59-61}	-230	(22)
$Cs_2NaLaCl_6$(c)	-571.6^{66}		

(Table continued on p. 98)

TABLE 1 (*continued*)

Substance	ΔH_f° (*kcal mol*$^{-1}$)	ΔG_f° (*kcal mol*$^{-1}$)	S° (*cal K*$^{-1}$ *mol*$^{-1}$)
$\mathrm{La(BrO_3)_3\cdot 9H_2O(c)}$	$\mathit{-857.9}^{72}$		
$\mathrm{LaI_3(c)}$	$\mathit{-159.4}^{73}$		
$\mathrm{LaI_3(g)}$	$\mathit{-79}^{56}$		
$\mathrm{La(IO_3)_3(c)}$	-334.6^{75}	-270.2^{75}	60.1^{75}
$\mathrm{LaS(c)}$	-110	-109	$(17)^{76-78}$
$\mathrm{LaS(g)}$	31^{7}	19	$(\mathit{60})^{76,77,79,80}$
$\mathrm{LaS_2(c)}$			$(21._5)^{77}$
$\mathrm{La_2S_3(c)}$	$\mathit{-289}^{84}$	-286	39.43^{81}
$\mathrm{La_2O_2SO_4(c)}$	$\sim -539^{85}$	$\sim -516^{85}$	104^{85} (?)
$\mathrm{La(SO_4)^+(aq)}$	$\mathit{-383.1}^{88,89}$	$\mathit{-346.2}^{88,89}$	$\mathit{-20}^{88,89}$
$\mathrm{La(SO_4)_2^-(aq)}$	$\mathit{-599.2}^{89}$	$\mathit{-526.7}^{89}$	$\mathit{-3}^{89}$
$\mathrm{La_2(SO_4)_3(c)}$	$\mathit{-942.0}^{17}$		
$\mathrm{La_2(SO_4)_3\cdot 9H_2O(c)}$	$\mathit{-1589}^{17}$		
$\mathrm{LaSe(c)}$	$\sim \mathit{-97}^{97}$	~ -96	$19._4^{77}$
$\mathrm{LaSe(g)}$	$\mathit{43}^{95-97}$	31	$(62.85)^{77}$
$\mathrm{La_2Se_3(c)}$	$\sim \mathit{-223}^{77}$	~ -220	48.33^{98}
$\mathrm{La_2(SeO_3)_3(c)}$	$\mathit{-688.2}^{99}$	$\mathit{-629.5}$	$\mathit{81}$
$\mathrm{LaTe(c)}$			$21._1^{77}$
$\mathrm{LaTe(g)}$	59^{95}	47	$(64._7)^{77}$
$\mathrm{La_2Te_3(c)}$			55.36^{100}
$\mathrm{LaN(c)}$	$-72._5^{102}$	-66	$(13._5)$
$\mathrm{La(NO_3)_3(c)}$	$\mathit{-299.8}^{104}$		
$\mathrm{La(NO_3)_3\cdot 3H_2O(c)}$	$\mathit{-520.0}^{104}$		
$\mathrm{La(NO_3)_3\cdot 4H_2O(c)}$	$\mathit{-592.3}^{104}$		
$\mathrm{La(NO_3)_3\cdot 6H_2O(c)}$	$\mathit{-732.2}^{104}$		
$\mathrm{LaAs(c)}$	-73^{106}	-72	$(18._5)$
$\mathrm{LaSb(c)}$			$\mathit{21.22}^{108}$
$\mathrm{LaBi(c)}$	$-53._0^{109}$	$-52._1$	$\mathit{24.10}^{108}$
$\mathrm{La_4Bi_3(c)}$	-173^{109}		
$\mathrm{LaC_2(c)}$	$-21^{111,113}$	$-21._5$	$18^{111,113}$
$\mathrm{LaC_2(g)}$	$142^{110-113}$	128	$62._6^{113}$
$\mathrm{LaC_3(g)}$	$\sim 191^{113}$		
$\mathrm{LaC_4(g)}$	$\sim 182^{113}$	~ 166	$71._4^{113}$
$\mathrm{La_2O_2C_2(c)}$	-320^{114}		$\sim 25^{114}$
$\mathrm{La_2(CO_3)_3(c)}$		$\mathit{-750.9}^{115}$	
$\mathrm{La_2(CN_2)_3(c)}$	$\mathit{-199}^{116}$		
$\mathrm{LaSn_3(c)}$	$-60._6^{117}$		
$\mathrm{La_2Sn_3(c)}$	$-140._4^{117}$		
$\mathrm{LaPb_2(c)}$	-43^{120}		
$\mathrm{LaPb_3(c)}$	-55^{120}		
$\mathrm{La_3Pb_4(c)}$	-107^{120}		
$\mathrm{La_4Pb_3(c)}$	-117^{120}		
$\mathrm{La_5Pb_3(c)}$	-138^{120}		
$\mathrm{La_5Pb_4(c)}$	-148^{120}		
$\mathrm{LaB_6(c)}$			19.87^{121}
$\mathrm{LaAl_2(c)}$			$\mathit{23.60}^{123}$
$\mathrm{LaNi_5(c)}$			$\mathit{50.98}^{124}$
$\mathrm{LaAu(g)}$	$\mathit{110.8}$	$\mathit{98.2}$	$\mathit{67}$
$\mathrm{LaRh(g)}$	$108._5^{127}$	$96._6$	61^{127}
$\mathrm{LaY(g)}$	$\mathit{157}$		

TABLE 1 (*continued*)

Substance	ΔH_f° (*kcal mol*$^{-1}$)	ΔG_f° (*kcal mol*$^{-1}$)	S° (*cal K*$^{-1}$ *mol*$^{-1}$)
$La_2Zr_2O_7$(c)	~ −919[128]		
$La_2(CrO_4)_3$(c)	−947[129]		
$La_2(CrO_4)_3$(amorph)	−939[129]		
$La_2(CrO_4)_3 \cdot 2H_2O$(c)	−1093[129]		
$La_2(CrO_4)_3 \cdot 7H_2O$(c)	−1447[129]		
$La(MoO_4)^+$(aq)		$-369._3$[130]	
$La_2(MoO_4)_3 \cdot 2H_2O$(c)		$-1070._0$[130]	
$LaFe(CN)_6$(aq, undiss)	−33.7[132,133]	$5._7$[24,25,132]	33[132,133]
LaFe(CN)M(aq)		$-4._2$[136]	

[a] All values in italics are the same as listed in NBS 270-7[2]. All of our values are consistent with auxiliary data from NBS 270-3[1]. Estimated values are in parentheses.

Widely divergent ΔH_f° values for La_2O_3(c) have been reported, but several recent investigations have apparently resolved nearly all of the earlier uncertainties. The first reliable investigation appears to be that of Huber and Holley[10], who reported $\Delta H_f^\circ = -428.57$ kcal mol^{-1} on the basis of their combustion measurements. Subsequently, investigations by solution calorimetry in two laboratories led Fitzgibbon et al.[11] to report $\Delta H_f^\circ = -428.82$ and -428.97 kcal mol^{-1}. More recent solution calorimetry by Gvelesiani and Yashvili[12] has led to $\Delta H_f^\circ = -429.7$ kcal mol^{-1}. We adopt $\Delta H_f^\circ = -428.7$ kcal mol^{-1} for La_2O_3(c), as also listed in NBS 270-7, on the basis of the investigations by Holley et al.[10,11].

Heat capacity measurements by Goldstein et al.[13] led to $S^\circ = 30.58$ cal K^{-1} mol^{-1} for La_2O_3(c) at 298 K. Later measurements by King et al.[14] led to a reported $S^\circ = 30.73$ cal K^{-1} mol^{-1}. We can improve on this latter value by combining their experimental $(S_{298}^\circ - S_{51}^\circ)$ with S_{51}° from other investigators[13,15] who made measurements at lower temperatures and thereby obtain $S^\circ = 30.25$ or 30.46 cal K^{-1} mol^{-1}. Finally, the excellent measurements by Justice and Westrum[15] led them to $S^\circ = 30.43$ cal K^{-1} mol^{-1} for La_2O_3(c) at 298 K, which we adopt for our Table 1 (also listed in NBS 270-7).

We have high temperature $(H_T^\circ - H_{298}^\circ)$ and related thermodynamic properties of La_2O_3(c) from the work of King et al.[14].

Combination of auxiliary data from NBS 270-3 with results of solution calorimetry by Spedding and Flynn[16] and Montgomery[17] leads to $\Delta H_f^\circ = -256.0$ kcal mol^{-1} for $LaCl_3$(c) and $\Delta H_f^\circ = -169.0$ kcal mol^{-1} for La^{3+}(aq). Both of these values, which we adopt for our Table 1, are the same as listed in NBS 270-7. Enthalpies of solution of La(c) and La_2O_3(c) in hydrochloric acid by Fitzgibbon et al.[11] in combination with "reasonable" estimated enthalpies of dilution lead to the same ΔH_f° of La^{3+}(aq). Further (approximate) support is provided for these adopted ΔH_f° values by results from other investigators[18–21].

We note that Tsvetkov and Rabinovich[20] have reported enthalpies of solution of $LaCl_3$(c) in both H_2O(liq) and D_2O(liq), while Clark and Bear[18] have done the same for H_2O(liq) and DMSO(liq). Krestkov et al.[21] have reported standard enthalpies of solution of $LaCl_3$(c) in water at several temperatures.

Enthalpies of dilution of aqueous lanthanum chloride have been reported by Spedding and Flynn[16] and by Nathan et al.[22].

We obtain $S^\circ = -52._0$ cal K^{-1} mol^{-1} for La^{3+}(aq) from data for $LaCl_3 \cdot 7H_2O$(c) as summarized by Hinchey and Cobble[23]. This value, which is the same as in NBS 270-7, is adopted for our Table 1 and combined with the ΔH_f° to obtain $\Delta G_f^\circ = -163.4$ kcal mol^{-1} and thence the standard potential:

$$La^{3+}(aq) + 3e^- = La(c) \qquad E^\circ = -2.36\ V$$

A more accurate entropy of La^{3+}(aq) might be obtained by way of a more accurate third law entropy for $LaCl_3 \cdot 7H_2O$(c) or a third law entropy for $La(IO_3)_3$(c) as discussed later in connection with the properties of this latter compound.

For hydrolysis or hydroxide complexing of La^{3+}(aq) we have

$$La^{3+}(aq) + H_2O(liq) = La(OH)^{2+}(aq) + H^+(aq) \qquad (1)$$

as the first step in a possibly complicated sequence leading ultimately to precipitation of hydroxide. Older investigations reviewed by Sillén[24,25] suggest that $K \cong 10^{-10}$ for reaction (1). The thorough investigation of Biedermann and Ciavatta[26] (3 M $NaClO_4$) provides evidence for such species as $La_2(OH)^{5+}$(aq) and $La_5(OH)_9^{6+}$(aq) or $La_6(OH)_{10}^{8+}$(aq). More recently, however, Amaya et al.[27] have carried out a similar investigation (3 M $LiClO_4$) and found no evidence for the di- and polynuclear species postulated by Biedermann and Ciavatta[26]. Largely on the basis of recent investigations (dilute solutions) by Usherenko and Skorik[28] we choose $K = 2 \times 10^{-9}$ for reaction (1) and calculate $\Delta G_f^\circ = -208._2$ kcal mol^{-1} for $La(OH)^{2+}$(aq). We also note that Usherenko and Skorik[28] have investigated reaction (1) in 25 and 50 volume percent ethanol and that Amaya et al.[29] have investigated the D analog of reaction (1) in D_2O(liq).

Investigations reviewed by Sillén[24,25] and Aksel'rud[30] lead to a wide range of reported solubility products for lanthanum hydroxide; we adopt the following from Moisa and Spivakovskii[31]:

$$La(OH)_3(\text{aged ppt}) = La^{3+}(aq) + 3OH^-(aq) \qquad K_{sp} = 2 \times 10^{-23}$$

This K_{sp} leads to $\Delta G_f^\circ = -307._1$ kcal mol^{-1} for $La(OH)_3$(aged ppt). We use von Wartenburg's[32] enthalpy of hydration of La_2O_3(c) to obtain $\Delta H_f^\circ = -337.0$ kcal mol^{-1} for lanthanum hydroxide. The NBS 270-7 has listed $\Delta H_f^\circ = -337.0$ kcal mol^{-1} for $La(OH)_3$(c). Combination of this ΔH_f° with the ΔG_f° above leads to $S^\circ = 34$ cal K^{-1} mol^{-1} for material that we represent by $La(OH)_3$(aged ppt). Had we adopted a larger K_{sp} as suggested by several earlier investigations[24,25,30], we would have obtained a smaller S° for lanthanum hydroxide. A third law entropy based on low temperature heat capacities would be of interest. On the basis of uncertain entropies for other hydroxides, we suggest that this S° may be less than 34 cal K^{-1} mol^{-1}.

We now use free energies to calculate the following:

$$0.5\,La_2O_3(c)+1.5\,H_2O(liq) = La^{3+}(aq)+3\,OH^-(aq) \qquad K_{sp} = 5\times10^{-10}$$

$$La_2O_3(c)+3\,H_2O(liq) = 2\,La(OH)_3(aged\ ppt) \qquad \Delta G^\circ = -36._4\ kcal\ mol^{-1}$$

Thus $La(OH)_3$(aged ppt) is quite stable with respect to La_2O_3(c) and H_2O(liq), in contrast to $Sc(OH)_3$(ppt), which is unstable[33] with respect to Sc_2O_3(c) and H_2O(liq).

Moisa and Spivakovskii[31] have also investigated the precipitation of La^{3+}(aq) by OH^-(aq) in presence of Cl^-(aq) and have found evidence for precipitates that they represent by $La(OH)_2Cl$ and $La(OH)_{2.5}Cl_{0.5}$. From their table of results we select the following [expressed in terms of $La_2(OH)_5Cl$ instead of $La(OH)_{2.5}Cl_{0.5}$]:

$$La(OH)_2Cl(fresh\ ppt) = La^{3+}(aq)+2OH^-(aq)+Cl^-(aq) \qquad K_{sp} = 3\times10^{-16}$$

$$La(OH)_2Cl(aged\ ppt) = La^{3+}(aq)+2OH^-(aq)+Cl^-(aq) \qquad K_{sp} = 2\times10^{-17}$$

$$La_2(OH)_5Cl(aged\ ppt) = 2La^{3+}(aq)+5OH^-(aq)+Cl^-(aq) \qquad K_{sp} = 8\times10^{-36}$$

We use these K_{sp} values to calculate $\Delta G_f^\circ = -291._1$ kcal mol^{-1} for $La(OH)_2Cl$(fresh ppt), $\Delta G_f^\circ = -292._7$ kcal mol^{-1} for $La(OH)_2Cl$(aged ppt), and $\Delta G_f^\circ = -594._0$ kcal mol^{-1} for $La_2(OH)_5Cl$(aged ppt). We use K_{sp} values given above to calculate the following:

$$2La(OH)_2Cl(aged\ ppt)+OH^-(aq) = La_2(OH)_5Cl(aged\ ppt)+Cl^-(aq) \qquad K = 5\times10^1$$

$$2La(OH)_5Cl(aged\ ppt)+OH^-(aq) = 2La(OH)_3(aged\ ppt)+2Cl^-(aq) \qquad K = 2\times10^{10}$$

These K values show that the hydroxychlorides are converted to hydroxides in presence of excess OH^-(aq).

Libowitz[34] and Beavis[35] have reviewed properties of lanthanum (and other) hydrides. We also call attention to the equilibrium investigation of Messer and Hung[36] and the summary of "thermochromatographic" investigations by Gaifutdinova et al.[37]. We adopt $\Delta H_f^\circ = -48._3$ kcal mol^{-1} for LaH_2(c) and $\Delta H_f^\circ = -45._2$ kcal mol^{-1} for LaD_2(c), as listed for both of these phases in NBS 270-7. We may also obtain $S^\circ = 9$ cal K^{-1} mol^{-1} for LaH_2(c) from the ΔS_f° tabulated by Beavis[35]; our interpretation of the data leads to $S^\circ \cong 12$ as listed in our Table 1 with the corresponding ΔG_f°. A third law entropy is needed. Experimental results are inadequate to yield an accurate ΔH_f° to be attributed to LaH_3(c).

Ferris et al.[38] have made high temperature equilibrium distribution measurements with results that lead us to $\Delta G_f^\circ \cong -409$ kcal mol^{-1} for LaF_3(c) at 298 K. Other high temperature equilibrium investigations by Polyachenok[39] have led to a reported $\Delta H_f^\circ = -405 \pm 7$ kcal mol^{-1} for LaF_3(c) at 298 K. Our own uncertain interpretation of these[39] results leads to a somewhat more negative ΔH_f°, which we take to be ~ -408 kcal mol^{-1}. Spedding and Henderson[40] have made high temperature ($H^\circ_T - H^\circ_{298}$) measurements and have estimated $S^\circ_{298} = (27.5)$ cal K^{-1} mol^{-1} for LaF_3(c), which we use with $\Delta H^\circ_f \cong -408$ kcal mol^{-1} to obtain $\Delta G^\circ_f = -390$ kcal mol^{-1} for LaF_3(c). Another approach is to relate the K_{sp} for the lanthanum fluoride in fluoride selective electrodes to the ΔG°_f of LaF_3(c). Taking $K_{sp} = 10^{-29}$ from Frant and Ross[41] leads to $\Delta G^\circ_f = -403$ kcal mol^{-1} for LaF_3(c). Or we might accept Butler's[42] interpretation ($K_{sp} = 3 \times 10^{-25}$) of the results of Frant and Ross[41], which leads to $\Delta G^\circ_f = -397$ kcal mol^{-1}. The more recent $K_{sp} = 10^{-24}$ from Baumann[43] leads to $\Delta G^\circ_f = -396$ kcal mol^{-1}. We are unable to resolve the spread (-390 to -409 kcal mol^{-1}) in these ΔG°_f values and therefore omit LaF_3(c) from our Table 1. Because of the importance of LaF_3(c) in several respects, we suggest the following further investigations: fluorine combustion calorimetry leading to ΔH°_f, low temperature calorimetry leading to S°_{298}, and high temperature e.m.f. measurements leading to ΔG°_f.

Several groups[44–47] have investigated the vapor pressure of LaF_3(c) at high temperatures, with results in only fair agreement with each other. Entropies calculated for LaF_3(g) at 298 K are 78.7 cal K^{-1} mol^{-1} in NBS 270-7 and 73.6 cal K^{-1} mol^{-1} by Krasnov and Danilova[48]. Investigation of the thermodynamics of high temperature exchange reactions of LaF_3(g) could lead to properties of LaF_3(g) that are independent of those of LaF_3(c) and thus permit useful comparisons of properties by way of the thermodynamics of sublimation derived from the vapor pressure results.

Entropies of LaF(g) from NBS 270-7 and from Krasnov and Danilova[48] are in good agreement. We adopt S° for LaF_2(g) from Krasnov and Danilova[48]. For LaF_3(g) we adopt the S° from NBS 270-7 rather than the smaller value calculated by Krasnov and Danilova[48].

There have been several investigations of the solubility of precipitated lanthanum fluoride, which we represent by $LaF_3 \cdot \frac{1}{2}H_2O$(ppt). Combination of Kury's[49] experimental results ($\mu = 0.5$ M) with estimated activity coefficients leads to $K_{sp} = 1.9 \times 10^{-20}$. Lingane's[50] results led him to $K_{sp} = 3 \times 10^{-19}$, while Butler's[42] recalculations have led to K_{sp} between 1.6×10^{-21} and 6.3×10^{-23}. Da Silva and Queimado[51] have reported $K_{sp} = 1.3 \times 10^{-19}$ for 0.1 M $NaNO_3$(aq) solutions. Still more recent results from Pan et al.[52] have led to a reported $K_{sp} = 1.1 \times 10^{-18}$. These various K_{sp} values lead to ΔG°_f from -416.2 to -422.0 kcal mol^{-1} for $LaF_3 \cdot \frac{1}{2}H_2O$(ppt).

Pan et al.[52] have reported K_{sp} values at both 20 and 25°C, and have used these values to calculate both ΔH° and ΔS° for the solubility reaction. If we assume that the solid phase was LaF_3(c) [as assumed by Pan et al.[52]], we obtain $S^\circ_{298} = 101$ cal K^{-1} mol^{-1} for LaF_3(c). Making the more reasonable (to us) assumption that the solid phase of their precipitate was $LaF_3 \cdot \frac{1}{2}H_2O$(ppt), we obtain $S^\circ = 109$ cal K^{-1} mol^{-1} for this substance. Because both of these entropies are some three or four times as large as reasonable estimates, we feel justified in ignoring all calculations based on their $d \ln K_{sp}/dT$ results.

The NBS 270-7 lists $\Delta H^\circ_f = -440.9$ kcal mol^{-1} for $LaF_3 \cdot \frac{1}{2}H_2O$(c). We do not know the source of this value, but use it for the following calculations. Combination of the NBS 270-7 ΔH_f° with the ΔG_f° values cited above leads to S_{298}° between 31 and 51 cal K^{-1} mol^{-1} for $LaF_3 \cdot \frac{1}{2}H_2O$(ppt); values near the lower of these are consistent with reasonable estimates of this entropy.

For $LaF_3 \cdot \frac{1}{2}H_2O$(ppt) we adopt $\Delta H_f^\circ = -441$ kcal mol^{-1}, $\Delta G_f^\circ = -417$ kcal mol^{-1}, and $S^\circ = (32)$ cal K^{-1} mol^{-1}. This ΔG_f° is consistent with $K_{sp} = 3 \times 10^{-19}$ which is consistent with some of the values cited above.

It would be interesting to have a third law entropy for $LaF_3 \cdot \frac{1}{2}H_2O$(c or ppt), as well as the equilibrium vapour pressure of H_2O(g) over a mixture of this latter compound with LaF_3(c).

Results from Kury et al.[53] and Walker and Choppin[54] are consistent with the ΔG_f° of LaF^{2+}(aq) in NBS 270-7 and the following equilibrium constants:

$$La^{3+}(aq) + F^-(aq) = LaF^{2+}(aq) \qquad K = 9.5 \times 10^2$$

$$La^{3+}(aq) + HF(aq) = LaF^{2+}(aq) + H^+(aq) \qquad K = 6.6 \times 10^{-1}$$

Estimates of ΔH° and ΔS° for these reactions can be obtained[53,54] from d ln K/dT.

We have already adopted $\Delta H_f^\circ = -256.0$ kcal mol^{-1} for $LaCl_3$(c), on the basis of apparently reliable calorimetric measurements[16,17]. Unfortunately, we have no reliably established free energy of formation or entropy for this compound. Distribution studies by Ferris et al.[55] have led to approximate ΔG_f° values at high temperatures, which we use to obtain $\Delta G_f^\circ \cong -227$ kcal mol^{-1} for $LaCl_3$(c) at 298 K. Combination of this value with our adopted ΔH_f° leads to a negative S_{298}°, which in turn leads us to omit the ΔG_f° from Ferris et al.[55] from our further considerations of lanthanum chloride (and lanthanum oxychloride) that follow.

Vapor pressures of $LaCl_3$(c)[56,57] and $LaCl_3$(liq)[58] have been measured. The results of Shimazaki and Niwa[56] lead to $\Delta H_f^\circ = 84$ kcal mol^{-1} and $\Delta S^\circ = 60$ cal K^{-1} mol^{-1} for sublimation of $LaCl_3$(c) at 298 K, while results of Polyachenok et al.[57] similarly lead to $\Delta H_f^\circ = 80$ kcal mol^{-1} and $\Delta S^\circ = 54$ cal K^{-1} mol^{-1} for sublimation. Combining these values with our ΔH_f° for $LaCl_3$(c) leads to $\Delta H_f^\circ = -172$ and -176 kcal mol^{-1}, respectively, for $LaCl_3$(g). To use the results of Moriarty[58] we have estimated the enthalpy of $LaCl_3$(liq) at 1200 K relative to that of $LaCl_3$(c) at 298 K. Although there is considerable uncertainty in our estimate, it appears that the derived enthalpy of sublimation is substantially larger than is consistent with the results of the other investigations cited above[56,57].

Glybin and Dobrotin[59] have reported results of solution calorimetry that lead us to $\Delta H_f^\circ = -234._9$ kcal mol^{-1} for LaOCl(c), based on our ΔH_f° values for La_2O_3(c) and $LaCl_3$(c).

Novikov et al.[60] and Koch et al.[61] have investigated

$$LaCl_3(c) + H_2O(g) = LaOCl(c) + 2HCl(g)$$

at high temperatures with results that lead us to ΔH_f° values for LaOCl(c) less negative than the calorimetric value above and to $S^\circ[LaCl_3(c)] - S^\circ[LaOCl(c)] = 10._5$ cal K^{-1} mol^{-1} at 298 K.

High temperature equilibrium investigations of

$$3\,\mathrm{LaOCl(c)} = \mathrm{La_2O_3(c)} + \mathrm{LaCl_3(g)}$$

by Patrikeev et al.[62] lead us to $\Delta H_f^\circ[\mathrm{LaCl_3(g)}] - 3\Delta H_f^\circ[\mathrm{LaOCl(c)}] = 558$ kcal mol^{-1}. Other high temperature equilibrium results from Smagina et al.[63] lead us to 532 kcal mol^{-1} for the above difference in enthalpies of formation.

Krasnov and Danilova[48] have calculated $S^\circ = (80.7)$ cal K^{-1} mol^{-1} for $\mathrm{LaCl_3(g)}$ on the basis of estimated molecular parameters; our estimates lead to a larger entropy. Montgomery[64] has estimated $S^\circ_{298} = (34.5)$ cal K^{-1} mol^{-1} for $\mathrm{LaCl_3(c)}$ and $S^\circ_{298} = (24)$ cal K^{-1} mol^{-1} for LaOCl(c); our estimates are smaller.

There is no single set of thermodynamic properties of $\mathrm{LaCl_3(c)}$, $\mathrm{LaCl_3(g)}$, and LaOCl(c) that is consistent with all of the results cited above. We choose to ignore the results from Moriarty[58] and from Smagina et al.[63], and then choose the properties listed in Table 1 as reasonably consistent with other experimental results and estimates. Entropies for $\mathrm{LaCl_3(c)}$ and LaOCl(c) based on low temperature heat capacities would be useful.

We note that Atchayya and Dadape[65] have investigated the reaction of gaseous aluminum chloride with $\mathrm{La_2O_3(c)}$ at high temperatures to form LaOCl(c) and AlOCl(g). Because of substantial uncertainties in the reported ΔH_f° of AlOCl(g), we are unable to use their results to obtain information about LaOCl(c). It might, however, be useful to combine their results with our tabulated properties of LaOCl(c) to obtain the thermodynamic properties of AlOCl(g).

We adopt the ΔH_f° of $\mathrm{LaCl_3\cdot 7H_2O(c)}$ listed in NBS 270-7 as consistent with the calorimetric results of Spedding and Flynn[16]. We also adopt the $S^\circ_{298} = 110.6$ cal K^{-1} mol^{-1} obtained by Hinchey and Cobble[23] from the low temperature heat capacities of Pfeffer, as listed in NBS 270-7.

Calorimetric measurements by Morss[66] have led to $\Delta H^\circ = -19.9$ kcal mol^{-1} for the enthalpy of solution of $\mathrm{Cs_2NaLaCl_6(c)}$. Combination of this value with our ΔH_f° of $\mathrm{La^{3+}(aq)}$, ΔH_f° values for $\mathrm{Na^+(aq)}$ and $\mathrm{Cl^-(aq)}$ from NBS 270-3, and $\Delta H_f^\circ = -62.7$ kcal mol^{-1} for $\mathrm{Cs^+(aq)}$ [based on results cited by Morss[66]] leads to $\Delta H_f^\circ = -571.6$ kcal mol^{-1} for $\mathrm{Cs_2NaLaCl_6(c)}$. Morss[66] has also presented an interesting discussion of lattice and hydration energies.

Vanderzee and Nutter[67] have measured enthalpies of dilution of aqueous lanthanum perchlorate over a wide range of concentration. Lietzke et al.[68] have made e.m.f. measurements and related thermodynamic calculations on aqueous $\mathrm{LaCl_3}$–HCl solutions up to 175°C while Lietzke and Danford[69] have made similar measurements on HCl–NaCl–$\mathrm{LaCl_3}$ at 25°C. Measurements by Dunn[70] and by Spedding et al.[71] have led to apparent and partial molal volumes for aqueous lanthanum chloride and lanthanum perchlorate.

Ferris et al.[55] provide an approximate ΔG_f° of $\mathrm{LaBr_3(c)}$ at 640°C. Sublimation pressures of $\mathrm{LaBr_3(c)}$ have been measured by Shimazaki and Niwa[56], who have also calculated ΔH° and ΔS° of sublimation. Combination of their ΔS° of sublimation with $S^\circ_{298} = 88.5$ cal K^{-1} mol^{-1} for $\mathrm{LaBr_3(g)}$ from Krasnov and Danilova[48] (based on estimated molecular parameters) leads to $S^\circ_{298} = 29.$ cal K^{-1} mol^{-1} for $LaBr_3$(c), which seems to us to be considerably smaller than is reasonable.

The ΔH°_f for $La(BrO_3)_3 \cdot 9H_2O$(c) in NBS 270-7 is consistent with the enthalpy of solution reported by Staveley et al.[72] and is adopted for our Table 1.

For LaI_3(c) we have $\Delta H^\circ_f = -159.4$ kcal mol^{-1} listed in NBS 270-7, consistent with the calorimetric results of Hohmann and Bommer[73]. Shimazaki and Niwa[56] have measured sublimation pressures of LaI_3(c) at several temperatures and have calculated ΔH° and ΔS° of sublimation at 298 K. We use their ΔH° of sublimation with the above ΔH°_f of LaI_3(c) to calculate our tabulated ΔH°_f of LaI_3(g). Krasnov and Danilova[48] have used estimated molecular parameters in calculating $S^\circ_{298} = 94.7$ cal K^{-1} mol^{-1} for LaI_3(g). Combination of this S° with ΔS° of sublimation from Shimazaki and Niwa[56] leads to $S^\circ_{298} = 32.4$ cal K^{-1} mol^{-1} for LaI_3(c). We consider this last S° to be considerably smaller than is reasonable and therefore choose to omit entropies and related free energies of LaI_3(c) and LaI_3(g) from Table 1.

Dworkin and Bredig[74] have made calorimetric measurements of $(H^\circ_T - H^\circ_{298})$ at high temperatures for LaI_3(c and liq).

Krasnov and Danilova[48] have used estimated molecular parameters for calculation of thermodynamic functions for various gaseous lanthanum halides that are not listed in Table 1.

Bertha and Choppin[75] have measured the solubility of $La(IO_3)_3$(c) and have derived $K_{sp} = 1.02 \times 10^{-11}$ for

$$La(IO_3)_3(c) = La^{3+}(aq) + 3IO_3^-(aq)$$

at 25°C. They have also made calorimetric measurements of the enthalpy of precipitation, leading to $\Delta H^\circ = 6.9$ kcal mol^{-1}for the above reaction. We combine these results with the properties of La^{3+}(aq) listed in Table 1 and those of IO_3^-(aq) from NBS 270-3 to obtain our tabulated properties of $La(IO_3)_3$(c), which are close to those listed in NBS 270-7. An entropy of $La(IO_3)_3$(c) based on low temperature heat capacities would be useful.

Cater et al.[76] have estimated $S^\circ_{298} = (17.5)$ cal K^{-1} mol^{-1} for LaS(c), as listed in NBS 270-7. Mills[77] has considered this value along with his own estimate and has selected $S^\circ_{298} = (17.0 \pm 2)$ cal K^{-1} mol^{-1}. We also note that Gordienko and Fenochka[78] have estimated $S^\circ_{298} = (16.00)$ cal K^{-1} mol^{-1}. We choose $S^\circ_{298} = (17)$ cal K^{-1} mol^{-1} for LaS(c).

Cater et al.[76], Cater and Steiger[79], Fenochka et al.[80], and Mills[77] have used estimated molecular parameters to calculate $S^\circ_{298} = (61.66)$, (60.3), (60.55), and (59.9) cal K^{-1} mol^{-1}, respectively, for LaS(g). The NBS 270-7 has listed $S^\circ = 60$ cal K^{-1} mol^{-1}. We also adopt $S^\circ_{298} = (60)$ cal K^{-1} mol^{-1} for LaS(g).

Low temperature heat capacity measurements have led Paukov et al.[81] to $S^\circ_{298} = 39.43$ cal K^{-1} mol^{-1} for La_2S_3(c), which is the value we adopt for this substance.

For LaS_2(c) we accept $S^\circ_{298} = (21._5)$ cal K^{-1} mol^{-1} from Mills[77].

We use the dissociation energy from Drowart et al.[7] to obtain $\Delta H_f^\circ = 31 \pm 3$ kcal mol^{-1} for LaS(g), which is the value we adopt. Slightly larger values with larger uncertainties can be obtained from other sources already cited[76,79] and those cited in the next paragraph.

Cater et al.[76], Cater and Steiger[79], and Gordienko et al.[82] are all in agreement with $\Delta H_{298}^\circ = 141._5$ kcal mol^{-1} for sublimation of LaS(c) to LaS(g). Combination of this enthalpy of sublimation with the ΔH_f° above for LaS(g) leads to $\Delta H_f^\circ = -110$ kcal mol^{-1} for LaS(c), which we adopt. Although the results reported recently by Gordienko and Fenochka[83] for sublimation and dissociation of lanthanum monosulfide are not quite internally consistent, they are in reasonable agreement with the ΔH_f° values we have selected for LaS(g) and LaS(c).

For La_2S_3(c) we adopt $\Delta H_f^\circ = -289$ kcal mol^{-1}, which is consistent with results of old calorimetric measurements[84] and has also been listed in NBS 270-7. Because of uncertainties in interpretation of the calorimetric results[84], we do not list a ΔH_f° for LaS_2(c).

Grizik et al.[85] have made high temperature equilibrium measurements with results that lead us to the properties listed in Table 1 for $La_2O_2SO_4$(c). Because the tabulated entropy is considerably larger than seems reasonable, we suggest that there may be a substantial error or uncertainty in the results[85].

Soshchin[86] and Gschneidner et al.[87] have estimated thermodynamic properties of technologically important La_2O_2S(c); measurements are needed.

Relying on the results of Fay and Purdie[88] and Izatt et al.[89], we choose $K = 3.5 \times 10^3$ for

$$La^{3+}(aq) + SO_4^{2-}(aq) = La(SO_4)^{+}(aq) \tag{2}$$

and thence calculate $\Delta G_f^\circ = -346.2$ kcal mol^{-1} for $La(SO_4)^+$(aq), as also listed in NBS 270-7. Our adopted $\Delta H_f^\circ = -383.1$ kcal mol^{-1} for $La(SO_4)^+$(aq) is the same as listed in NBS 270-7; this value is in precise agreement with the calorimetric results of Izatt et al.[89] and is in close agreement with the calorimetric results of Fay and Purdie[88]. Izatt et al.[89] and Fay and Purdie[88] cite results of earlier equilibrium investigations that provide additional support for the K value given above for reaction (2).

Fisher and Davis[90] have made conductance measurements at different pressures to find corresponding K values for formation of $La(SO_4)^+$(aq) as in reaction (2). Their results lead to $K = 4._2 \times 10^3$ at 1 atm and $K = 1._2 \times 10^3$ at 2000 atm, and thence to a positive ΔV° for the association reaction (2).

We also have data (equilibrium and calorimetric) from de Carvalho and Choppin[91] for reaction (2) in 2 M $NaClO_4$ solution.

We have $K = 72$ for

$$La(SO_4)^{+}(aq) + SO_4^{2-}(aq) = La(SO_4)_2^{-}(aq)$$

from the results of Izatt et al.[89], in accord with the ΔG_f° listed in NBS 270-7. We also have the ΔH_f° and S° for $La(SO_4)_2^-$(aq) from Izatt et al.[89], as also listed in NBS 270-7.

Conductance measurements by Farrow and Purdie[92] have led to K for reaction (2) in D_2O(liq).

Lietzke et al.[93,94] have measured the solubilities of lanthanum sulfate in water, in aqueous uranyl sulfate solutions, and in sulfuric acid solutions at several high temperatures.

The ΔH_f° values for $La_2(SO_4)_3$(c) and $La_2(SO_4)_3 \cdot 9H_2O$(c) that are listed in NBS 270-7 are consistent with the calorimetric results of Montgomery[17] and are adopted for our Table 1.

Results from Bergman et al.[95], from Ni and Wahlbeck[96], and from Nagai et al.[97] are in good agreement on the dissociation energy and thence lead to our $\Delta H_f^\circ = 43$ kcal mol^{-1} for LaSe(g). Combination of this value with further results from Nagai et al.[97] leads to $\Delta H_f^\circ \cong -97$ kcal mol^{-1} for LaSe(c). For LaSe(c) we also have $S_{298}^\circ = 19._4$ cal K^{-1} mol^{-1} as calculated by Mills[77] from results of heat capacity measurements. Mills[77] has used estimated molecular parameters to calculate $S_{298}^\circ = (62.85)$ cal K^{-1} mol^{-1} for LaSe(g). We combine the ΔH_f° and S° values to obtain corresponding free energies that are also listed in Table 1.

Heat capacity measurements by Paukov et al.[98] have led to $S_{298}^\circ = 48.33$ cal K^{-1} mol^{-1} for La_2Se_3(c). Mills[77] has cited $\Delta H_f^\circ = -223 \pm 5$ kcal mol^{-1} for this compound, on the basis of calorimetric results that are unavailable to us. We combine these values to obtain our tabulated ΔG_f° for La_2Se_3(c).

We adopt $\Delta H_f^\circ = -688.7$ kcal mol^{-1} for $La_2(SeO_3)_3$(c) as listed in NBS 270-7. This value is consistent with the calorimetric results of Maier et al.[99]. We also cite the ΔG_f° and S° values listed in NBS 270-7 for this compound, but are unable to identify the source of these properties.

For LaTe(c) we have only $S_{298}^\circ = 21._1$ cal K^{-1} mol^{-1} as calculated by Mills[77] from heat capacities. The dissociation energy from Bergman et al.[95] leads to $\Delta H_f^\circ = 59$ kcal mol^{-1} for LaTe(g). We combine this value with $S_{298}^\circ = (64._7)$ cal K^{-1} mol^{-1} calculated[77] from estimated molecular parameters to obtain our tabulated ΔG_f°.

A reliable $S_{298}^\circ = 55.36$ cal K^{-1} mol^{-1} for La_2Te_3(c) is obtained from the heat capacity measurements of Nogteva et al.[100]. Mills[77] cites $\Delta H_f^\circ = -187.5 \pm 6.1$ kcal mol^{-1} on the basis of calorimetric results that are unavailable to us, while the NBS 270-7 lists $\Delta H_f^\circ = -173$ kcal mol^{-1} from an un-cited source that we cannot identify. We do not list either ΔH_f° or ΔG_f° for La_2Te_3(c). Sokolov and Doroshenko[101] have reported vapor pressures for decomposition of La_2Te_3(c); neither solid phases nor gaseous species are adequately identified to justify thermodynamic calculations.

We adopt $\Delta H_f^\circ = -72._5$ kcal mol^{-1} for LaN(c), which is consistent with the calorimetric results of Neumann et al.[102] and with the value listed in NBS 270-7. Combination of this value with our estimated $S_{298}^\circ = (13._5)$ cal K^{-1} mol^{-1} leads to the tabulated ΔG_f° of LaN(c). Although there have been two investigations[103] of the low temperature heat capacity of LaN(c), the published results (graphs of C_p vs. T) do not permit calculation of S_{298}°.

We adopt ΔH_f° values for compounds of type $La(NO_3)_3 \cdot nH_2O$(c) that are consistent with results[104] of vapor pressure and calorimetric measurements, and as listed in NBS 270-7. We also note that Spedding et al.[105] have reported accurate densities and apparent molal volumes of aqueous solutions of lanthanum nitrate.

We adopt $\Delta H_f^\circ = -73$ kcal mol^{-1} for LaAs(c) from the calorimetric results of Hanks and Faktor[106].

Gschneidner et al.[87] have summarized the high temperature e.m.f. results of Russian investigations of several La–Sb phases ranging from La$_2$Sb(c) to La$_{0.53}$Sb$_{0.47}$(c). On the basis of these[87] results we can choose $\Delta H_f^\circ = -71$ kcal mol^{-1} for LaSb(c). On the other hand, Chua and Pratt[107] have cited $\Delta H_f^\circ = -52$ kcal mol^{-1} for LaSb(c) on the basis of unpublished vapor pressure studies by Pratt and Underhill. We are unable to resolve this discrepancy. For LaSb(c) we therefore list only the entropy $S_{298}^\circ = 21.22$ cal K^{-1} mol^{-1} from the heat capacity results of Wallace et al.[108].

The heat capacity measurements of Wallace et al.[108] have led to $S_{298}^\circ = 24.10$ cal K^{-1} mol^{-1} for LaBi(c), and we have $\Delta H_f^\circ = -53._0$ kcal mol^{-1} from the calorimetric measurements of Borsese et al.[109]. These values lead to our tabulated ΔG_f° for LaBi(c). We also have $\Delta H_f^\circ = -173$ kcal mol^{-1} for La$_4$Bi$_3$(c) from the results of Borsese et al.[109].

Results of four high temperature investigations[110–113] lead to the thermodynamic properties we list in Table 1 for LaC$_2$(c) and LaC$_2$(g). Unfortunately, the desired thermodynamic properties have been obtained by combination of the actual experimental results with thermal functions that are partly based on estimated molecular parameters. Furthermore, there are some substantial differences between the results of different investigators and between second and third law treatments, all of which indicate the presence of systematic experimental errors and/or errors in the thermal functions used in data treatment. As a result, uncertainties are several kcal mol^{-1} in ΔH_f° and ΔG_f° values. A third law entropy for LaC$_2$(c) would be useful. Finally, as Stearns and Kohl[113] have written, the phase we have represented by LaC$_2$(c) probably is represented better by LaC$_{2-x}$(c).

The results of Stearns and Kohl[113] also permit us to calculate our tabulated properties of LaC$_3$(g) and LaC$_4$(g).

High temperature equilibrium measurements by Butherus and Eick[114] lead to our tabulated properties for the oxide carbide La$_2$O$_2$C$_2$.

Jordanov and Havezov[115] have reported the solubility product $K_{sp} = 3.8 \times 10^{-34}$ for La$_2$(CO$_3$)$_3$(c), which leads to $\Delta G_f^\circ = -750.9$ kcal mol^{-1} for La$_2$(CO$_3$)$_3$(c), as also listed in NBS 270-7.

Hartmann and Eckelmann[116] have measured the heat of combustion of lanthanum cyanamide, leading to $\Delta H_f^\circ = -199$ kcal mol^{-1} for La$_2$(CN$_2$)$_3$(c), as also listed in NBS 270-7.

Calorimetric measurements by Guadagno et al.[117] lead to $\Delta H^\circ = -60._6$ kcal mol^{-1} for LaSn$_3$(c) and to $\Delta H_f^\circ = -140._4$ kcal mol^{-1} for La$_2$Sn$_3$(c). High temperature e.m.f. results from Matigorova and Bayancv[118] are in fair agreement with the above ΔH_f° for LaSn$_3$(c).

We have $\Delta H_f^\circ = -49.18$ ($\pm 5\%$) kcal mol^{-1} for $LaPb_3$(c) from the calorimetric measurements of Palenzona and Cirafici[119]. From Ferro et al.[120] we have $\Delta H_f^\circ = -54.8$ (± 1.5) kcal mol^{-1} for this same compound, along with ΔH_f° for other compounds of type La_nPb_m(c). In Table 1 we list ΔH_f° values from Ferro et al.[120], although it is possible that the ΔH_f° for $LaPb_3$(c) from Palenzona and Cirafici[119] is better.

For LaB_6(c) we have a reliable $S_{298}^\circ = 19.87$ cal K^{-1} mol^{-1} from Westrum[121]. Gschneidner et al.[87] have reviewed results of Russian investigators and cite ΔH_f° values ranging from -27.7 to -30.9 kcal mol^{-1} for LaB_6(c), with uncertainties of ± 4 to ± 6 kcal mol^{-1}. These values are in reasonable agreement with $\Delta H_f^\circ = -31$ kcal mol^{-1} that is listed in NBS 270-7. The most recent investigation, by Ames and McGrath[122], casts doubt on these and other investigations in which it appeared that LaB_6(c) vaporized to a LaB_n(g) compound or to La(g) and solid boron. Ames and McGrath[122] have found that LaB_6(c) vaporized congruently to La(g) and 6B(g) and have obtained $\Delta H^\circ = 854.6 \pm 37.0$ kcal mol^{-1} for this vaporization reaction at 298 K. Combination of this ΔH_f° of vaporization with our ΔH° of La(g) and ΔH_f° from NBS 270-3 for B(g) [note that there is probably an uncertainty of about 3 kcal mol^{-1} in this quantity] leads us to $\Delta H_f^\circ = +55$ kcal mol^{-1} for LaB_6(c). Because of the large uncertainties and the disagreements between various workers, we do not list a ΔH_f° for LaB_6(c).

Heat capacity measurements by Deenadas et al.[123] lead to $S_{298}^\circ = 23.60$ cal K^{-1} mol^{-1} for $LaAl_2$(c). Similar measurements by Marzouk et al.[124] lead to $S_{298}^\circ = 50.98$ cal K^{-1} mol^{-1} for $LaNi_5$(c).

It has been observed by van Vucht et al.[125] that $LaNi_5$(c) and phases of type $La_{1-x}Ce_xNi_5$(c) absorb and desorb large quantities of hydrogen rapidly at room temperature; the hydride $LaNi_5H_{6.7}$(c) has been formed at H_2(g) pressure of 2.5 atm. An estimate of the ΔH of dissociation of this compound is obtained[125] from decomposition pressures at several temperatures.

For LaAu(g) we adopt the thermodynamic properties listed in NBS 270-7; these values are in fair agreement with the results of Gingerich and Finkbeiner[126]. Our tabulated properties of LaRh(g) are based on the high temperature investigations by Cocke et al.[127].

Calorimetric results from Korneev et al.[128] lead us to $\Delta H_f^\circ \cong -979$ kcal mol^{-1} for lanthanum zirconate, $La_2Zr_2O_7$(c).

Our tabulated ΔH_f° values ($\pm \sim 3$ kcal mol^{-1}) for lanthanum chromates are based on the enthalpies of solution determined calorimetrically by Tsyrenova et al.[129].

Results from Davidenko et al.[130] lead to the following equilibrium constants and thence to the free energies of $La_2(MoO_4)_3 \cdot 2H_2O$(c) and $La(MoO_4)^+$(aq):

$$La_2(MoO_4)_3 \cdot 2H_2O(c) = 2La^{3+}(aq) + 3MoO_4^{2-}(aq) + 2H_2O(liq) \qquad K_{sp} = 10^{-21}$$

$$La^{3+}(aq) + MoO_4^{2-}(aq) = La(MoO_4)^+(aq) \qquad K = 10^4$$

For these calculations we use $\Delta G_f^\circ = -200.4$ kcal mol^{-1} for MoO_4^{2-}(aq) from a recent review[131].

The association of $La^{3+}(aq)$ with $Fe(CN)_6^{3-}(aq)$ is an interesting problem in electrolyte solution chemistry that has been investigated several times[24,25,132]. We adopt the following equilibrium constant and the corresponding ΔG_f° for $LaFe(CN)_6$ (aq, undiss):

$$La^{3+}(aq) + Fe(CN)_6^{3-}(aq) = LaFe(CN)_6(aq, undiss) \qquad K = 6 \times 10^3$$

The d ln K/dT investigation of Davies and James[133] leads to $\Delta H^\circ = 2.02$ kcal mol^{-1} and $\Delta S^\circ = 23.9$ cal K^{-1} mol^{-1} for the above reaction, while the calorimetric measurements of Stampfli and Choppin[132] lead to $\Delta H^\circ = 0.85$ kcal mol^{-1} and $\Delta S^\circ = 19.8$ cal K^{-1} mol^{-1}. We weight the latter results most heavily in obtaining our ΔH_f° and S° values for $LaFe(CN)_6$(aq, undissoc.). We also note that Hamann et al.[134] have investigated the above reaction at pressures up to 2000 atm and from d ln K/dP have calculated that $\Delta V^\circ = 8.0$ cm^3 mol^{-1} for this association reaction.

Matheson[135] has discussed the effect of the "distance of closest approach" parameter on calculated values of stability constants, with particular reference to lanthanum ferricyanide.

Panckhurst and Woolmington[136] have found $K = 1.1 \times 10^5$ for

$$La^{3+}(aq) + Fe(CN)_6^{4-}(aq) = LaFe(CN)_6^-(aq)$$

Our ΔG_f° of $LaFe(CN)_6^-(aq)$ is based on this equilibrium constant and the ΔG_f° of $Fe(CN)_6^{4-}$ listed in NBS Tech. Note 270-4.

Results of several investigations[137-139] are consistent with $K = 5 \times 10^3$ for

$$La^{3+}(aq) + Co(CN)_6^{3-}(aq) = LaCo(CN)_6(aq, undiss)$$

The results of James and Monk[137] permit an estimate of ΔH° and ΔS° for the above reaction.

Sillén[24,25] has cited several equilibrium investigations leading to reported solubility products and stability constants for complex ions involving lanthanum and various P(V) species such as PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_9^{3-}$, etc. We do not use these results for our Table I because it is our opinion that too little attention was paid to such matters as hydrolysis reactions, ion pairing, and characterization of solid phases supposedly in equilibrium with saturated solutions.

We also note that Sillén[24,25] has cited (apparently reliable) formation constants for various inorganic complex ions of $La^{3+}(aq)$. Because these formation constants are generally small, we have not used them for calculation of ΔG_f° values of the corresponding complexes.

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