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Thermodynamics of the Interaction of the Lanthanides with Other Elements

A.P.Bayanov

The thermodynamic characteristics (Gibbs free energies, enthalpies, and entropies) of the interaction of the lanthanides with various elements to form binary compounds and solid or liquid alloys are described. The dissociation energies of gaseous compounds are briefly analysed and experimental and calculated data are compared. The variation of the thermodynamic characteristics of the compounds in the lanthanum-lutetium series is considered from the standpoint of the electronic structures of the components. The thermodynamic behaviour of europium and yttrium in relation to the other lanthanides is discussed.
The bibliography includes 360 references.

CONTENTS

I. Introduction 122
II. Halides 122
III. Chalcogenides 124
IV, Pnictides 126
V. Carbides, silicides, and borides 126
VI. Hydrides 127
VII. Metallic alloys with *p* elements 127
VIII. Alloys of lanthanides with *s* and *d* elements 128
IX. General characteristics 129

I. INTRODUCTION

The bulk of the thermodynamic data for the lanthanides was obtained in the last two—three decades. The thermodynamic properties of numerous simple and complex lanthanide compounds both in the solid state and in solution were investigated during this period[1-4]. Towards the end of the 1960s refractory lanthanide compounds and alloys began to be studied. The experimental technique of the investigation of such systems is fairly complex and the number of the relevant experimental studies increased slowly. For this reason, the thermodynamic characteristics of many such compounds have been calculated.

The early investigations of the thermodynamic properties of lanthanide compounds are described in Serebrennikov's[5] and Gschneidner's[6] monographs and in Montgomery's review[7]. We shall consider some of these early studies because the data obtained in them have been transferred without due critical analysis from handbook to handbook, owing to the lack of other results, and have served in many publications as "reference" experimental data. During the last 5—7 years, reviews have been published on the thermodynamics of lanthanide halides[8,9] and oxides[10-14], certain refractory compounds of lanthanides with *p* elements[11,15,16], and alloys[17]. Krestov's monograph[3] deals with the thermodynamic characteristics of the lanthanide ions in the gaseous state and in solution, the temperature variation of the properties of certain lanthanide compounds, and the changes which they undergo in ionisation, hydration, dissolution, formation and ionic sublimation reaction.

The aim of the present review was to give a systematic account and to carry out a critical analysis of the experimental data for the thermodynamics of the interaction of the lanthanides with other elements and to compare them with calculated values. Particular attention was devoted to the relation between the thermodynamic characteristics and the electronic structures of the system components.

II. HALIDES

The trichlorides have been most thoroughly investigated among lanthanide halides. Systematic calorimetric studies on crystalline lanthanide trichlorides were carried out by Bommer and Hohmann[18-20]. Their results agree with those of Matignon[21,22], but in both sets of investigations insufficiently pure lanthanides were used. In later studies by Spedding and coworkers[23-25], Montgomery[26,27], Stuve[28-31], and Polyachenok[32] purer lanthanides were employed. Comparison of the enthalpies of formation of lanthanide trichlorides (Table 1) shows that the corresponding values for $EuCl_3$ and $YbCl_3$ are more positive than the enthalpies of formation of the adjacent lanthanide trichlorides. This apparent anomaly has been accounted for theoretically[35,36].

Table 1. Enthalpies of formation of lanthanide trichlorides.

Lanthanide trichloride	$-\Delta H^\circ_{298}$, mole^{-1}	Refs.	Lanthanide trichloride	$-\Delta H^\circ_{298}$, kcal mole^{-1}	Lanthanide trichloride
$LaCl_3$	255.91±0.20	25	$GdCl_3$	240.09±0.30	25
	255.9	33		239.6	33
	256.18±0.28	26	$TbCl_3$	238.33±1.50	30
$CeCl_3$	252.84±0.02	23, 24		238.4	33
	251.5	33	$DyCl_3$	236.6	33
$PrCl_3$	252.09±0.02	25		235	34
	252.0	33	$HoCl_3$	240.29±1.70	30
$NdCl_3$	245.62±0.02	23, 24		237.8	33
	248.97±0.26	28	$ErCl_3$	239.07±0.20	25
	247.4	33		238.0	33
	246.5	32	$TmCl_3$	235.82±0.40	31
$SmCl_3$	244.18±0.41	27		236.3	33
	244.1	33	$YbCl_3$	229.37±0.72	31
$EuCl_3$	218.74±0.65	29		229.4	33
	219.5	33	$LuCl_3$	234.5	33

While the majority of lanthanides in the solid state under standard external conditions have three valence electrons, europium and ytterbium have only two valence electrons under the same conditions[5]. In the trichlorides all the lanthanides are tervalent. The interaction with chlorine entails a change in the number of valence electrons of europium and ytterbium from two to three and the associated rearrangement of the electronic structure:

$$\mathrm{Eu\,[II,\ 4}f^{7}5d^{0}6s^{2}\mathrm{]} \rightarrow \mathrm{Eu\,[III,\ 4}f^{6}5d^{1}6s^{2}\mathrm{]},$$

$$\mathrm{Yb\,[II,\ 4}f^{14}5d^{0}6s^{2}\mathrm{]} \rightarrow \mathrm{Yb\,[III,\ 4}f^{13}5d^{1}6s^{2}\mathrm{]}.$$

It has been established[35,36] that the energy required for the completion of the above processes is 22 kcal mole^{-1} for europium and 9 kcal mole^{-1} for ytterbium. Other lanthanides are not involved in processes of this kind. As a result the Gibb's free energies and enthalpies of formation of $EuCl_3$ and $YbCl_3$ are more positive than the corresponding values for the trichlorides of the adjacent lanthanides.

Latimer[37] calculated the entropy of formation of lanthanide trichlorides by combining their absolute entropies and the entropies of the initial elements. His entropy data[37] and the experimental enthalpies of formation served as a basis for the calculation of the Gibbs free energies of formation of lanthanide trichlorides[7,37]. The Gibbs free energies for the lanthanide trichlorides were also determined by Karapet'yants[38] by the method of comparative calculation. The thermodynamic characteristics of the formation of individual lanthanide trichlorides have also been investigated[39-47].

Some authors[43-46] calculated the thermodynamic functions of formation of liquid lanthanide dichlorides. The enthalpies of formation of crystalline samarium, ytterbium[48,49], europium[50], and neodymium[32] dichlorides have been determined calorimetrically at 298 K as -195.6 ± 1.0, -184.5 ± 1.7, -197.0 ± 1.3, and -163.2 kcal mole^{-1} respectively. These results are consistent with the values calculated for praseodymium, neodymium, samarium, europium, erbium, and ytterbium dichlorides from the fusion diagrams and vapour pressures in systems of the type $Ln-LnCl_3$.[51-56] According to Turnbull and Watts[57] and Valentine et al.[58] the Gibbs free energy of the formation of $PrCl_2$ is -156 kcal mole^{-1} and its enthalpy of formation is -158 kcal mole^{-1} [57] or -167 kcal mole^{-1}.[58] The enthalpies of formation of all the lanthanide dichlorides have been calculated from the Born–Haber cycle[51,59,60]. The enthalpies of formation of the crystalline dichlorides exhibit double periodicity in the series of lanthanides—there are extrema corresponding to $EuCl_2$ and $YbCl_2$ (Fig. 1). The difluorides exhibit a similar relation[59]. The standard enthalpy of formation of EuF_2 evaluated from tensimetric data[61] is -284 ± 17 kcal mole^{-1}.

Experimental enthalpies of formation of lanthanide trifluorides were obtained by Polyachenok[62,63]: -405, -401, -395, -389, and -378 kcal mole^{-1} for LaF_3, PrF_3, NdF_3, GdF_3, and ErF_3 respectively. Their accuracy is to within 5–7 kcal mole^{-1}. The data for the above five trifluorides were also used to estimate by interpolation the enthalpies of formation of the trifluorides of other lanthanides[63]. The enthalpies of formation of trifluorides at 298 K have been determined in a calorimetric study of the precipitation of lanthanide trifluorides from aqueous solutions[64,65] and the following values were obtained (in kcal mole^{-1}): -403.7 ± 1.5 for LaF_3, -402.0 ± 1.5 for CeF_3, -401.5 ± 1.5 for PrF_3, -398.5 ± 0.5 for NdF_3, -398.6 ± 4.0 for SmF_3, -373.8 ± 4.0 for EuF_3, -397.5 ± 0.5 for GdF_3, -388.6 ± 2.0 for ErF_3, and -382.1 ± 2.0 for YbF_3.

The following expressions for the Gibbs free energies of formation of lanthanide trifluorides have been obtained by an e.m.f. method using a solid electrolyte (anionic conductor):

$\Delta G = -(411.38 \pm 0.81) + (57.46 \pm 0.9) \cdot 10^{-3}T \pm 1.4$ kcal/mole LaF_3, (Refs.66,67),

$\Delta G = -405 + 52.71 \cdot 10^{-3}T$ kcal/mole NdF_3, (Ref.68),

$\Delta G = -402 + 50.77 \cdot 10^{-3}T$ kcal/mole GdF_3, (Ref.68),

$\Delta G = -400.5 + 48.42 \cdot 10^{-3}T$ kcal/mole DyF_3, (Ref.68),

$\Delta G = -397.5 + 45.66 \cdot 10^{-3}T$ kcal/mole ErF_3, (Ref.68),

$\Delta G = -394.5 + 44.89 \cdot 10^{-3}T$ kcal/mole β-LuF_3, (Ref.68).

$\Delta G = -387 + 37.08 \cdot 10^{-3}T$ kcal/mole α-LuF_3, (Ref.68).

The enthalpies of formation of lanthanide trifluorides calculated[59] from the Born–Haber cycle are higher by 30–50 kcal mole^{-1} than the experimental values. The data of Brewer et al.[69], which have been used in a number of texts[3,8,70,71], are also higher than the experimental results. On the other hand, the data in the handbook of Wicks and Block[72] are lower than the experimental enthalpies of formation of the trifluorides[62-68,73]. The thermodynamic functions of formation of certain lanthanide fluorides were studied in other investigations also[74-81]. Certain data[4,65,72] reflect the energy of the change in the number of valence electrons of europium[36]. In others this factor[3,34,63,78] is disregarded.

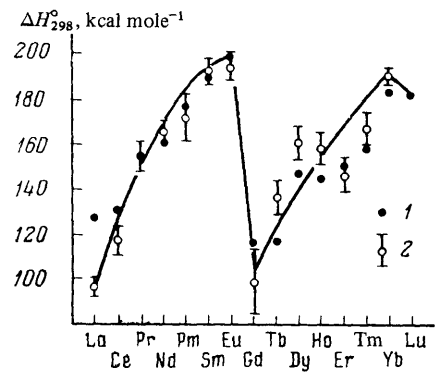


Figure 1. The standard enthalpies of formation of solid lanthanide dichlorides: 1) Novikov and Polyachenok's data[59]; 2) Johnson's data[60].

Estimates of the enthalpies of formation of crystalline lanthanide tribromides have been published[8,47,69,72,79,80]. The data quoted by Wicks and Block[72] are appreciably lower in absolute magnitude than those in other publications. The effect of the change in the number of valence electrons of europium and ytterbium from two to three has been reflected in the enthalpies quoted by Thoma[8], but has been disregarded by other authors[34,78,79]. The thermodynamic functions of europium tribromide[82] and dibromide[83] have been determined experimentally. The enthalpy and Gibbs free energy of formation of $EuBr_3$ at 293.15 K are respectively -186 ± 3.0 and -179.3 ± 3.0 kcal mole^{-1}. For solid $EuBr_2$, $\Delta H^{\circ}_{298} = -178.0 \pm 3.0$ kcal mole^{-1}, $\Delta S^{\circ}_{298} = -16.2 \pm 3.0$ e.u., and $\Delta G^{\circ}_{298} = -173.2 \pm 3.0$ kcal mole^{-1}. Estimates are available for samarium, europium, and ytterbium dibromides[69].

The experimental determinations of the enthalpies of formation of lanthanide tri-iodides[8,20] are inconsistent. The Gibbs free energies have been calculated[37,38]. The data in handbooks[71,72] for the tri-iodides have only been estimated, as in other publications[69,78,84]. The formation of solid EuI_2 at 298.15 K is accompanied by the evolution of -138.0 ± 5 kcal mole^{-1} of heat[85].

The enthalpies of formation and dissociation energies of gaseous lanthanide monohalides, dihalides, and trihalides have been studied[86-97]. According to tensimetric data, the dissociation energies of EuI_2,[95] $EuCl_2$,[95] and $YbCl_2$,[96] are respectively 156.0 ± 5.0, 212.0 ± 2.3, and 193.5 ± 3.2 kcal mole^{-1}. Certain problems of the energetics and stability of gaseous lanthanide halides have been solved by Polyachenok[94] by estimating the thermodynamic quantities using methods of comparative calculation. The atomisation energies of various groups of lanthanide halides in the lanthanum–lutetium series exhibit a double periodicity with minima corresponding to europium and ytterbium. The standard enthalpies of formation of lanthanide monohalides and dihalides show that their stability increases from lanthanum to europium and from gadolinium to ytterbium. The enthalpies of formation of lanthanide trihalides vary monotonically in the series La–Lu with extrema at Eu and Yb. The accuracy of the estimates[94] obtained by methods of comparative calculation is to within ±10–15 kcal mole^{-1}.

III. CHALCOGENIDES

The principal data for the enthalpies of formation of the oxides were obtained calorimetrically by the combustion of lanthanum[21,98-102], cerium[99,100,103-105], Ce_2O_3,[106,107] neodymium[99,105,108], samarium[105,106,109,110], europium[111,112], gadolinium[113], dysprosium[114,115], holmium[116], erbium[105,117], thulium[118], ytterbium[114], and lutetium[119] in oxygen and by low-temperature calorimetric measurements for the dissolution of the lanthanides and the oxides La_2O_3,[21,26,120,121] Pr_2O_3 (hexagonal)[122,123], Pr_2O_3 (cubic)[123,124], $PrO_{1.833}$,[122,123] PrO_2,[124] $PrO_{1.717}$,[122] $PrO_{1.804}$,[122] Nd_2O_2 (hexagonal)[14], Sm_2O_3,[110] Eu_2O_3,[29,112] $TbO_{1.500}$,[125,126] $TbO_{1.710}$,[125] $TbO_{1.805}$,[125] $TbO_{1.510}$,[126] $TbO_{1.709}$,[126] $TbO_{1.817}$,[126] $TbO_{1.975}$,[126] $TbO_{2.000}$,[126] and Dy_2O_3.[115] The available entropies of the lanthanide oxides have been recently analysed[10,14] by a method for the calculation of entropy based on Latimer's scheme for the resolution of the entropy of a compound into those of its atomic components. The entropies of formation of the latter were calculated by combining the entropies of the lanthanides and their oxides[14]. The enthalpies, Gibbs free energies, and entropies of formation of various lanthanide oxides are compiled in Tables 2 and 3.

Having analysed various high-temperature data for the oxides, Holley et al.[14] tabulated the enthalpies ΔH°_T, entropies ΔS°_T, and Gibbs free energies ΔG°_T of formation of the lanthanide oxides in the temperature range 100–2000 K.

The oxides with a cubic structure have more negative enthalpies of formation than those of the oxides with monoclinic or hexagonal structures. The Gibbs free energies and entropies of formation of europium and ytterbium sesquioxides are lower than the values for the corresponding oxides of the adjacent lanthanides.

The thermodynamic functions of the oxides in the composition range CeO_2–Ce_2O_3 have been investigated[128-131] by an electromotive force method in cells with a solid oxide electrolyte (an anionic conductor). The equilibrium oxygen pressures over cerium oxides were measured in the same composition range[128,132,133] at temperatures from 600° to 1170°C by a dynamic method in an H_2O–H_2 or CO_2–CO gas stream. The thermodynamic properties of the oxides $PrO_{1.5}$–$PrO_{1.714}$ were also studied electrochemically[134]. Data obtained by various experimental methods for solid lanthanide oxides agree satisfactorily with one another.

Table 2. Thermodynamic characteristics of the formation of lanthanide oxides[14,110,112].

Oxide	$-\Delta H^0_{298.15}$, kcal mole^{-1}	$-\Delta S^0_{298.15}$, e.u.	$-\Delta G^0_{298.15}$ kcal mole^{-1}
La_2O_3 (hexag.)	428.7±0.18	70.04±0.45	407.82±0.23
CeO_2	260.6±0.2	52.24±0.18	245.0±0.3
Ce_2O_3 (hexag.)	430.9±3.8	73.5±0.62	409.0±3.8
Pr_2O_3 (hexag.)	435.8±1.6	70.5±1.0	414.8±1.6
$PrO_{1.833}$	227.6±0.8	43.5±0.5	214.7±0.8
Nd_2O_3 (hexag.)	432.37±0.21	72.12±0.46	411.17±0.25
Sm_2O_3 (monocl.)	435.86±0.45	70.65±0.35	414.8±0.5
Sm_2O_3 (cubic)	436.76		
Eu_2O_3 (monocl.)	394.7±0.8	76.0±2.0	372.0±0.9
Eu_2O_3 (cubic)	397.7±0.9		
Gd_2O_3 (monocl.)	433.94±0.87	68.3±1.7	413.4±1.0
Tb_2O_3 (cubic)	445.6±1.8	71.0±1.0	424.4±1.8
$TbO_{1.709}$	227.4±0.9	40.3±0.5	215.4±0.9
Dy_2O_3 (cubic)	445.19±0.85	66.10±0.27	425.5±0.9
Ho_2O_3 (cubic)	449.5±1.15	71.9±0.55	428.1±1.15
Er_2O_3 (cubic)	453.59±0.45	71.86±0.41	432.16±0.47
Tm_2O_3 (cubic)	451.4±1.4	72.4±1.0	428.8±1.4
Yb_2O_3 (cubic)	433.68±0.53	70.32±0.30	412.71±0.54
Lu_2O_3 (cubic)	448.9±1.8	71.9±1.0	427.5±1.8

The enthalpy of formation of crystalline $EuO_{1.02}$ was determined calorimetrically[135] at 298 K as -145.2 ± 2.8 kcal mole^{-1}. The Gibbs free energies of formation of EuO, YbO, and SmO are respectively −10, 7, and 13 kcal mole^{-1}.[136]

Table 3. Enthalpies of formation of cerium, praseodymium, and terbium oxides[122-127].

Oxide	$-\Delta H^\circ_{298.15}$, kcal mole^{-1}	Oxide	$-\Delta H^\circ_{298.15}$, kcal mole^{-1}	Oxide	$-\Delta H^\circ_{298.15}$, kcal mole^{-1}
Ce_2O_3 (hexag.)	435.0	Pr_2O_3 (hexag.)	435.8±1.6	Tb_2O_3	445.6±1.8
$CeO_{1.67}$ (cubic)	233	Pr_2O_3 (cubic)	436.8±1.6	$TbO_{1.709}$	227.4±0.9
$CeO_{1.72}$ (orthorhomb.)	238	$PrO_{1.717}$	224.0±0.9	$TbO_{1.817}$	229.7±0.9
$CeO_{1.78}$ (orthorhomb.)	244	$PrO_{1.804}$	226.5±0.8	$TbO_{2.000}$	232.0±0.7
$CeO_{1.81}$ (orthorhomb.)	247	$PrO_{1.833}$	225.2±0.2	—	—
CeO_2 [110]	260.6	$PrO_{1.833}$	227.6±0.8	—	—
—	—	$PrO_{2.000}$	232.9±1.5	—	—

Although rough estimates of the dissociation energies D°_0 of gaseous lanthanide monoxides had been obtained in earlier studies[137-139], the first accurate values of D°_0 were apparently obtained for LaO,[140-143] NdO,[141-143] SmO,[141-143] GdO,[142,143] TbO,[143] and LuO[142,143] by the mass-spectrometric method in combination with Knudsen's method. These characteristics were investigated in greatest detail by Ames[144,145]. Subsequent studies[146-150] yielded similar results. The dissociation energy of LaO was found to be 192.5,[140] 187.0 ± 4.6,[141] 186.4 ± 4.6,[142] 190.5 ± 4.6,[143] 193.5,[145] 192.5,[146] 189.5,[146] 190.3 ± 1.0,[147]

and 189.9 ± 1.0 [148] kcal mole^{-1}. The following dissociation energies have been obtained for other lanthanide monoxides (in kcal mole^{-1}): 190.5,[143] 193.5,[145] 185.2,[151] and 188.6 [152] for CeO, 175.8,[143] 182,[145] and 171.0 ± 6.9 [151] for PrO, 171.0 ± 4.6,[141] 163.4 ± 4.9,[142] 168.1 (169),[143] 172.1 (174.5),[145] 163.0,[151] and 170.3 [16] for NdO, 142.7 [143] and 142.4 ± 4 [145] for SmO, 133.3,[143] 134.7 ± 1.3,[145] and 133.9 [153] for EuO, 162.0 ± 6.9 [143] and 173 ± 3 [145] for GdO, 170.3 [143] and 173.8 [145] for TbO, 150.4 ± 0.6 for DyO,[145] 152.7 ± 2.0 for HoO,[145] 151.6 ± 0.8 for ErO,[145] 139.2 ± 0.7 for TmO,[145] 88.4 ± 0.8 for YbO,[145] and 159.5 ± 6.9 [143] and 167 ± 3 [145] for LuO. The corresponding enthalpies of formation of the gaseous monoxides are also quoted in the above studies. Gordienko et al.[16] recommend the following values of ΔH_0° (kcal mole^{-1}):

LaO	CeO	PrO	NdO	SmO	EuO	GdO	TbO	DyO	HoO
31.3	22.3	33.3	36.2	34.5	32.7	17.8	20.0	20.1	23.8
ErO	TmO	YbO	LuO						
17.1	20.8	—7.2	5.5						

Table 4. Enthalpies of formation of solid lanthanide monosulphides and dissociation energies of the gaseous monosulphides at 298 K.

Lanthanide monosulphide	$-\Delta H_{298}^\circ$, kcal mole^{-1}	References	D_{298}°, kcal mole^{-1}	References
LaS	113±1	156, 157	141.3±4.9	159
	113.3	159–161	138.8±6	159
	110.5	159	145.3	161
	108±4	162		
CeS	112±1	156	—	—
	118±2	154		
	109±1	7		
PrS	111±1	156	118.3	159, 163, 164
	109	16, 164, 170	117.7±1.1	170
NdS	111±1	156	113	159, 164
	104.8	161	118.1	161
	108.5	16, 164		
SmS	103.2	170	93	170
EuS	97.5	16, 170	—	—
	106.7±1.3	166		
GdS	105±1	156	109.5	161
	78.5	161		
YbS	97.9	170		

The thermodynamic characteristics of lanthanide sulphides were apparently obtained for the first time by Matignon[22] and Biltz[102]. Subsequently these investigations were assessed critically[154–156] using for the calculation of the enthalpies of formation of the solid sulphides the heats of solution of the lanthanides quoted in other reports[23–25]. After recalculation, the relevant values were found to be close to the enthalpies of formation of the sulphides based on data derived from systematic calorimetric studies[156–158]. The enthalpies of formation of the sulphides and the dissociation energies of the gaseous lanthanide monosulphides are quoted in Table 4. The studies were carried out mass-spectrometrically[159–166]. The enthalpies of formation of solid sulphides of different compositions are compiled in Table 5. The entropies and Gibbs free energies of formation of lanthanide sulphides have been estimated[7,37,76,167] and the high-temperature thermodynamic characteristics of solid lanthanide monosulphides have been tabulated[16,163,164,168,169].

Table 5. Enthalpies of formation of lanthanide sulphides at 298 K (kcal mole^{-1}).

Lanthanide	Ln_2S_3		Ln_3S_4		LnS_2	
	$-\Delta H_{298}^\circ$	references	$-\Delta H_{298}^\circ$	references	$-\Delta H_{298}^\circ$	references
La	282±3	156	401.4	157	144.4	157
	282±10	155	—	—	149±8	7
	192±16	7	—	—	—	—
Ce	277±3	156	392.0	157	142.2	157
	300±8	154	394.8	7	146.3±2.0	7
	282±2	7	—	—	—	—
Pr	273±3	156	391.0	157	141.0	147
Nd	269±3	156	388.0	157	138.8	147
	285.9	22				
	277	7				

The dissociation energies of the gaseous sulphides were determined mass-spectrometrically[170–175]. The variation of the dissociation energies of the gaseous monosulphides, monoxides, monoselenides[176,177], and monotellurides[176] in the La–Lu series is illustrated in Fig. 2. The dissociation energies[161,178] of PrSe, NdSe, and SmSe are much higher[176]. The standard enthalpies of formation of LaSe, PrSe, NdSe, SmSe, and EuSe calculated from mass-spectrometric data are −82, −123.5, −151.5, −147.0, and −107.5 kcal mole^{-1} respectively. The considerable difference between the enthalpies of formation of SmSe and EuSe is unexpected, because samarium and europium in the monoselenides are both bivalent[179].

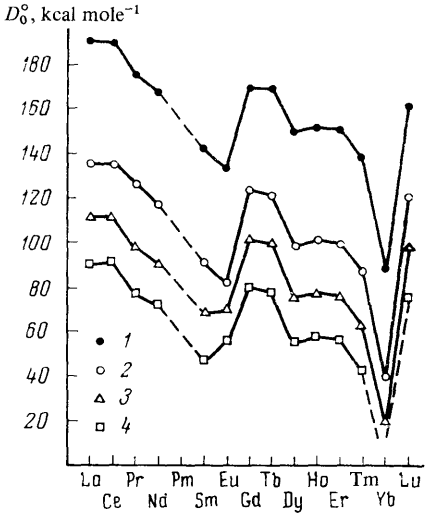


Figure 2. Variation of the dissociation energies of the monochalcogenides in the series of lanthanides: 1) monoxides; 2) monosulphides; 3) monoselenides; 4) monotellurides[176].

The enthalpies of formation of Gd_2Se_3 (−255.3 ± 8.1 kcal mole^{-1}),[180] Gd_2Te_3 (−221.4 ± 5.3 kcal mole^{-1}),[180] and La_2Te_3 (−187.5 ± 6.1 kcal mole^{-1})[181] were determined calorimetrically. The Gibbs free energies, enthalpies, and

entropies of formation of the higher lanthanum tellurides were calculated from e.m.f. data[182]:

	$-\Delta G_{880°K}$, kcal g-atom^{-1}	$-\Delta H$, kcal g-atom^{-1}	$-\Delta S$, e.u.
$La_{0,25}Te_{0,75}$	27.30±0.01	28.26 ± 0.16	1.42 ± 0.22
$La_{0,286}Te_{0,714}$	31.30±0.01	32.30±0.15	1.62±0.20

IV. PNICTIDES

The enthalpy of formation of LaN is lower[183-186] than that of CeN (Table 6) in which cerium is partly present in the quadrivalent state[6]. In the series of lanthanide arsenides[187] the enthalpy of formation of YbAs has the highest (least negative) value in consequence of the expenditure of energy in the change of the number of valence electrons of ytterbium from two to three[36]. The enthalpies of formation of the monoarsenides have been determined by differential calorimetry within wide confidence limits. The intermediate compounds in the lanthanum–antimony system and gadolinium antimonide have high enthalpies of formation and negative entropies of formation in the temperature range 653–803 K investigated by an e.m.f. method[188-191] (Table 7). The heats of atomisation of praseodymium monopnictides decrease from arsenic to bismuth[192].

Table 6. Enthalpies of formation of lanthanide mononitrides[183-186] and monoarsenides[187].

Compound	$-\Delta H°$, kcal mole^{-1}	Compound	$-\Delta H°$, kcal mole^{-1}
LaN	72±3	GdAs	74.4±3.2
CeN	78±3	TbAs	75.0±3.4
LaAs	73.0±4.5	DyAs	78.1±5.0
CeAs	68.9±3.0	HoAs	72.3±3.3
PrAs	73.4±3.1	ErAs	75.6±3.2
NdAs	72.7±3.5	TmAs	72.8±3.2
SmAs	72.0±3.5	YbAs	61.8±2.9
		LuAs	75.6±3.1

Table 7. Thermodynamic characteristics of the formation of lanthanum and gadolinium antimonides[188-191].

Phase	$-\Delta H$, kcal g-atom^{-1}	$-\Delta S°$, e.u.	$-\Delta G°_{730°K}$, kcal g-atom^{-1}
$LaSb_2$	23.25±0.19	1.28±0.26	22.32±0.01
$La_{0,53}Sb_{0,47}$	35.42±0.44	2.94±0.65	33.25±0.01
La_4Sb_3	35.58±0.51	2.81±0.74	33.53±0.01
La_5Sb_3	35.34±0.65	3.07±0.83	33.14±0.01
La_2Sb	33.96±0.87	3.53±1.23	31.36±0.02
$Gd_{0,52}Sb_{0,48}$	32.77±0.60	1.80±0.79	31.46±0.01

V. CARBIDES, SILICIDES, AND BORIDES

The main studies on the thermodynamics of the formation of lanthanide dicarbides have been carried out mass-spectrometrically in combination with Knudsen's tensimetric method[193-223]. The dissociation energies of the gaseous dicarbides and the heats of evaporation, atomisation, and formation of solid dicarbides were calculated in these investigations using the Second and Third Laws of thermodynamics. The thermodynamic characteristics of formation of a number of dicarbides and sesquicarbides have been studied by an e.m.f. method[224,225] and calorimetrically[105]. The enthalpies of formation of the lanthanide dicarbides calculated from the results of different investigations agree provided that the Third Law was used in the calculations. The standard enthalpies of formation of lanthanide dicarbides calculated from e.m.f. data using the Second Law differ appreciably from tensimetric data[225].

Table 8. Standard enthalpies of formation of lanthanide dicarbides.

Lanthanide dicarbide	$-\Delta H°_{298}$, kcal mole^{-1}	References	Lanthanide dicarbide	$-\Delta H°_{298}$, kcal mole^{-1}	References
LaC_2	19	199	EuC_2	16.1±1.0	200
	21	195		9.17±1.15	205
	21.3	203		16.0±1.3	204
	20.9	225		30.6	197
CeC_2	25	199	GdC_2	30±9	196, 198
	17	201		24.2	225
	19.5	201			
	15±5	213	DyC_2	11±1	214
	21.2	225		22.5	225
	23.2±1.3	105	HoC_2	19.8	212
PrC_2	20.2	225		21±1	214
				19.83	226
NdC_2	12.5	199	ErC_2	18.5±0.4	215
	21.2	225		26.5	225
SmC_2	15.6±1.6	199	YbC_2	18.0±1.0	206
	15.2±2.0	200	LuC_2	18±5	220
	18.4±1.3	207			
	23.4±2.0	208			

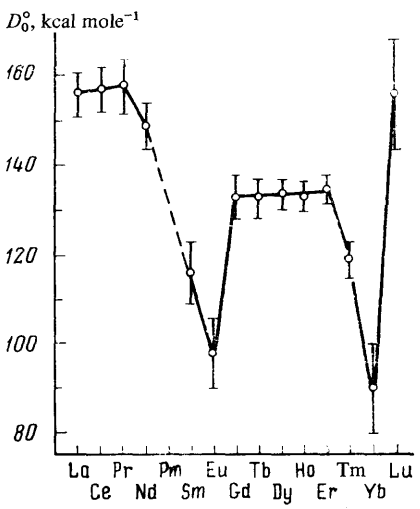


Figure 3. Variation of the Ln–C_2 bond energy in the series of lanthanides[218-220].

The enthalpies of formation of various lanthanide dicarbides are compiled in Table 8. They vary about 20 kcal mole^{-1}. The variation of the Ln–C_2 bond energy in the series of gaseous lanthanide dicarbides exhibits double periodicity (Fig. 3).

The Gibbs free energies of formation of lanthanum, cerium, praseodymium, and neodymium sesquicarbides from the liquid lanthanides and solid graphite, determined by an e.m.f. method[224], are higher than the values calculated for Ce_2C_3 from the phase diagram[227]. The enthalpy of formation of $CeC_{1.5}$ was found to be -21.1 ± 0.7 kcal mole^{-1} at 298.15 K by combustion in a bomb calorimeter[105]. The standard enthalpy and entropy of formation of Ho_2C_3 are -11.1 kcal mole^{-1} and 5.1 e.u. respectively according to tensimetric data[226].

The thermodynamic studies on the silicides are apparently limited to LaSi, β-$LaSi_2$, and β-$CeSi_2$, whose enthalpies of formation are respectively -30.0,[228] -44.4,[228] and -50 [229] or -45 [230] kcal mole^{-1}.

The first enthalpies of formation of lanthanum, cerium, and yttrium borides were obtained in Refs. 231–237. They were used to calculate by the thermochemical logarithmic rule the enthalpies of formation of the hexaborides of the entire series of lanthanides[234,235]. However, the monotonic increase of the modulus of this quantity in the series from lanthanum to lutetium is unlikely.

The heats of dissociation of the gaseous hexaborides and the enthalpies of formation of the solid compounds have been determined from mass-spectrometric measurements[236-242] by the method of Langmuir and Knudsen. The heats of dissociation decrease steadily from LaB_6 to SmB_6 (Table 9). A similar variation has been observed also for lanthanide diborides[243].

Table 9. Enthalpies of dissociation and formation of lanthanide hexaborides[241,242].

Lanthanide hexaboride	Temp. range, K	Enthalpy of dissociation, kcal mole^{-1}	Enthalpy of formation, kcal mole^{-1}
LaB_6	2045–2300	134.2±2.7	−28±4
CeB_6	1846–2220	123.1±2.8	−11±4
PrB_6	1943–2200	111.5±2.5	−23.5±4
NdB_6	1983–2300	107.9±2.2	−29.5±3
SmB_6	2050–2370	102.8±2.3	−54±3
GdB_6	2170–2500	127.0±2.8	−31±4
TbB_6	1980–2350	128.7±3.4	−34±5

VI. HYDRIDES

The thermodynamic characteristics of the formation of the dihydrides of the majority of lanthanides and also of some of their dideuterides have been calculated from the temperature variation of the pressure of hydrogen formed on dissociation of these compounds (Table 10).[244-256] On passing from the hydrides to the deuterides, the thermodynamic functions of formation diminish. Gschneidner reported[257] that the enthalpies of formation of terbium, dysprosium, thulium, and lutetium dihydrides are close to the enthalpies of formation of the dihydrides of the adjacent lanthanides. The equilibrium pressure and partial thermodynamic characteristics of hydrogen were also studied for lanthanum[258,259] and gadoliunium[260] dihydrides. The enthalpies of dissociation of the higher non-stoichiometric lanthanide hydrides to the dihydrides have been calculated[261-263] as 10–20 kcal/mole H_2. There has been only one calorimetric study[264] on $LaH_{2.8}$, $CeH_{2.7}$, and $PrH_{2.7}$.

VII. METALLIC ALLOYS WITH *p* ELEMENTS

The first studies[265-267] carried out by an e.m.f. method using a liquid electrolyte (a cationic conductor) already demonstrated a marked interaction of the lanthanides with bismuth and lead. The results of studies up to 1969 on the thermodynamics of lanthanide alloys have already been reviewed[17]. The intermediate phases in the cerium–lead, praseodymium–lead, and neodymium–lead systems were investigated[268] by a modified Knudsen method.

Table 10. Enthalpies and entropies of formation of lanthanide dihydrides.

Lanthanide dihydride	$-\Delta H^\circ_{298}$, kcal/mole H_2	$-\Delta S^\circ_{298}$, e.u.	Refs.	Lanthanide dihydride	$-\Delta H^\circ_{298}$, kcal/mole H_2	$-\Delta S^\circ_{298}$, e.u.	Refs.
LaH_2	49.6±1.0	35.5±1.0	244	GdH_2	45.2±0.1	43.1±0.1	248
LaD_2	46.5±1.0	33.1±1.0	244	GdH_2	46.9±0.7	—	249
LaH_2	49.7±0.1	—	245	HoH_2	52.7	35.6	250
CeH_2	49.2±1.0	35.4±1.0	244	HoD_2	52.3	35.8	250
CeD_2	46.3±1.0	33.5±1.0	244	ErH_2	53.5	36.5	247
CeH_2	33.9±0.9	—	245	ErH_2	52.6±0.3	35.2±0.3	251
CeH_2	48.3	34.1	246	ErH_2	48.3	32.3	252
PrH_2	49.7±1.0	35.0±1.0	244	ErH_2	55.2	51.1	253
PrH_2	47.8	—	245	ErD_2	52.2	48.6	253
NdH_2	50.5±1.0	34.8±1.0	244	ErD_2	53.0±0.2	36.3±0.2	254
NdH_2	44.8	—	245	YbH_2	43.3	33.4	255
SmH_2	53.3	—	247	YbH_2	42.9±1.2	29.2±1.7	256
SmH_2	43.0±0.5	39.4±0.2	248				

E.m.f. studies on the cerium–lead system[269] yielded appreciably different thermodynamic characteristics of formation of $CePb_3$, particularly as regards the Gibbs free energy. The ytterbium–aluminium system was studied tensimetrically over a wide range of compositions and the equation $\Delta G^\circ_T = -17\,473.16 + 9.405\,T$ (cal mole^{-1}) was fitted to the Gibbs free energies of formation of $YbAl_2$ in the range 773–873 K.[270] The alloys of lanthanides with aluminium gallium, indium, thallium, tin, lead, and bismuth were studied mainly in the range of compositions with a high content of the non-lanthanide metal. The thermodynamic characteristics of formation of compounds of the lanthanides with the above *p* elements found by an e.m.f. method and the equations for the temperature variation of the activity coefficients of the lanthanides in the liquid alloys are presented in Table 11. When a galvanic cell of the amalgam type is used in the study of the thermodynamic properties of lanthanide–aluminium alloys, it is necessary to take into account the displacement of the lanthanide ion from the electrolyte by aluminium. This factor was neglected in a number of the investigations[271,272,297,298], which probably accounts for certain discrepancies between the data of Kober et al.[272] and Degtyar' et al.[299], the latter having been obtained by a method based on the distribution in the system aluminium–lanthanum–bismuth. Calorimetric studies on the enthalpies of mixing of the lanthanides with aluminium were begun recently[297,298,300]. Palenzona and Cirafici[301] determined the enthalpies of formation of thirteen compounds of lanthanides and lead of the type $LnPb_3$ by dynamic differential calorimetry. Ferris et al.[302] calculated with a low accuracy the activity coefficients of lanthanum, cerium, neodymium, gadolinium, and dysprosium in liquid, bismuth-based alloys. Smith[303] estimated the heat of solution of samarium in lead as 15 kcal g-atom^{-1}.

The enthalpies of formation of $LaSn_3$ found by an e.m.f. method[288], high-temperature calorimetry of the dissolution process[304,305], and dynamic differential calorimetry[306] agree with one another. The enthalpies of formation of lanthanide–tin compounds of the type $LnSn_3$ and the relative partial molar enthalpies of solution of the lanthanides in tin are compiled in Table 12.

Table 11. Thermodynamic characteristics of the formation of compounds in liquid mixtures of lanthanides and *p* elements.

Compound	$-\Delta H^\circ_T$, kcal mole^{-1}	$-\Delta S^\circ_T$, e.u.	$-\Delta G^\circ_T$ kcal mole^{-1}	T, °K	Coefficients of the equation $\lg\gamma = a - bT^{-1}$ a	b	Temp. range, K	Refs.
1	2	3	4	5	6	7	8	9
$LaAl_4$	57.7±0.5	19.6±0.4	38.2±0.1	1000	2.973	9 872	953—1123	271
$CeAl_4$	52.0±0.7	12.2±0.7	42.1±0.1	900	—	—	—	272
$CeAl_4$	63.0±1.3	24.2±1.3	38.8±0.1	1000	3.384	10 530		272
$LaGa_2$	68.6	15.5	53.5	975	5.134	13 853	675—975	273,274
$CeGa_2$	73.2	26.3	47.6	975	7.568	15 173	675—975	275
	—	—	—	—	5.745	13 445	673—973	276
$PrGa_2$	69.4	18.7	51.2	975	5.781	14 091	675—975	277
$NdGa_2$	70.5	19.6	51.4	975	6.024	14 200	675—975	278
$GdGa_2$	(82)	(48)	35.2	975	10.50	15 908	675—975	279
$DyGa_2$	98	66	31	973	7.65	15 078	675—975	280
$ErGa_2$	68	36	33	973	—	—		281
$TmGa_3$	50	23.7	29	873	—	—		282
$LaIn_3$	51.3	10.5	41.1	975	3.170	10 023	725—975	283
$CeIn_3$	57.6	21.1	37.1	975	5.780	11 868	725—975	284
$PrIn_3$	55.3	15.5	40.2	975	3.793	10 531	725—975	285
$NdIn_3$	55.9	17.0	39.3	975	4.186	10 806	725—975	286
$GdIn_3$	47.2±1.2	12.3±1.6	40.1±0.1	773	—	—	673—875	287
$ErIn_3$	40.4±2.4	9.7±3.1	33.0±0.2	773	—	—	673—875	287
$LaTl_3$	45.3	11.0	34.6	975	2.784	8 679	775—975	283
$LaSn_3$	62.7	8.2	54.7	975	4.70	13 900	673—973	288
$NdSn_3$	62.1±0.8	12.9±0.9	49.6±0.1	973	—	—	773—973	289
$GdSn_3$	53.2±2.0	10.3±2.3	42.2±0.2	973	—	—	773—973	290
$LaPb_3$	55.4±1.1	14.2±1.1	41.2±0.2	1000	—0.068	6 618	950—1120	271
$CePb_3$	57.6±0.4	17.4±0.5	39.2±0.1	1000	1.744	8 220	700—1033	269
$NdPb_3$	47.1±0.6	5.2±0.7	42.5±0.2	873	—	—	796—873	291
$GdPb_3$	33.1±0.3	2.26±0.3	31.3±0.1	873	—	—	773—879	292
$ErPb_3$	31.9±0.2	3.8±0.2	28.6±0.1	873	—	—	773—873	293
$LaBi_x$	66.1±0.3	15.1±0.3	52.5±0.1	900	0.844	11 070	753—953	294
$CeBi_x$	64.9±0.5	15.2±0.6	51.2±0.1	900	2.03	11 400	773—923	295,296

Table 12. Enthalpies of formation of compounds of the type $LnSn_3$ and enthalpies of solution of the lanthanides in liquid tin-based alloys.

Lanthanide	$-\Delta H_{LnSn_3}$, kcal mole^{-1}	Temp., K	References	$-\Delta\bar{H}_{Ln(Sn)}$, kcal g-atom^{-1}	Temp., K	References
La	62.7±1.8	773—973	288	61.5±2.0	773—973	288
La	60.6±0.8	273	304	64.4—66.7	725—775	304
La	65.18 (60.25) *	510	306	66.2±0.6	632	305
Ce	54.01 (49.08)	510	306	68.4±0.4	634	305,307
Pr	60.87 (55.94)	520	306	61.3±0.4	750	305
Pr	—	—	—	70.0±2.5	750	308
Nd	70.89 (65.96)	620	306	58±2	750	308
Nd	57.1±0.8	773—973	289	57.1±1.4	773—973	289
Sm	58.48 (53.55)	570	306	53±2	750	308
Sm	53.8	295	309,310	—	—	—
Eu	50.48±1.85	295.7	311	$40.4+167\ C_{Eu}$**	958	311
Gd	49.65±1.65	299.7	312	$41.9+225C_{Gd}$	969	312
Gd	53.72 (48.78)	600	306	—	—	—
Gd	48.2±2.0	773—973	290	51.4±2.6	773—973	290
Dy	—	—	—	$36.44-34.4C_{Dy}$	957	313
Er	—	—	—	$29.25+1.2C_{Er}$	963	313
Yb	50.80 (45.86)	540	306	35.2±0.3	770	305
Yb	42.1	294	314	35.3	857	314
Lu	37.4±0.8***	800	315	—	—	—

* The values of ΔH_{LnSn_3} at 298 K are indicated in brackets.

** c_{Ln} = at.% of the lanthanide.

*** $\Delta\bar{H}_{Ln}$.

It has been established on the basis of the magnetic properties of $EuSn_3$, $YbSn_3$, $EuPb_3$ and $YbPb_3$ that europium and ytterbium in these compounds are bivalent[316,317]. The enthalpies of formation of $EuSn_3$ and $YbSn_3$ (Table 12) are close to the values which can be obtained by interpolation from the enthalpies of formation of compounds of the type $LnSn_3$ of the adjacent tervalent lanthanides. The lanthanide–lead compounds of the type $LnPb_3$ exhibit a similar behaviour[301].

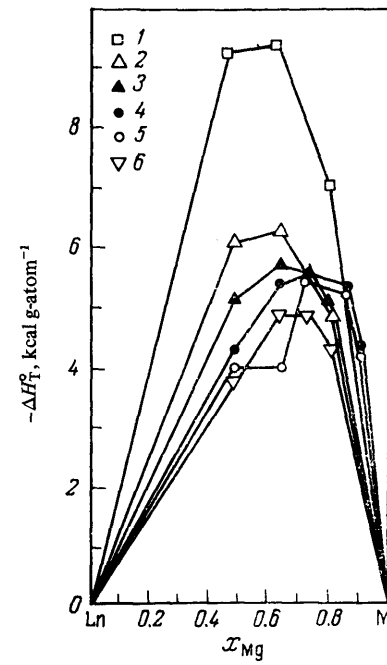


Figure 4. Enthalpies of formation of the intermediate compounds in different systems[318]: 1) Lu–Mg; 2) Er–Mg; 3) Gd–Mg; 4) Nd–Mg; 5) Ce–Mg; 6) Dy–Mg.

VIII. ALLOYS OF LANTHANIDES WITH *s* AND *d* ELEMENTS

The magnesium alloys have been most thoroughly investigated in this group. The intermediate compounds in systems formed by magnesium with cerium, neodymium, gadolinium, dysprosium, erbium, and lutetium have been studied by Knudsen's method[318]. The maximum in the thermodynamic characteristics of formation shift from the composition $CeMg_3$ to $GdMg_2$ and then to LuMg (Figs. 4 and 5). In liquid lanthanum–magnesium melts[319] the maximum Gibbs free energy of mixing of the components is also displaced towards $LaMg_3$. The Gibbs free energies of formation of 12 compounds having the composition LnMg (except for europium and ytterbium) have been studied in the temperature range 700—800 K.[320] The results of two studies[318,320] for the heavy lanthanides differ appreciably. The partial thermodynamic characteristics of cerium in magnesium-based solutions have been calculated at 1083 K: $\Delta\bar{H}^\infty_{Ce}$ = −26.8 kcal g-atom^{-1},[321] $\Delta\bar{S}^{exc\,\infty}_{Ce}$ = −9.8 e.u.,[321] and $\Delta\bar{G}^{exc\,\infty}_{Ce}$ = −16.4 [321] or −15.5 [322] kcal g-atom^{-1}. The partial thermodynamic characteristics

of magnesium have been determined for neodymium–magnesium and samarium–magnesium alloys[323]. The authors[324] explain the negative enthalpy of solution of cerium in sodium by the influence of impurities.

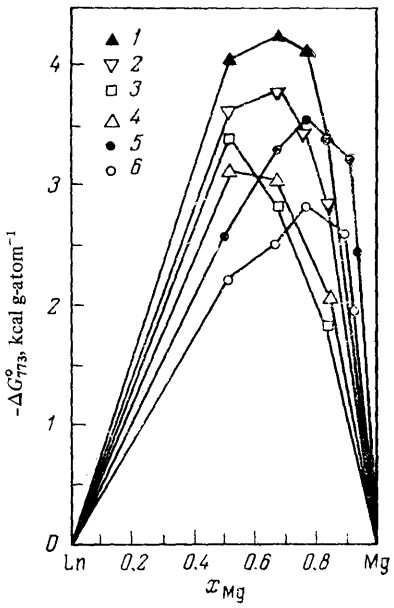


Figure 5. Gibbs free energies of formation of the intermediate compounds at 773 K in different systems[318]: 1) Gd–Mg; 2) Dy–Mg; 3) Lu–Mg; 4) Er–Mg; 5) Nd–Mg; 6) Ce–Mg.

The fairly high volatility of zinc and its remoteness in the electrochemical series from the lanthanides made it possible to investigate lanthanide–zinc alloys by Knudsen's tensimetric method[325-328] and by e.m.f. methods[329-333]. The solid intermediate compounds have been studied in the systems cerium–zinc[325], samarium–zinc[326], praseodymium–zinc[327], and neodymium–zinc[328] and in some of the investigations[325,327] the liquid alloys were also studied. Chiotti[334] showed, using a new method for the integration of the Gibbs–Duhem equation, that some of his earlier results[327] were incorrect. The thermodynamic characteristics obtained by Chiotti and Mason[325,326] were analysed by the present authors in an earlier publication[17].

Alloys of lanthanum, cerium, and praseodymium with zinc and cadmium (Table 13) have been studied by an e.m.f. method[329-333]. The behaviour of lanthanum, cerium, and praseodymium in liquid zinc- and cadmium-based alloys is consistent with Henry's Law. The enthalpies of formation of $NdZn_{11}$, $NdCd_{11}$, and $SmCd_{11}$ have also been estimated[333] by a method of comparative calculation as -86.16, -69.65, and -68.34 kcal mole^{-1} respectively. The Gibbs free energies of formation of compounds of the type LnCd vary about -7 kcal g-atom^{-1} as a function of the atomic number of the lanthanide[320]. The results of thermodynamic studies on the samarium–mercury system by tensimetric[335] and e.m.f. [336] methods do not agree, particularly as regards the enthalpies and entropies (these differ in sign). The interpretation of the e.m.f. of the cell

$$Sm\,|\,Sm(ClO_4)_3 + LiClO_4 + \text{dimethylformamide}\,|\,Sm(Hg)$$

requires further consideration.

Table 13. Thermodynamic characteristics of the formation of lanthanide–zinc and lanthanide–cadmium compounds of the type LnM_{11}.

Compound	$-\Delta H^{\circ}_T$, kcal mole^{-1}	$-\Delta S^{\circ}_T$, e.u.	$-\Delta G^{\circ}_{723°K}$, kcal mole^{-1}	Temp. range, K	References
$LaZn_{11}$	97.4	53.3	56.2		329
$LaZn_{11}$	93.6±0.2	49.1±0.2	55.6±0.1	715—1022	330,332
$LaZn_{11}$	92.58±0.18	48.02±0.24	57.85±0.02	705—793	333
$CeZn_{11}$	86.3±0.6	42.9±0.9	53.1±0.4	723—1020	331,332
$CeZn_{11}$	87.85±0.18	44.98±0.21	55.31±0.09	710—1018	333
$CeZn_{11}$	92.32	46.7	58.56		325
$PrZn_{11}$	85.26±0.19	42.65±0.25	54.42±0.04	696—875	333
$PrZn_{11}$	89.35	45.48	56.47		327
$NdZn_{11}$	91.93	50.56	55.50		328
$LaCd_{11}$	72.34±0.17	48.58±0.22	40.83±0.03	670—804	333
$CeCd_{11}$	70.52±0.15	44.57±0.21	38.29±0.03	638—884	333
$PrCd_{11}$	69.07±0.23	44.82±0.31	36.26±0.06	635—825	333

The thermodynamic characteristics of $LaIr_2$ [337,338] and of the intermediate compounds in the cerium–iridium system[338,339] have been determined by an e.m.f. method using a solid electrolyte (an anionic conductor). The Gibbs free energies of formation (in kcal mole^{-1}) of $LaIr_2$ and $CeIr_2$ in the temperature range 950–1200 K are described by the equations

$$\Delta G^{\circ}_{LaIr_2}(\pm 0.45) = -(44.0 \pm 2) + (1.13 \pm 2)\cdot 10^{-3}T,$$

$$\Delta G^{\circ}_{CeIr_2}(\pm 4) = -(62.5 \pm 4) + (0.10 \pm 3.3)\cdot 10^{-3}T.$$

The thermodynamic characteristics of $CeIr_3$, $CeIr_5$, and Ce_2Ir_7 differ little from those of $CeIr_2$.

Gingerich and coworkers[340-342] demonstrated the high stability of the gaseous monaurides. Their dissociation energies are as follows (in kcal mole^{-1}): 79.5 ± 5.0 for LaAu, 75.5 ± 3.5 for CeAu, 73.0 ± 5.0 for PrAu, 69.5 ± 6.0 for NdAu, 66.8 for TbAu, 60 ± 3 for HoAu, and 78.5 for LuAu. The dissociation energy of HoAg (28.6 ± 4 kcal mole^{-1}) is lower than that of HoAu (59.7 ± 3 kcal mole^{-1})[341]. The atomisation energies of lutetium, holmium, and terbium diaurides have been calculated[342]. The calculation of the bond energies in lanthanide monaurides and diaurides using Pauling's model of a single polar bond yielded results in good agreement with experiment. The dissociation energies of EuAg have been determined experimentally (31.0 ± 3.0 kcal mole^{-1}) and calculated theoretically on the basis of Pauling's model (33.4 kcal mole^{-1})[343].

IX. GENERAL CHARACTERISTICS

The present author calculated the energies of mutual exchange between 14 lanthanides and various elements for 1078 systems from the properties of the initial components by the Hildebrand–Mott method[344]. The most positive energies were found for the mutual exchange between the majority of lanthanides (with the exception of europium and ytterbium) and s^1 elements. Negative values are characteristic of the energies of mutual exchange between

all the lanthanides and *p* elements. Compared with other lanthanides, the energies are higher for the mutual exchange between europium and ytterbium and d^5 elements and lower for the mutual exchange with *s* elements.

The Gibbs free energies and enthalpies of formation of europium and ytterbium compounds are consistent with the general variation of these characteristics for compounds of the type $LnSn_3$ (Table 12) and $LnPb_3$,[301] monosulphides (Table 4), and dicarbides (Table 8) in the series of lanthanides. The Gibbs free energies and enthalpies of formation of the sesquioxides (Table 2), monoarsenides (Table 6), trichlorides (Table 1), and trifluorides are more positive for the europium and ytterbium compounds than for the compounds of the adjoining lanthanides. According to the present author's data[345,346] the interaction of calcium and cadmium with europium and ytterbium is more favourable on energy grounds than the interaction with the adjacent lanthanides. These features of the thermodynamic characteristics of europium and ytterbium compounds, which distinguish them from those of the compounds of other lanthanides, are probably determined by the nature of the interaction of various elements with the 5*d* electrons of the lanthanides.

If the formation of the compound requires three valence electrons of the lanthanide, then in the case of europium and ytterbium, which have only two valence electrons in the metallic state under standard conditions[6], $4f-5d$ transitions, accompanied by an increase in the number of valence electrons to three and a corresponding energy expenditure (22 ± 2 kcal mole^{-1} for europium and 9 ± 2 kcal mole^{-1} for ytterbium), take place. The Gibbs free energies and enthalpies of formation of the europium and ytterbium compounds are then smaller than the corresponding quantities for the formation of similar compounds of the adjacent lanthanides.

When the enthalpies of formation of europium or ytterbium compounds fit the general variation of the enthalpies of formation of lanthanide compounds, it is postulated[315] that the third valence electron of the lanthanide (a 5*d* electron[6,347]) is not involved in the formation of the chemical bond (or its contribution to the bond energy is small), is delocalised, and is responsible for the metallic conduction. Europium and ytterbium compounds of this type (for example monochalcogenides[179]), in which there are only two valence electrons (i.e. in europium and ytterbium)[179], may prove to be semiconductors or insulators.

We shall consider the thermochemical behaviour of europium and ytterbium, involving a greater ease (on energy grounds) of the interaction of a non-lanthanide element with europium or ytterbium than with adjacent lanthanides, from the standpoint of the configurational model of matter developed by Samsonov and coworkers[348-350] using as an example lanthanide–calcium alloys. The valence electrons of calcium in the excited state do not include more than one *d* electron per atom and tend to assume the d^0 configuration. The valence electrons of the lanthanides (except for europium and ytterbium) include one–two *d* electrons per atom and also tend to assume the d^0 configuration. In the calcium–lanthanide system each component tends to give up its valence *d* electron to the other component. This leads to an antagonism between calcium and the lanthanide, the separation of the liquid alloys into two phases[6], and positive Gibbs free energies, enthalpies, and entropies of mixing of the components[346]. Europium and ytterbium do not have 5*d* electrons and their mixing with calcium involves a decrease in enthalpy[346].

In compounds of the type LnN and $LnIr_2$ lanthanum is tervalent and cerium is quadrivalent[6] (the "true" valence is determined by the number of electrons delocalised from the given atom[351]). The Gibbs free energies and enthalpies of formation of CeN and $CeIr_2$ are higher than those for LaN and $LaIr_2$ respectively. This combination of the thermodynamic characteristics of the lanthanum and cerium compounds shows that the contribution of the fourth valence electron of cerium to the energy of the chemical bond with nitrogen and iridium is fairly large, particularly since the increase of the number of valence electrons of cerium from three in the pure metal to four in the compound requires an energy of about 50 kcal g-atom^{-1}.[36] It has been established that the change in the number of valence electrons from three in metallic samarium to two in the compound involves a change in the Gibbs free energy and enthalpy of 6.2 ± 1.7 kcal g-atom^{-1} under standard external conditions[352].

The variation of the Gibbs free energies and enthalpies of formation of binary lanthanide compounds as a function of the atomic number of the element is complex. On passing from lanthanide trichlorides to oxides, the stability series is inverted. Whereas in the trichloride series the maximum enthalpy of formation corresponds to $LaCl_3$ (Table 1), in the series La_2O_3–Gd_2O_3–Lu_2O_3 the maximum corresponds to Lu_2O_3 (Table 2). The enthalpies of formation of lanthanide dicarbides (Table 8) and dihydrides (Table 10) remain virtually constant from lanthanum to lutetium. The variation of the enthalpies of formation of the solid lanthanide compounds has been considered on the basis of the concepts of the energy of stabilisation by the crystal field[1,3,34,353,354], the promotion energy, and bond multiplicity[355,356]. The observed relations are largely qualitative.

The dissociation energies of gaseous lanthanide compounds decrease in the series from lanthanum to europium and from gadolinium to ytterbium. Charkin[357] showed that the variation of the dissociation energies in the series of lanthanide compounds is determined by the variation of the excitation energies of the valence electron configurations of the lanthanides. It has also been shown[16,165] that the dissociation energies of the compounds vary with the degree of involvement of the lanthanide *d* electrons in the formation of chemical bonds. However, the nature of the relation between the dissociation energies of lanthanide monoxides or monosulphides and the same series of degrees of involvement of *d* electrons, calculated[358] from the properties of the lanthanides alone, remains obscure. Apparently the degrees of involvement of $4f$, $5d$, $6s$, and $6p$ valence electrons of the lanthanide in the formation of chemical bonds and hence the set of valence electron configurations can nevertheless change on passing from one class of lanthanide compounds to another (particularly in the solid state). This in fact leads to different changes in the thermodynamic characteristics in the series of solid lanthanide compounds. The proposed explanation of the variation of the Gibbs free energies or enthalpies of formation in the series of lanthanide compounds is consistent with Gschneidner's study[359], where four types of relations between the degree of involvement of $4f$ electrons in the chemical bond and the atomic number of the element were established on the basis of 33 series of lanthanide compounds.

In conclusion we may note that the thermodynamic characteristics of lanthanide compounds have been used[191,360] to determine the type of chemical bond. Comparison of the experimental and calculated enthalpies of formation of intermetallic lanthanide compounds showed[360]

that there is a predominantly metallic type of bond in the intermediate compounds of the lanthanide–magnesium systems; in lanthanide alloys with *p* elements there is a considerable contribution by ionic-covalent bonding. Thus the study of the thermodynamics of the interaction of the lanthanides with various elements permits certain conclusions concerning the nature of the valence electrons involved in the formation of the chemical bond and the type of bond in the compounds formed.

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Kuban State University,
Krasnodar