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Enthalpies of formation, entropies & heat capacities of lanthanide monohalides

Standard enthalpies of formation, entropies and heat capacities of the lanthanide monohalides, LnX_{g} , $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$

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Abstract. Molecular constants and dissociation energies reported in the literature, supplemented by some estimated parameters, have been used to derive the molar heat capacities, molar entropies and molar standard enthalpies of formation for the lanthanide monohalides, LnX_{g} , for $\text{Ln} = \text{Ba}, \text{La}$ to Lu and $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$.

1. Introduction

The lanthanide monohalides, LnX_{g} , are important radiating species in high pressure plasmas derived from doses containing lanthanide(III) halides. To understand the characteristics of these plasmas and to determine the role of the lanthanide monohalides it is necessary to calculate the chemical composition of the plasma from the coolspot temperature (typically 1000 to 1500 K) to the arc centre temperature (typically in the range 4000 to 6000 K). Such calculations are usually based on the assumption of local thermodynamic equilibrium, LTE. A typical chemical system used in a ceramic metal halide discharge lamp might contain a mixture of the iodides of Sodium, Thallium, Holmium and Thulium (collectively known as the 'lamp dose') together with Mercury and Argon. The coolspot temperature of the vessel containing the plasma determines the composition of the liquid and hence the elemental composition of the gas phase above the dose. These compositions in turn determine the elemental composition and hence the species concentration throughout the plasma chamber from the wall temperature to the highest temperatures found in the centre of the arc.

Detailed knowledge of the temperature variation of chemical composition within the plasma is an essential precursor to predicting the corresponding transport coefficients. The temperature variation of the transport coefficients not only govern the microscopic properties of the plasma but also have to be taken into consideration in the design and fabrication of the lamp and its components. Of the transport coefficients: viscosity controls convection within the plasma chamber and has a major influence on the power loss and hence the efficiency of the lightsource; the electrical conductivity of the plasma determines the voltage of the lamp and plays a vital role in the design of the ballasts needed to control the electrical characteristics of high intensity discharge lamps; the thermal conductivity of the plasma is another contributor to power loss and determines the wall temperature of the plasma chamber which in turn has a major influence on the failure mechanisms and life of the device. The temperature variation of the heat capacity of the plasma reflects changes in chemical composition. These changes are responsible for the concentrations of radiating and charged species.

To calculate the plasma composition, thermodynamic functions for all of the species under consideration must be available and held in the appropriate database format. None of the readily available thermochemical databases contain a complete set of self consistent values for the lanthanide monohalides. This paper outlines the determination of the molar standard enthalpies of formation, molar entropies and molar heat capacities for the series LnX_{g} ($\text{Ln} = \text{Ba}, \text{La}$ to Lu and $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) from dissociation energies and molecular constants.

In lamps with electrodes the use of lanthanide halides is restricted to the bromides and iodides. Electrodeless plasma lamps, however, allow chloride-containing systems to be used. Fluorides are not used in discharge lamps but they are included here to complete the LnX_{g} series. Promethium, Pm, is an unstable element

and does not occur naturally but it is included in all theoretical considerations of lanthanide compounds. Although Barium is not a lanthanide element it is often included in studies of the lanthanide series because of its position in the Periodic Table. Preliminary accounts of this work have been given earlier [1], [2].

A detailed account of the behaviour and use of metal halides and other molten salts in high intensity discharge lamps is given in [3].

2. Molecular constants

Molecular constants for $\text{LnF}<\text{g}>$ and $\text{LnCl}<\text{g}>$ except $\text{BaF}<\text{g}>$, $\text{BaCl}<\text{g}>$, $\text{LaF}<\text{g}>$ and $\text{LaCl}<\text{g}>$ were taken from reference [4]. Molecular constants for $\text{LaF}<\text{g}>$, $\text{LaCl}<\text{g}>$, $\text{LaBr}<\text{g}>$ and $\text{LaI}<\text{g}>$ were taken from reference [5]. Molecular constants for $\text{BaF}<\text{g}>$ and $\text{BaCl}<\text{g}>$ were taken from the NIST Chemistry WebBook [6].

In the absence of a published set of self consistent values for the molecular constants for the series $\text{LnBr}<\text{g}>$ and $\text{LnI}<\text{g}>$, these parameters were estimated. As the molecular constants had to be estimated, the terms for anharmonicity contributions to the molar heat capacities and entropies, i.e. the anharmonicity constant ($\omega_e x_e$), the rotational constant (B_e) and the rotational - vibrational constant (α_e), were omitted. Values of the vibrational wavenumbers (ω_e) and the equilibrium interatomic distances (R_e) for the series $\text{LnBr}<\text{g}>$ and $\text{LnI}<\text{g}>$ were estimated using the ratios of the corresponding values for $\text{LaCl}:\text{LaBr}$ and $\text{LaCl}:\text{LaI}$ from [5].

The energy levels and quantum weights selected for the $\text{LnX}<\text{g}>$ molecules were those for the corresponding Ln(II) species [7]. A similar approach to representing the energy levels of $\text{LnX}<\text{g}>$ molecules [4] and $\text{LnI}_3<\text{g}>$ molecules [8] has been used previously to reflect the ionic character of the Ln-X bonds.

The molecular constants used in this work are listed in tables 1 to 4.

3. Heat capacities and entropies at 298.15 K

The heat capacities for the $\text{LnX}<\text{g}>$ series were calculated from 298.15 to 6000 K using the 'StatMech' software [9] with input values for the molecular constants listed in tables 1 to 4. The coefficients for the temperature variations of the molar heat capacities ($C_{p,m}(T)$) of the lanthanide monohalides, expressed as (1) are listed in tables 5 to 8.

$$C_{p,m}(T)/\text{J.K}^{-1}.\text{mol}^{-1} = A + BT + CT^2 + DT^{-2} \quad (1)$$

where T = temperature (K)

Molar heat capacities for $\text{Ln}<\text{g}>$ and $\text{X}<\text{g}>$ were calculated using energy levels for Ln(I) and X(I) as listed in [7].

These calculations also provide the molar entropies (S_m) at 298.15 K for the lanthanide monohalides, these are listed in table 9.

4. Derivation of standard enthalpies of formation from dissociation energies

The standard enthalpies of formation for $\text{LnX}<\text{g}>$ were derived from scheme 1. The dissociation energies for $\text{LnX}<\text{g}>$ were taken from reference [10], the standard enthalpies of formation for $\text{Ln}<\text{g}>$ and $\text{X}<\text{g}>$ were taken from the SGTE Substance Database [11].

Scheme 1. Derivation of standard enthalpy of formation from dissociation energy

$$1/2X_{2< r >} = X_{< g >} \quad \Delta H = \text{Standard enthalpy of formation of } X_{< g >} \quad (5)$$

where $< r >$ is the standard state of the element at the reference temperature (298.15 K)

$$(2) = (4) + (5) - (3) \quad (6)$$

Dissociation energies in table 10 are taken to be at 0 K, the corresponding enthalpies of dissociation at 298.15 K were determined from equations (3), (7) and (8).

$$\Delta C_p(T) = C_p(\text{Ln}, g, T) + C_p(X, g, T) - C_p(\text{LnX}, g, T) \quad (7)$$

$$\Delta H(T) = \Delta H(298.15 \text{ K}) + \int_{298.15 \text{ K}}^T \Delta C_p(T) dT \quad (8)$$

Molar standard enthalpies of dissociation at 298.15 K for the lanthanide monohalides derived from this study are presented in table 11. The molar standard enthalpies of formation for the lanthanide monohalides are shown in table 12.

5. Discussion

While the molecular constants have a substantial effect of the calculated values of the molar heat capacities ($C_{p,m}$) and entropies ($S_m(T)$) it is the impact on the temperature variation of the standard Gibbs free energy of formation ($\Delta G_m(T)$) that is important when considering the effect of these parameters on the calculated chemical composition of a plasma. The values between 1000 and 6000 K are therefore of most interest in this application. Taking $\text{LaBr}_{< g >}$ as an example, the value of $S_m(1000 \text{ K})$ is $330.656 \text{ J.K}^{-1}.\text{mol}^{-1}$ with energy levels included in the calculation and $312.307 \text{ J.K}^{-1}.\text{mol}^{-1}$ without the energy levels. The corresponding values at 6000 K are 379.305 and $409.017 \text{ J.K}^{-1}.\text{mol}^{-1}$. The impact of these changes on the standard Gibbs free energy can be illustrated by $\Delta G_m(1000 \text{ K})$ with energy levels included in the calculation of $C_{p,m}(T)$ and $S_m(T)$ is $-190641 \text{ J.mol}^{-1}$ whereas without the energy levels the value would be $-208862 \text{ J.mol}^{-1}$. The corresponding values at 6000 K are $-1936006 \text{ J.mol}^{-1}$ and $-2113460 \text{ J.mol}^{-1}$ respectively. The inclusion of energy levels has an impact of approximately 9 per cent on the value of $\Delta G_m(\text{LaBr}, g, T)$ in the range 1000 to 6000 K.

The effect of changing the value of the vibrational wavenumber (ω_e) on the calculated value for the standard Gibbs free energy of formation for $\text{LaBr}_{< g >}$ can be illustrated by varying the selected value (237.8 cm^{-1}) by ± 10 per cent. Such changes result in differences of less than 1 per cent in the values of $\Delta G_m(T)$ in the range 1000 to 6000 K.

Similar effects are seen if the value of the equilibrium interatomic distance (R_e) for $\text{LaBr}_{< g >}$ is changed by ± 10 per cent. These changes also result in differences of less than 1 per cent in the values of $\Delta G_m(T)$ in the range 1000 to 6000 K.

Anharmonicity contributions to the molar heat capacities and entropies were included for $\text{LnF}_{< g >}$ and $\text{LnCl}_{< g >}$ but not included for $\text{LnBr}_{< g >}$ and $\text{LnI}_{< g >}$. The anharmonicity contributions for the $\text{LnX}_{< g >}$ series increase with temperature and with the increasing atomic mass of the halogen. However, as described above, it is the impacts on the values of the standard Gibbs free energies of formation that are important for this application. The anharmonicity contributions to the molar heat capacities of $\text{LaF}_{< g >}$ and $\text{LaCl}_{< g >}$ at 1000 K are $0.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ and $0.399 \text{ J.K}^{-1}.\text{mol}^{-1}$ respectively. These represent 0.007 and 0.008 of the values of the molar heat capacities. The corresponding values at 6000 K are 0.040 and 0.049. The impacts on the values of the molar entropies are lower, being 0.001 for both $\text{LaF}_{< g >}$ and $\text{LaCl}_{< g >}$ at 1000 K and 0.005 and 0.006 respectively at 6000 K. The differences between $\Delta G_m(\text{LaCl}, g, T)$ calculated with and without anharmonicity contributions are less than 1 per cent throughout the temperature range 1000 to 6000 K. The equivalent differences for the $\text{LnBr}_{< g >}$ and $\text{LnI}_{< g >}$ series are estimated to be less than 2 per cent.

The molar standard enthalpies of formation at 298.15 K and the molar entropies at 298.15 K for the Barium monohalides are listed in the SGTE Substance database [11] and are shown in table 13 together with the corresponding values from reference [6] (although this source does not provide values for BaCl<g>). Comparison of these values with the results reported in table 9 show that the molar entropies at 298.15 K are within 1.2 J.K⁻¹.mol⁻¹ for all four of the Barium monohalides.

Values for the molar standard enthalpies of formation at 298.15 K, however, show substantial differences between the three sources. While the ranges of values for BaF<g> are 6527 J.mol⁻¹ and 3320 J.mol⁻¹ for BaCl<g>, the ranges for BaBr<g> and BaI<g> are much greater. The SGTE database lists a values of -75324 J.mol⁻¹ for $\Delta_f H_m(\text{BaBr}, \text{g}, 298.15 \text{ K})$, the NIST source gives -110590 J.mol⁻¹ compared to -63048 J.mol⁻¹ from this work. There are also large differences in the values reported for $\Delta_f H_m(\text{BaI}, \text{g}, 298.15 \text{ K})$: -10237 J.mol⁻¹ (SGTE); -42420 J.mol⁻¹ (NIST); -29265 J.mol⁻¹ (this work).

This spread of values exemplifies the need for a set of self consistent values for lanthanide and Barium monohalides.

6. Conclusions

From the molar standard enthalpies of formation, the molar entropies at 298.15 K and the temperature variation of the molar heat capacities a dataset for each of the LnX<g> series can be derived in the SGTE format [11], or equivalent, for use with integrated thermochemical databank packages.

For the calculation of chemical compositions in high pressure plasmas it is the temperature variations of the standard Gibbs free energies of formation for all of the species being considered that are important. Thus, for example, values for $\Delta_f G_m(\text{LnX}, \text{g}, T)$ must be consistent with those for $\Delta_f G_m(\text{Ln}, \text{g}, T)$, $\Delta_f G_m(\text{X}, \text{g}, T)$, $\Delta_f G_m(\text{Ln}^+, \text{g}, T)$ and $\Delta_f G_m(\text{LnX}^+, \text{g}, T)$.

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Table 1. Molecular constants for $\text{LnF}_{\langle g \rangle}$ used in this work.

Ln	Molar mass (g.mol ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)	R_e (cm)	Reference
Ba	156.338	468.9	1.790	0.2158	1.2000E-03	2.162E-08	6
La	157.908	575.2	2.133	0.2464	1.2217E-03	2.023E-08	5
Ce	159.118	581.2	2.170	0.2483	1.2400E-03	2.048E-08	4
Pr	159.905	586.9	2.210	0.2505	1.2600E-03	2.005E-08	4
Nd	163.238	592.1	2.250	0.2521	1.2800E-03	1.996E-08	4
Pm	163.998	596.7	2.280	0.2542	1.3000E-03	1.987E-08	4
Sm	169.348	600.8	2.320	0.2553	1.3100E-03	1.978E-08	4
Eu	170.958	493.1	1.900	0.2300	1.2100E-03	1.935E-08	4
Gd	176.248	607.6	2.380	0.2582	1.3400E-03	1.963E-08	4
Tb	177.922	605.4	2.400	0.2599	1.3600E-03	1.955E-08	4
Dy	181.498	607.4	2.420	0.2612	1.3700E-03	1.948E-08	4
Ho	183.928	613.9	2.440	0.2626	1.3800E-03	1.941E-08	4
Er	186.258	615.0	2.450	0.2640	1.3900E-03	1.935E-08	4
Tm	187.932	615.5	2.450	0.2654	1.4000E-03	1.928E-08	4
Yb	192.038	505.5	1.900	0.2422	1.2500E-03	2.016E-08	4
Lu	193.968	615.1	2.450	0.2676	1.4100E-03	1.917E-08	4

Table 2. Molecular constants for $\text{LnCl}<\text{g}>$ used in this work.

Ln	Molar mass (g.mol^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	R_e (cm)	Reference
Ba	172.793	279.3				2.683E-08	6
La	174.363	341.6	0.98	0.1	3.6000E-04	2.498E-08	5
Ce	175.573	344.3	1.00	0.1	3.6600E-04	2.486E-08	4
Pr	176.360	346.9	1.02	0.1	3.7200E-04	2.475E-08	4
Nd	179.693	349.1	1.05	0.1	3.7800E-04	2.464E-08	4
Pm	180.453	351.0	1.06	0.1	3.8400E-04	2.453E-08	4
Sm	185.803	352.6	1.09	0.1	3.5600E-04	2.442E-08	4
Eu	187.413	288.7	0.89	0.1	3.9400E-04	2.571E-08	4
Gd	192.703	354.9	1.12	0.1	4.0000E-04	2.423E-08	4
Tb	194.377	355.6	1.14	0.1	4.0500E-04	2.413E-08	4
Dy	197.953	356.0	1.15	0.1	4.1000E-04	2.404E-08	4
Ho	200.383	356.1	1.17	0.1	4.1500E-04	2.396E-08	4
Er	202.713	355.9	1.18	0.1	4.2000E-04	2.388E-08	4
Tm	204.387	355.3	1.18	0.1	3.8000E-04	2.379E-08	4
Yb	208.493	291.1	0.92	0.1	2.3660E-04	2.488E-08	4
Lu	210.423	353.4	1.19	0.1	3.6399E-04	2.366E-08	4

Table 3. Molecular constants for LnBr<g> used in this work.

Ln	Molar mass (g.mol ⁻¹)	ω_e (cm ⁻¹)	R_e (cm)
Ba	217.244	194.4	2.840E-08
La	218.814	237.8	2.644E-08
Ce	220.024	239.7	2.631E-08
Pr	220.811	241.5	2.620E-08
Nd	224.144	243.0	2.608E-08
Pm	224.904	244.4	2.596E-08
Sm	230.254	245.5	2.585E-08
Eu	231.864	201.0	2.721E-08
Gd	237.154	247.1	2.565E-08
Tb	238.828	247.6	2.554E-08
Dy	242.404	247.8	2.544E-08
Ho	244.834	247.9	2.536E-08
Er	247.164	247.8	2.527E-08
Tm	248.838	247.3	2.518E-08
Yb	252.944	202.7	2.633E-08
Lu	254.874	246.0	2.504E-08

Table 4. Molecular constants for LnI<g> used in this work.

Ln	Molar mass (g.mol ⁻¹)	ω_e (cm ⁻¹)	R_e (cm)
Ba	264.244	153.2	3.082E-08
La	265.814	187.4	2.869E-08
Ce	267.024	188.9	2.855E-08
Pr	267.811	190.3	2.843E-08
Nd	271.144	191.5	2.830E-08
Pm	271.904	192.6	2.817E-08
Sm	277.254	193.5	2.805E-08
Eu	278.864	158.4	2.953E-08
Gd	284.154	194.7	2.783E-08
Tb	285.828	195.1	2.772E-08
Dy	289.404	195.3	2.761E-08
Ho	291.834	195.4	2.752E-08
Er	294.164	195.3	2.743E-08
Tm	295.838	194.9	2.732E-08
Yb	299.944	159.7	2.858E-08
Lu	301.874	193.9	2.718E-08

Table 5. Coefficients for the temperature variation of the molar heat capacities of the lanthanide monofluorides as expressed in equation (1), 298.15 to 6000 K.

Ln	A	B	C	D	T _{max}
BaF	3.9487E+01	-6.9904E-03	6.4499E-06	-2.8676E+05	900
	9.4870E+00	2.7479E-02	-4.0859E-06	5.7968E+06	1600
	2.9618E+01	1.9553E-02	-4.1888E-06	-1.2598E+07	2700
	8.3099E+01	-1.2628E-02	1.0845E-06	-4.9295E+07	5200
	4.1514E+01	-4.9070E-04	9.0780E-08	9.5070E+07	6000
LaF	1.2776E+01	9.4742E-02	-6.4110E-05	9.1960E+04	600
	7.1988E+01	-2.7690E-02	7.0616E-06	-4.0030E+06	1600
	4.1701E+01	-1.0918E-03	3.9272E-07	8.2930E+06	4600
	1.1920E+01	8.7033E-03	-5.1407E-07	9.1047E+07	6000
CeF	3.0739E+01	3.1653E-02	-9.1755E-06	-2.0780E+04	800
	4.3332E+01	1.9666E-02	-7.3462E-06	-2.6914E+06	1600
	7.8992E+01	-1.3928E-02	1.4188E-06	-1.3825E+07	4100
	4.5365E+01	-1.4267E-03	1.1034E-07	5.9576E+07	6000
PrF	3.3229E+01	1.8073E-02	-4.6550E-06	-3.6900E+03	1400
	6.8879E+01	-8.8117E-03	7.6430E-07	-1.6926E+07	3400
	5.0355E+01	-2.7802E-03	2.4115E-07	3.0077E+07	6000
NdF	3.6780E+01	1.6719E-02	-6.1974E-06	-2.3120E+05	900
	4.0243E+01	8.6624E-03	-1.5880E-06	-1.8882E+05	3400
	7.3773E+01	-7.1694E-03	4.8510E-07	-4.2561E+07	6000
PmF	3.5320E+01	4.7616E-03	-9.8968E-07	-2.4467E+05	1400
	3.9815E+01	1.3861E-03	-1.8855E-07	-2.8738E+06	4500
	4.5296E+01	-9.9170E-04	8.3320E-08	-8.6346E+06	6000
SmF	3.6651E+01	2.8354E-02	-1.5563E-05	-1.2250E+05	900
	6.2314E+01	-1.2368E-02	2.4113E-06	-3.0168E+06	2500
	4.8603E+01	-9.7310E-04	5.8410E-08	-3.4653E+06	6000
EuF	3.0190E+01	2.0213E-02	-9.9722E-06	-6.0190E+04	900
	4.8668E+01	-8.2348E-03	2.3319E-06	-2.3624E+06	2700
	1.4176E+01	1.2073E-02	-9.6631E-07	2.4644E+07	5600
	5.7160E+01	3.7570E-04	-7.4010E-08	-1.4672E+08	6000
GdF	4.3845E+01	-2.8997E-03	3.7786E-06	-2.7556E+05	1000
	4.2442E+01	4.9399E-03	-1.1271E-06	-1.8069E+06	2800
	5.7553E+01	-3.7802E-03	2.7788E-07	-1.5200E+07	6000
TbF	3.7386E+01	4.7645E-03	3.2000E-06	-3.8448E+05	800
	2.4676E+01	2.9931E-02	-1.0059E-05	2.9537E+05	1500
	6.6845E+01	-1.1992E-02	1.4698E-06	-1.1455E+07	3700
	3.8702E+01	-5.9730E-04	1.6295E-07	4.1523E+07	6000
DyF	4.1725E+01	-7.3400E-04	-1.0704E-06	-5.2049E+05	700
	3.6867E+01	1.6932E-03	6.9605E-07	6.0312E+05	2000
	3.0644E+01	7.8199E-03	-8.2667E-07	8.4000E+05	4600
	6.2021E+01	-2.6069E-03	1.4505E-07	-8.3279E+07	6000

Enthalpies of formation, entropies & heat capacities of lanthanide monohalides

HoF	4.6171E+01	-1.2221E-02	5.4954E-06	-5.1932E+05	1300
	3.1495E+01	5.3892E-03	-3.2125E-07	2.2046E+06	4600
	1.9059E+01	8.7658E-03	-5.7046E-07	4.8312E+07	6000
ErF	4.0852E+01	-5.8382E-03	3.4667E-06	-2.5498E+05	1600
	2.4623E+01	1.1372E-02	-1.4166E-06	2.7987E+06	4000
	6.4267E+01	-4.1406E-03	2.8049E-07	-7.3116E+07	6000
TmF	3.6633E+01	1.1547E-03	-1.9325E-07	-1.6409E+05	1500
	4.5053E+01	-6.1464E-03	1.6888E-06	-3.9973E+06	4100
	-1.1691E+02	4.6291E-02	-3.1072E-06	4.5983E+08	6000
YbF	3.6741E+01	1.1405E-03	-2.2318E-07	-2.3660E+05	1900
	5.0065E+01	-6.6010E-03	1.0785E-06	-1.2206E+07	5600
	-3.7399E+01	1.5871E-02	-5.4455E-07	3.8053E+08	6000
LuF	3.6475E+01	1.7236E-02	-6.4462E-06	-2.3387E+05	900
	4.0237E+01	8.6659E-03	-1.5885E-06	-2.2206E+05	3400
	7.3769E+01	-7.1679E-03	4.8500E-07	-4.2586E+07	6000

Table 6. Coefficients for the temperature variation of the molar heat capacities of the lanthanide monochlorides as expressed in equation (1), 298.15 to 6000 K.

Ln	A	B	C	D	T _{max}
BaCl	4.0921E+01	-1.0289E-02	8.0811E-06	-2.0528E+05	1000
	-7.8160E+00	4.4604E-02	-9.0096E-06	1.0728E+07	2300
	1.0006E+02	-1.9696E-02	1.8065E-06	-8.0256E+07	4100
	9.1621E+03	-2.8633E+00	2.5260E-04	-2.7299E+10	4300
	8.9394E+01	-1.2733E-02	9.0864E-07	-1.3464E+08	6000
LaCl	1.5585E+01	8.9004E-02	-6.0637E-05	1.5723E+05	600
	7.2227E+01	-2.7851E-02	7.1297E-06	-3.7762E+06	1600
	4.3104E+01	-1.7595E-03	4.9872E-07	7.3716E+06	4100
	-1.4727E+03	4.7324E-01	-4.1317E-05	4.5664E+09	4400
	-5.5162E+01	2.5467E-02	-1.6767E-06	4.0872E+08	6000
CeCl	1.5228E+01	7.7964E+00	-3.5540E-05	2.8050E+05	900
	8.5905E+01	-1.9605E-02	2.4571E-06	-1.0771E+07	3200
	5.3456E+01	-4.1090E-03	3.7150E-07	3.2415E+07	4100
	1.0531E+03	-3.1724E-01	2.7912E-05	-2.9729E+09	4400
	9.2439E+01	-1.3060E-02	9.2608E-07	-1.7084E+08	6000
PrCl	3.5666E+01	1.3799E-02	-2.5295E-06	7.1900E+04	1100
	4.7939E+01	6.0749E-03	-2.1115E-06	-5.1093E+06	2400
	7.0106E+01	-9.6704E-03	9.3051E-07	-1.6053E+07	4100
	7.8100E+00	8.8231E-03	-6.2926E-07	1.9729E+08	5600
	3.9506E+01	9.8400E-05	3.9430E-08	7.7868E+07	6000
NdCl	3.9961E+01	1.0488E-02	-2.7080E-06	-1.7814E+05	1200
	4.1448E+01	7.9677E-03	-1.4543E-06	-5.6551E+05	3500
	7.9502E+01	-8.9566E-03	6.5530E-07	-5.7650E+07	4100
	1.3018E+03	-3.9146E-01	3.4270E-05	-3.7399E+09	4400
	1.2279E+02	-1.9140E-02	1.3154E-06	-2.7929E+08	6000
PmCl	3.6503E+01	2.9481E-03	-4.6811E-07	-1.1632E+05	3800
	4.3835E+01	-9.0090E-04	5.2300E-08	-3.2629E+06	6000
SmCl	3.8830E+01	2.4678E-02	-1.3723E-05	-3.0680E+04	900
	6.1454E+01	-1.1462E-02	2.2085E-06	-2.4631E+06	2600
	4.9408E+01	-1.1405E-03	8.0620E-08	-5.2082E+06	6000
EuCl	3.1375E+01	1.8247E-02	-8.9498E-06	4.0550E+04	900
	4.8693E+01	-8.1420E-03	2.3348E-06	-2.1536E+06	2700
	5.0840E+00	1.5653E-02	-1.3318E-06	4.2252E+07	4100
	-1.2171E+04	3.8375E+00	-3.3853E-04	3.6594E+10	4300
	2.2465E+03	-6.4604E-01	5.3528E-05	-7.5409E+09	4600
	4.8667E+01	2.5191E-03	-2.1082E-07	-1.0285E+08	6000
GdCl	4.5911E+01	-6.2115E-03	5.3515E-06	-1.7750E+05	1000
	4.2483E+01	5.0108E-03	-1.1231E-06	-1.4965E+06	2800
	5.8022E+01	-3.8542E-03	2.9375E-07	-1.5797E+07	6000
TbCl	3.9838E+01	4.1890E-04	5.4904E-06	-3.0128E+05	800
	2.4844E+01	2.9872E-02	-1.0018E-05	5.6771E+05	1500

Enthalpies of formation, entropies & heat capacities of lanthanide monohalides

	6.6163E+01	-1.1492E-02	1.4051E-06	-1.0627E+07	3800
	3.7753E+01	-2.4650E-04	1.4382E-07	4.5562E+07	6000
DyCl	4.5857E+01	-9.6211E-03	4.4914E-06	-4.9082E+05	900
	3.1239E+01	7.0602E-03	-6.2349E-07	2.5455E+06	3100
	5.0593E+01	7.8520E-04	-1.1937E-07	-4.3079E+07	5600
	6.1652E+01	-2.4160E-03	1.3845E-07	-8.1271E+07	6000
HoCl	4.8603E+01	-1.6282E-02	7.4702E-06	-4.3277E+05	1100
	3.0377E+01	6.1379E-03	-4.1707E-07	3.3273E+06	4100
	-1.0575E+04	3.3339E+00	-2.9391E-04	3.1856E+10	4300
	1.4103E+02	-2.8371E-02	2.5928E-06	-3.2179E+08	4800
	1.8980E+01	8.8916E-03	-5.7178E-07	4.9062E+07	6000
ErCl	4.2667E+01	-8.4063E-03	4.5347E-06	-1.4486E+05	1400
	2.2250E+01	1.2705E-02	-1.5863E-06	5.4576E+06	3900
	6.6026E+01	-4.5009E-03	3.1540E-07	-7.9696E+07	6000
TmCl	3.8641E+01	-1.5923E-03	8.5743E-07	-6.5410E+04	2700
	3.8906E+01	-3.6543E-03	1.4329E-06	8.0168E+06	4100
	-3.1152E+04	9.7861E+00	-8.6224E-04	9.3661E+10	4300
	6.6834E+03	-1.9567E+00	1.6258E-04	-2.2649E+10	4600
	-1.3195E+02	5.0212E-02	-3.3768E-06	5.2838E+08	6000
YbCl	3.7619E+01	1.8870E-04	1.0764E-07	-1.2072E+05	3300
	5.8011E+01	-9.3309E-03	1.3623E-06	-2.8843E+07	4100
	-1.1856E+04	3.7280E+00	-3.2815E-04	3.5781E+10	4300
	3.0234E+03	-8.8186E-01	7.3461E-05	-1.0130E+10	4600
	-1.0950E+00	7.3355E-03	3.6680E-08	1.9302E+08	6000
LuCl	3.7566E+01	-8.3700E-05	3.2980E-07	-1.5781E+05	1600
	5.3512E+01	-1.6942E-02	5.1250E-06	-3.3542E+06	2900
	-1.5202E+02	7.9306E-02	-7.6046E-06	2.7814E+08	4100
	-2.6908E+04	8.4812E+00	-7.4923E-04	8.0535E+10	4300
	3.7481E+03	-1.0774E+00	8.8738E-05	-1.2796E+10	4600
	2.0986E+02	-2.8245E-02	1.4245E-06	-9.5129E+08	6000

Table 7. Coefficients for the temperature variation of the molar heat capacities of the lanthanide monobromides as expressed in equation (1), 298.15 to 6000 K.

Ln	A	B	C	D	T _{max}
BaBr	4.1318E+01	-1.1200E-02	8.6494E-06	-1.7040E+05	1100
	-1.0092E+01	4.6353E-02	-9.3768E-06	1.1824E+07	2300
	9.5727E+01	-1.7795E-02	1.5770E-06	-7.4012E+07	4600
	4.4865E+01	-1.7192E-03	1.4561E-07	7.8415E+07	6000
LaBr	1.6025E+01	8.7671E-02	-6.0071E-05	2.0897E+05	600
	7.2256E+01	-2.8280E-02	7.1379E-06	-3.6993E+06	1600
	4.1060E+01	-1.0781E-03	3.4691E-07	9.2553E+06	4800
	1.1805E+01	8.4236E-03	-5.1846E-07	9.1840E+07	6000
CeBr	3.4994E+01	2.2013E-02	-3.4062E-06	6.4870E+04	700
	3.6268E+01	2.7597E-02	-9.9898E-06	-8.9364E+05	1500
	7.9719E+01	-1.4586E-02	1.4614E-06	-1.4265E+07	4100
	4.5396E+01	-1.7531E-03	1.1097E-07	5.9859E+07	6000
PrBr	3.5915E+01	1.3002E-02	-2.3525E-06	1.3130E+05	1100
	4.7940E+01	5.6775E-03	-2.1115E-06	-5.0228E+06	2400
	6.0190E+01	-6.0219E-03	4.7877E-07	2.1881E+05	6000
NdBr	4.0475E+01	9.0901E-03	-2.1912E-06	-1.2838E+05	1300
	4.2837E+01	6.7187E-03	-1.3155E-06	-1.4135E+06	3600
	7.2453E+01	-7.1213E-03	4.5726E-07	-3.7267E+07	6000
PmBr	3.6601E+01	2.8636E-03	-4.5064E-07	-4.8930E+04	3900
	4.6301E+01	-1.5642E-03	1.0168E-07	-1.2667E+07	6000
SmBr	3.9152E+01	2.3704E-02	-1.3441E-05	2.7790E+04	900
	6.1460E+01	-1.1871E-02	2.2092E-06	-2.3760E+06	2600
	4.9249E+01	-1.4883E-03	7.5180E-08	-4.8093E+06	6000
EuBr	3.1531E+01	1.7467E-02	-8.8119E-06	8.6210E+04	900
	4.8696E+01	-8.6470E-03	2.3350E-06	-2.0942E+06	2700
	1.4175E+01	1.1679E-02	-9.6636E-07	2.4935E+07	5600
	5.5450E+01	3.8240E-04	-1.0044E-07	-1.3725E+08	6000
GdBr	4.6799E+01	-8.5965E-03	6.5390E-06	-1.3846E+05	900
	3.9740E+01	6.7717E-03	-1.5836E-06	-2.9527E+05	2600
	5.7624E+01	-4.1169E-03	2.7971E-07	-1.4955E+07	6000
TbBr	4.0205E+01	-6.7480E-04	5.8468E-06	-2.4349E+05	800
	2.4859E+01	2.9444E-02	-1.0014E-05	6.5405E+05	1500
	6.6164E+01	-1.1907E-02	1.4053E-06	-1.0536E+07	3800
	3.8160E+01	-7.7090E-04	1.5207E-07	4.4098E+07	6000
DyBr	4.6313E+01	-1.1056E-02	5.1611E-06	-4.3432E+05	1300
	2.8469E+01	8.4412E-03	-9.3674E-07	4.3041E+06	4500
	6.1938E+01	-2.9058E-03	1.4363E-07	-8.2444E+07	6000
HoBr	4.8877E+01	-1.7144E-02	7.6650E-06	-3.7164E+05	1100
	3.1231E+01	5.1727E-03	-3.2978E-07	2.9810E+06	4800

Enthalpies of formation, entropies & heat capacities of lanthanide monohalides

	1.9080E+01	8.4452E-03	-5.7013E-07	4.8652E+07	6000
ErBr	4.2875E+01	-9.1228E-03	4.6434E-06	-8.1270E+04	1400
	2.2251E+01	1.2278E-02	-1.5863E-06	5.5491E+06	3900
	6.4483E+01	-4.5134E-03	2.8468E-07	-7.3554E+07	6000
TmBr	3.8801E+01	-2.1990E-03	9.0621E-07	-1.5000E+02	2800
	2.4515E+01	1.5917E-03	8.0975E-07	3.4733E+07	4500
	-1.3027E+02	4.9368E-02	-3.3480E-06	5.2050E+08	6000
YbBr	3.7656E+01	-3.5300E-04	1.1276E-07	-6.9240E+04	3300
	4.0638E+01	-4.0831E-03	8.3124E-07	1.6321E+07	6000
LuBr	4.0471E+01	9.0946E-03	-2.1929E-06	-1.3004E+05	1300
	4.2837E+01	6.7183E-03	-1.3155E-06	-1.4158E+06	3600
	7.2451E+01	-7.1205E-03	4.5720E-07	-3.7258E+07	6000

Table 8. Coefficients for the temperature variation of the molar heat capacities of the lanthanide monoiodides as expressed in equation (1), 298.15 to 6000 K.

Ln	A	B	C	D	T _{max}
BaI	4.1415E+01	-1.1441E-02	8.8099E-06	-1.5478E+05	1200
	-1.0325E+01	4.6514E-02	-9.4079E-06	1.1980E+07	2300
	9.5727E+01	-1.7795E-02	1.5770E-06	-7.3991E+07	4600
	4.4849E+01	-1.7152E-03	1.4534E-07	7.8515E+07	6000
LaI	1.6115E+01	8.7479E-02	-5.9956E-05	2.3277E+05	600
	7.2260E+01	-2.8284E-02	7.1391E-06	-3.6702E+06	1600
	4.1060E+01	-1.0781E-03	3.4691E-07	9.2853E+06	4800
	1.1737E+01	8.4406E-03	-5.1966E-07	9.2184E+07	6000
CeI	3.5074E+01	2.1855E-02	-3.3168E-06	8.9340E+04	700
	3.6273E+01	2.7592E-02	-9.9882E-06	-8.6400E+05	1500
	7.9719E+01	-1.4585E-02	1.4613E-06	-1.4233E+07	4100
	4.5375E+01	-1.7475E-03	1.1055E-07	5.9974E+07	6000
PrI	3.5967E+01	1.2918E-02	-2.3151E-06	1.5706E+05	1100
	4.7943E+01	5.6752E-03	-2.1110E-06	-4.9927E+06	2400
	6.0191E+01	-6.0220E-03	4.7879E-07	2.4963E+05	6000
NdI	4.0518E+01	9.0257E-03	-2.1656E-06	-1.0203E+05	1300
	4.2837E+01	6.7183E-03	-1.3155E-06	-1.3820E+06	3600
	7.2451E+01	-7.1207E-03	4.5721E-07	-3.7225E+07	6000
PmI	3.6613E+01	2.8555E-03	-4.4935E-07	-2.0760E+04	3900
	4.6313E+01	-1.5673E-03	1.0190E-07	-1.2684E+07	6000
SmI	3.9219E+01	2.3584E-02	-1.3382E-05	5.3790E+04	900
	6.1461E+01	-1.1872E-02	2.2092E-06	-2.3441E+06	2600
	4.9250E+01	-1.4886E-03	7.5210E-08	-4.7798E+06	6000
EuI	3.1563E+01	1.7410E-02	-8.7833E-06	1.0503E+05	900
	4.8696E+01	-8.6474E-03	2.3351E-06	-2.0726E+06	2700
	1.4175E+01	1.1679E-02	-9.6635E-07	2.4956E+07	5600
	5.6113E+01	2.2510E-04	-8.9950E-08	-1.4070E+08	6000
GdI	4.6867E+01	-8.7183E-03	6.5998E-06	-1.1216E+05	900
	3.9740E+01	6.7715E-03	-1.5835E-06	-2.6271E+05	2600
	5.7625E+01	-4.1173E-03	2.7975E-07	-1.4924E+07	6000
TbI	4.0283E+01	-8.2210E-04	5.9249E-06	-2.1743E+05	800
	2.4861E+01	2.9442E-02	-1.0014E-05	6.8588E+05	1500
	6.6164E+01	-1.1907E-02	1.4053E-06	-1.0502E+07	3800
	3.8156E+01	-7.6960E-04	1.5197E-07	4.4147E+07	6000
DyI	4.6361E+01	-1.1125E-02	5.1885E-06	-4.0714E+05	1300
	2.8469E+01	8.4413E-03	-9.3675E-07	4.3371E+06	4500
	6.1972E+01	-2.9140E-03	1.4419E-07	-8.2574E+07	6000
HoI	4.8933E+01	-1.7235E-02	7.7053E-06	-3.4480E+05	1100
	3.1231E+01	5.1724E-03	-3.2975E-07	3.0136E+06	4800

Enthalpies of formation, entropies & heat capacities of lanthanide monohalides

	1.9002E+01	8.4640E-03	-5.7139E-07	4.9080E+07	6000
ErI	4.2918E+01	-9.1832E-03	4.6661E-06	-5.3920E+04	1400
	2.2251E+01	1.2278E-02	-1.5863E-06	5.5818E+06	3900
	6.4487E+01	-4.5145E-03	2.8477E-07	-7.3535E+07	6000
TmI	3.8819E+01	-2.2150E-03	9.0963E-07	2.8240E+04	2800
	2.4516E+01	1.5915E-03	8.0975E-07	3.4762E+07	4500
	-1.3029E+02	4.9373E-02	-3.3484E-06	5.2061E+08	6000
YbI	3.7663E+01	-3.5840E-04	1.1375E-07	-4.9040E+04	3300
	4.0646E+01	-4.0855E-03	8.3144E-07	1.6318E+07	6000
LuI	4.0517E+01	9.0284E-03	-2.1667E-06	-1.0314E+05	1300
	4.2837E+01	6.7187E-03	-1.3155E-06	-1.3829E+06	3600
	7.2450E+01	-7.1203E-03	4.5717E-07	-3.7227E+07	6000

Table 9. Molar entropies^a (S_m) for $\text{LnX}_{<\text{g}>}$ at 298.15 K.

Ln	LnF ($\text{J.K}^{-1}.\text{mol}^{-1}$)	LnCl ($\text{J.K}^{-1}.\text{mol}^{-1}$)	LnBr ($\text{J.K}^{-1}.\text{mol}^{-1}$)	LnI ($\text{J.K}^{-1}.\text{mol}^{-1}$)
Ba	246.143	257.805	269.902	277.791
La	252.320	264.332	275.522	283.351
Ce	257.090	268.003	282.493	290.316
Pr	259.955	271.799	283.119	290.938
Nd	258.612	270.484	281.745	289.551
Pm	278.456	290.411	301.573	309.374
Sm	252.742	264.677	275.819	283.600
Eu	258.973	270.451	282.569	290.404
Gd	261.455	273.448	284.495	292.255
Tb	263.034	275.043	286.025	293.784
Dy	264.051	276.088	287.020	294.772
Ho	262.477	274.590	285.488	293.222
Er	263.924	276.082	286.927	294.663
Tm	261.595	273.802	284.599	292.324
Yb	250.705	262.572	274.246	282.026
Lu	260.103	252.204	283.124	290.835

^a Values are expressed to 3 decimal place by convention and do not represent accuracy

Table10. Dissociation energies from reference [10].

Ln	LnF (cm ⁻¹)	LnCl (cm ⁻¹)	LnBr (cm ⁻¹)	LnI (cm ⁻¹)
Ba	48200	36500	29900	26700
La	55300	43600	37300	34500
Ce	51700	38200	31200	27900
Pr	48400	35400	28800	25600
Nd	45600	35000	28400	25200
Pm	46600	34600	28000	24800
Sm	46900	35000	27700	24500
Eu	45100	33900	27300	24100
Gd	49400	37700	31100	27900
Tb	53700	39300	32000	28100
Dy	44100	32800	26200	23000
Ho	43000	34200	26900	23000
Er	47600	37500	30200	26400
Tm	42300	31600	25000	21800
Yb	43600	31300	24700	21500
Lu	43500	31800	25200	22000

Table 11. Molar enthalpies of dissociation ($\Delta_{\text{dis}}H_{\text{m}}$) for LnX_{g} at 298.15 K.

Ln	LnF (J.mol ⁻¹)	LnCl (J.mol ⁻¹)	LnBr (J.mol ⁻¹)	LnI (J.mol ⁻¹)
Ba	580009	439272	359918	321028
La	665118	524380	448585	414888
Ce	621639	459956	375196	335516
Pr	581962	425654	346283	307799
Nd	548739	421142	341771	303285
Pm	561324	416994	337605	299119
Sm	565176	422051	334277	295791
Eu	542968	408445	328835	290374
Gd	594609	453874	374473	335986
Tb	647253	474193	386447	339584
Dy	531053	395078	315705	277217
Ho	517678	411603	323857	276994
Er	572601	450971	363224	317559
Tm	509114	380303	300931	262444
Yb	525054	377080	297742	259280
Lu	523435	383265	303285	264799

Table 12. Molar standard enthalpies of formation ($\Delta_f H_m$) for $\text{LnX}_{<\text{g}>}$ at 298.15 K.

Ln	$\text{LnF (J.mol}^{-1}\text{)}$	$\text{LnCl (J.mol}^{-1}\text{)}$	$\text{LnBr (J.mol}^{-1}\text{)}$	$\text{LnI (J.mol}^{-1}\text{)}$
Ba	-315629	-132970	-63048	-29265
La	-159888	22772	89135	117725
Ce	-125185	78420	153748	188321
Pr	-146769	51461	121400	154777
Nd	-142230	27289	97228	130607
Pm	-222781	-36529	33428	66807
Sm	-280199	-95152	-16810	16569
Eu	-287401	-110956	-40778	-7424
Gd	-116718	65939	135908	169288
Tb	-181817	33165	111479	153235
Dy	-166421	11476	81417	114798
Ho	-138107	9890	88204	129960
Er	-179394	-15842	62473	103031
Tm	-196975	-26242	43698	77078
Yb	-293188	-103292	-33386	-31
Lu	-16193	165899	236447	269826

Table 13. Molar standard enthalpies of formation ($\Delta_f H_m$) and molar entropies (S_m) for $BaX_{<g>}$ at 298.15 K from the SGTE Substance database [11] and the NIST Chemistry WebBook [6].

	Reference [11]		Reference [6]	
	$\Delta_f H_m$ (J.mol ⁻¹)	S_m (J.K ⁻¹ .mol ⁻¹)	$\Delta_f H_m$ (J.mol ⁻¹)	S_m (J.K ⁻¹ .mol ⁻¹) ^a
BaF<g>	-322156	246.116	-322170 _b	246.23 _b
BaCl<g>	-136290	258.727		
BaBr<g>	-75324	270.739	-110590	270.74
BaI<g>	-10237	278.465	-42420	278.72

^a Values given to 2 decimal places in [6]^b Value not listed