| | |
|---|---|
| $D$ | constant "scaling factor" |
| $h$ | Planck's constant |
| $H^*$ | ideal-gas enthalpy |
| $k$ | Boltzmann's constant; an index |
| $m$ | constant exponent |
| $N$ | number of data points |
| $R$ | gas constant |
| $S^*$ | temperature-dependent part of ideal-gas entropy |
| $T$ | absolute temperature |
| $T_c$ | absolute thermodynamic critical temperature |
| $\hat{T}$ | reduced temperature = $T/T_c$ |
| $w$ | equivalent wavenumber, cm$^{-1}$ |
| $x$ | independent variable = $B(\hat{T} - \tau)$ |
| $X$ | computed property |
| $y$ | dependent variable = $(\hat{c}_v - c_\alpha)/(c_\omega - c_\alpha)$ |
| $y_c$ | value of $y$ at $T = T_c$ |
| $z$ | independent variable = $T/(T + D)$ |

*Greek Letters*

| | |
|---|---|
| $\alpha$ | subscript denoting low temperature |
| $\eta$ | reduced reciprocal temperature = $h\nu/2kT$ |
| $\nu$ | molecular vibration frequency |
| $\tau$ | constant in the definition $x = B(\hat{T} - \tau)$ |

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# Thermodynamic Properties of Lanthanide Trihalide Molecules

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**The thermodynamic properties of lanthanide trihalide molecules have been calculated for the temperature range 298.15–2000 K using the methods of statistical mechanics. The necessary molecular data are incomplete, and the missing parameters have been estimated in a systematic manner.**

There has been considerable recent interest in the high-temperature thermodynamic properties of the lanthanide trihalides with particular emphasis on vapor pressure and sublimation pressure measurements (*17*). In most of these studies a "second law" treatment of the data was used to obtain enthalpies of vaporization or sublimation, although a "third law" treatment was used in some cases. However, the molecular parameters required to calculate the free energy functions ($-[G^\circ_T - H^\circ_{298.15}]/T$) for the gaseous molecules were developed on a case-by-case basis which makes systematic comparisons difficult. Free energy functions for the lanthanum trihalides have been published (*14*), but significant molecular data have become available more recently (*10, 11, 15, 20, 24*).

Because of an interest in systematic trends in properties of $LnX_3$ molecules and in view of the advantages of the third law treatment, it was decided to calculate their thermodynamic functions using the best data currently available and employing uniform methods for interpolation and extrapolation in the absence of published data.

## Method

The calculations were performed using STRETCH-TDF, a FORTRAN computer program (*5*) which employs the usual statistical-mechanical formulas (rigid rotor, harmonic oscillator approximation). The electronic contributions were calculated separately using QEL, an APL program written for that purpose, since the STRETCH-TDF program does not include electronic levels in the polyatomic molecule calculation mode. STRETCH-TDF inputs are molecular weight, symmetry number, moments of inertia, and vibrational frequencies together with their degeneracies. The QEL inputs are the energies and multiplicities of the electronic states of the molecule, including the multiplicity of the ground state. A description of the method may be found in the introduction to the JANAF Thermochemical Tables (*23*).

## Molecular Geometry

The molecular structures of $LnX_3$ molecules have been the subject of recent investigations (*10, 11, 13, 15, 20, 24*), but the picture is far from being complete. Infrared spectra of $LnF_3$ molecules trapped in inert matrices have been interpreted by some investigators (*24*) as supporting a planar $D_{3h}$ geometry, but others (*10, 11*) interpret similar data as supporting a pyramidal $C_{3v}$ geometry. Molecular beam experiments (*13*) on a number of trifluorides support a pyramidal geometry for some but not all of the molecules studied. Earlier electron diffraction studies (*1*) were interpreted as supporting a planar geometry, but more recent work (*6*) presents strong evidence for the pyramidal configuration. Extended Hückel molecular orbital calculations done in this laboratory (*18*) also support a pyramidal geometry.

The weight of evidence thus appears to favor the pyramidal geometry with reported X-Ln-X bond angles: $LaF_3$, 117° (*10*); $LuCl_3$, 111.0°; $LaBr_3$, 115.1°; $GdBr_3$, 113.8°; $LuBr_3$, 114.5° (*6*). The symmetry $C_{3v}$ would ordinarily lead to a symmetry number of 3. However, the rather large bond angles and the low frequencies of the totally symmetric bending vibration, $\nu_2$ (see below), lead to the conclusion that 6 is the preferred symmetry number in the absence of detailed information on the shape of the potential energy curve for $\nu_2$.

Using the "valence force field" approximation as discussed by Herzberg (*12*), the bending force constant, $k_\delta/l^2$, is calculated to be $1.0 \times 10^4$ dyn/cm for $LaF_3$, $6.0 \times 10^3$ for $LaCl_3$, $5.9 \times 10^3$ for $LaBr_3$, and $3.3 \times 10^3$ for $LaI_3$, assuming a bond angle of 115° in each case. These values may be used to estimate the inversion barrier by calculating the energy needed to expand the bond angles to 120°. The neglect of bond stretching during inversion is effectively cancelled by the neglect of anharmonicity. For example, the energy barrier in ammonia is $4 \times 10^{-13}$ erg (*9*) and the "angle-only" barrier, neglecting anharmonicity, is $3 \times 10^{-13}$ erg. The estimated inversion barriers are $6 \times 10^{-14}$ erg for $LaF_3$, $5 \times 10^{-14}$ for $LaCl_3$ and for $LaBr_3$, and $3 \times 10^{-14}$ for $LaI_3$, again assuming an equilibrium bond angle of 115°. These values are to be compared with the magnitude of $kT = 4 \times 10^{-14}$ erg at 300 K. That is, the thermal energy of the $LnX_3$ molecules is large compared to the inversion barrier at most temperatures of interest. With respect to the ratio of $kT$ to the inversion barrier, the $LnX_3$ molecules at, say, 800 K may be compared with $NH_3$ at 4600 K. At the latter temperature, the simple rigid rotor–harmonic oscillator treatment (*22*), with a symmetry number of 3, gives a value of $S°(NH_3)$ which is 1.2 cal mol$^{-1}$ K$^{-1}$ lower than that resulting from a treatment taking into account inversion, anharmonicity, and coupling (*9*). This difference is only 0.2 cal mol$^{-1}$ K$^{-1}$ less than $R \ln 2$, which is the amount by which entropy values using symmetry numbers of 6 and 3, respectively, would differ. Hence, the choice of a symmetry number of 6 is justified for the $LnX_3$ molecules.

In keeping with the foregoing conclusions, the moments of inertia were calculated for the trigonal-planar, $D_{3h}$, geometry.

The only published internuclear distance data come from electron diffraction studies for $LaX_3$ and $NdX_3$ (X = F, Cl, Br, I) molecules (*1*) and for $LuCl_3$, $LaBr_3$, $GdBr_3$, and $LuBr_3$ (*6*). These, together with octahedral radii for $Ln^{3+}$ ions (*21*) and crystal radii for the halide ions (*19*), were used in the manner described earlier (*16*) to estimate the needed distances: $R(gas)/R(spp) = 0.921$ for $LnF_3$, 0.914 for $LnCl_3$, 0.915 for $LnBr_3$, and 0.932 for $LnI_3$, where $R$(gas) is the distance in the gaseous molecule and $R$(spp) is the sum of the $Ln^{3+}$ radius (*21*) and the halide radius (*19*). The more recent data (*6*) were used for $LaBr_3$. The resulting Ln–X distances are given in Table I.

## Vibration Frequencies

The vibration frequencies for $LaF_3$, $CeF_3$, $NdF_3$, $EuF_3$, and $GdF_3$ given in Table I are based on the matrix isolation data of Hastie, Hauge, and Margrave (*10, 11*), corrected by the relation $\nu(\text{gas}) \approx \nu(\text{Ne}) + 0.8(\nu_{\text{Ne}} - \nu_{\text{Ar}})$ given by these authors (*10*) where $\nu$(gas) is the estimated frequency for the gaseous molecule and $\nu$(Ne) and $\nu$(Ar) are the respective frequencies in Ne and Ar matrices. Values for the asymetric stretching frequency, $\nu_3$, have been reported (*20*) for the gaseous molecules $ScX_3$ (X = Cl, Br, I) and $LnCl_3$ (Ln = Y, La, Pr, Nd, Gd), and the latter values are included in Table I. The remaining frequencies were estimated. For a given halogen, each frequency is essentially a linear function of the atomic number of the lanthanide: $\nu_1(LnF_3) = 544 + 4.1n$, $\nu_2(LnF_3) = 83 + 1.7n$, $\nu_3(LnF_3) = 515 + 5.1n$, $\nu_4(LnF_3) = 117 + 1.8n$, $\nu_3(LnCl_3) = 318 + 0.97n$, where $n$ is the position number in the lanthanide series ($n_{La} = 0$). The ratios $\nu_1/\nu_3$, $\nu_2/\nu_3$, and $\nu_4/\nu_3$ were also effectively linear for $LnF_3$ molecules. They were assumed to have the same value for all $LnX_3$ (X = Cl, Br, I) molecules. Lastly, the $\nu_3$ ratios for $ScCl_3/ScBr_3$ and $ScCl_3/ScI_3$ were assumed to apply to all $LnX_3$ (X = Cl, Br, I) molecules.

**Table I. Molecular Constants for $LnX_3$ Molecules**

| | $d$(Ln–X), Å[a] | $\nu_1$, cm$^{-1}$ | $\nu_2$, cm$^{-1}$ | $\nu_3$, cm$^{-1}$ | $\nu_4$, cm$^{-1}$ |
|---|---|---|---|---|---|
| $LaF_3$ | 2.22[b] | 540 | 82 | 511 | 125 |
| $CeF_3$ | 2.18 | 549 | 86 | 519 | 115 |
| $PrF_3$ | 2.17 | 552 | 86 | 525 | 121 |
| $NdF_3$ | 2.16[c] | 557 | 84 | 536 | 118 |
| $PmF_3$ | 2.16 | 560 | 90 | 535 | 124 |
| $SmF_3$ | 2.14 | 564 | 92 | 540 | 126 |
| $EuF_3$ | 2.13 | 570 | 92 | 544 | 130 |
| $GdF_3$ | 2.12 | 573 | 97 | 552 | 136 |
| $TbF_3$ | 2.10 | 579 | 97 | 554 | 131 |
| $DyF_3$ | 2.09 | 581 | 98 | 561 | 133 |
| $HoF_3$ | 2.08 | 585 | 109 | 569 | 120 |
| $ErF_3$ | 2.07 | 589 | 102 | 571 | 137 |
| $TmF_3$ | 2.05 | 593 | 103 | 576 | 139 |
| $YbF_3$ | 2.04 | 597 | 100 | 579 | 144 |
| $LuF_3$ | 2.04 | 598 | 106 | 585 | 147 |
| $LaCl_3$ | 2.62[b] | 335 | 51 | 316 | 79 |
| $CeCl_3$ | 2.58 | 335 | 52 | 319 | 80 |
| $PrCl_3$ | 2.57 | 336 | 52 | 320 | 80 |
| $NdCl_3$ | 2.56[b] | 336 | 53 | 324 | 81 |
| $PmCl_3$ | 2.55 | 377 | 54 | 322 | 82 |
| $SmCl_3$ | 2.53 | 337 | 55 | 323 | 82 |
| $EuCl_3$ | 2.52 | 338 | 55 | 324 | 83 |
| $GdCl_3$ | 2.51 | 338 | 56 | 326 | 84 |
| $TbCl_3$ | 2.50 | 339 | 57 | 326 | 84 |
| $HoCl_3$ | 2.49 | 339 | 58 | 327 | 85 |
| $DyCl_3$ | 2.47 | 340 | 58 | 328 | 85 |
| $ErCl_3$ | 2.46 | 340 | 59 | 329 | 86 |
| $TmCl_3$ | 2.44 | 341 | 59 | 330 | 87 |
| $YbCl_3$ | 2.43 | 341 | 60 | 331 | 87 |
| $LuCl_3$ | 2.42[d] | 342 | 60 | 331 | 88 |
| $LaBr_3$ | 2.74[d] | 265 | 41 | 252 | 63 |
| $CeBr_3$ | 2.71 | 265 | 41 | 252 | 63 |
| $PrBr_3$ | 2.70 | 265 | 42 | 253 | 64 |
| $NdBr_3$ | 2.68 | 266 | 42 | 254 | 64 |
| $PmBr_3$ | 2.68 | 266 | 43 | 255 | 65 |
| $SmBr_3$ | 2.66 | 267 | 43 | 256 | 65 |
| $EuBr_3$ | 2.65 | 267 | 44 | 257 | 66 |
| $GdBr_3$ | 2.64[d] | 268 | 44 | 257 | 66 |
| $TbBr_3$ | 2.63 | 268 | 45 | 258 | 67 |
| $DyBr_3$ | 2.62 | 269 | 45 | 259 | 67 |
| $HoBr_3$ | 2.61 | 269 | 46 | 260 | 68 |
| $ErBr_3$ | 2.60 | 270 | 46 | 261 | 68 |
| $TmBr_3$ | 2.58 | 270 | 47 | 261 | 69 |
| $YbBr_3$ | 2.57 | 271 | 47 | 262 | 69 |
| $LuBr_3$ | 2.56[d] | 271 | 48 | 263 | 70 |
| $LaI_3$ | 2.99[b] | 186 | 28 | 177 | 44 |
| $CeI_3$ | 2.96 | 186 | 28 | 178 | 44 |
| $PrI_3$ | 2.95 | 186 | 28 | 179 | 45 |
| $NdI_3$ | 2.93[b] | 187 | 29 | 179 | 45 |
| $PmI_3$ | 2.92 | 187 | 29 | 180 | 45 |
| $SmI_3$ | 2.91 | 188 | 30 | 180 | 46 |
| $EuI_3$ | 2.90 | 188 | 30 | 181 | 46 |
| $GdI_3$ | 2.89 | 188 | 31 | 181 | 46 |
| $TbI_3$ | 2.87 | 189 | 31 | 182 | 47 |
| $DyI_3$ | 2.86 | 189 | 32 | 182 | 47 |
| $HoI_3$ | 2.85 | 190 | 32 | 183 | 48 |
| $ErI_3$ | 2.84 | 190 | 33 | 184 | 48 |
| $TmI_3$ | 2.83 | 191 | 33 | 184 | 48 |
| $YbI_3$ | 2.82 | 191 | 34 | 185 | 49 |
| $LuI_3$ | 2.81 | 191 | 34 | 185 | 49 |

[a] Estimated, unless otherwise indicated. See text and ref 18. [b] Reference 10. [c] Smooth value. See ref 18. [d] Reference 11.

**Table II. Thermodynamic Properties of $LnX_3$ Molecules** [a]

| | $H°_T - H°_0$, kcal mol$^{-1}$ | | | $S°_T$, cal mol$^{-1}$ K$^{-1}$ | | | $-(G°_T - H°_{298.15})/T$, cal mol$^{-1}$ K$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | 298.15 K | 1000 K | 1500 K | 298.15 K | 1000 K | 1500 K | 500 K | 1000 K | 1500 K |
| Fluorides | | | | | | | | | |
| $LaF_3$ | 4.11 | 17.46 | 27.31 | 76.90 | 99.66 | 107.64 | 78.93 | 86.32 | 92.18 |
| $CeF_3$ | 4.12 | 17.78 | 28.16 | 80.54 | 103.72 | 112.13 | 82.58 | 90.06 | 96.14 |
| $PrF_3$ | 4.10 | 17.89 | 28.39 | 81.04 | 104.24 | 112.83 | 83.07 | 90.55 | 96.63 |
| $NdF_3$ | 4.10 | 17.86 | 28.47 | 81.42 | 104.72 | 113.32 | 83.45 | 90.96 | 97.07 |
| $PmF_3$ | 4.08 | 18.04 | 28.78 | 80.93 | 104.56 | 113.26 | 82.97 | 90.59 | 96.79 |
| $SmF_3$ | 4.08 | 18.40 | 29.26 | 80.08 | 104.31 | 113.11 | 82.18 | 89.99 | 96.33 |
| $EuF_3$ | 4.42 | 19.40 | 30.27 | 78.46 | 103.95 | 112.77 | 80.74 | 89.01 | 95.56 |
| $GdF_3$ | 4.02 | 17.28 | 27.11 | 80.12 | 102.71 | 110.68 | 82.13 | 89.45 | 95.29 |
| $TbF_3$ | 4.03 | 17.61 | 28.10 | 81.18 | 104.19 | 112.69 | 83.19 | 90.61 | 96.64 |
| $DyF_3$ | 4.01 | 17.32 | 27.45 | 81.50 | 104.14 | 112.34 | 83.50 | 90.83 | 96.71 |
| $HoF_3$ | 4.02 | 17.27 | 27.19 | 81.78 | 104.33 | 112.36 | 83.78 | 91.08 | 96.92 |
| $ErF_3$ | 3.99 | 17.22 | 27.07 | 81.26 | 103.78 | 111.76 | 83.26 | 90.55 | 96.38 |
| $TmF_3$ | 3.98 | 17.20 | 27.07 | 80.71 | 103.21 | 111.21 | 82.71 | 89.99 | 95.81 |
| $YbF_3$ | 3.97 | 17.17 | 26.99 | 79.68 | 102.15 | 110.11 | 81.67 | 88.95 | 94.76 |
| $LuF_3$ | 3.95 | 17.14 | 26.96 | 75.35 | 97.81 | 105.76 | 77.34 | 84.61 | 90.43 |
| Chlorides | | | | | | | | | |
| $LaCl_3$ | 4.61 | 18.30 | 28.20 | 85.21 | 108.72 | 116.74 | 87.37 | 95.02 | 101.01 |
| $CeCl_3$ | 4.60 | 18.62 | 29.06 | 88.57 | 112.51 | 120.98 | 90.74 | 98.49 | 104.67 |
| $PrCl_3$ | 4.60 | 18.66 | 29.33 | 89.35 | 113.34 | 121.98 | 91.51 | 99.28 | 105.49 |
| $NdCl_3$ | 4.59 | 18.73 | 29.41 | 89.45 | 113.56 | 122.22 | 91.62 | 99.42 | 105.67 |
| $PmCl_3$ | 4.59 | 18.95 | 29.75 | 89.19 | 113.64 | 122.40 | 91.38 | 99.28 | 105.62 |
| $SmCl_3$ | 4.61 | 19.32 | 30.24 | 88.43 | 113.50 | 122.35 | 90.66 | 98.78 | 105.26 |
| $EuCl_3$ | 4.99 | 20.34 | 31.28 | 86.90 | 113.24 | 122.12 | 89.31 | 97.89 | 104.59 |
| $GdCl_3$ | 4.57 | 18.25 | 28.15 | 88.76 | 112.24 | 120.27 | 90.91 | 98.56 | 104.54 |
| $TbCl_3$ | 4.57 | 18.58 | 29.08 | 89.68 | 113.59 | 122.15 | 91.84 | 99.58 | 105.76 |
| $DyCl_3$ | 4.56 | 18.31 | 28.51 | 90.02 | 113.57 | 121.84 | 92.17 | 99.82 | 105.87 |
| $HoCl_3$ | 4.56 | 18.25 | 28.24 | 90.10 | 113.59 | 121.69 | 92.25 | 99.90 | 105.90 |
| $ErCl_3$ | 4.56 | 18.24 | 28.16 | 89.89 | 113.37 | 121.41 | 92.04 | 99.69 | 105.68 |
| $TmCl_3$ | 4.55 | 18.23 | 28.19 | 89.39 | 112.86 | 120.93 | 91.54 | 99.18 | 105.17 |
| $YbCl_3$ | 4.55 | 18.22 | 28.12 | 88.40 | 111.87 | 119.89 | 90.55 | 98.19 | 104.18 |
| $LuCl_3$ | 4.54 | 18.22 | 28.12 | 84.22 | 107.68 | 115.70 | 86.37 | 94.01 | 99.99 |
| Bromides | | | | | | | | | |
| $LaBr_3$ | 4.82 | 18.60 | 28.52 | 91.68 | 115.38 | 123.42 | 93.87 | 101.59 | 107.62 |
| $CeBr_3$ | 4.82 | 18.93 | 29.39 | 95.21 | 119.34 | 127.82 | 97.40 | 105.23 | 111.44 |
| $PrBr_3$ | 4.81 | 18.97 | 29.65 | 95.85 | 120.04 | 128.69 | 98.05 | 105.88 | 112.13 |
| $NdBr_3$ | 4.81 | 19.05 | 29.75 | 96.02 | 120.34 | 129.01 | 98.22 | 106.10 | 112.38 |
| $PmBr_3$ | 4.81 | 19.26 | 30.08 | 95.73 | 120.32 | 129.05 | 97.94 | 105.92 | 112.30 |
| $SmBr_3$ | 4.83 | 19.64 | 30.57 | 94.98 | 120.25 | 129.11 | 97.25 | 105.44 | 111.95 |
| $EuBr_3$ | 5.21 | 20.65 | 31.61 | 93.38 | 119.93 | 128.82 | 95.83 | 104.48 | 111.22 |
| $GdBr_3$ | 4.80 | 18.58 | 28.49 | 95.32 | 119.01 | 127.04 | 97.51 | 105.23 | 111.25 |
| $TbBr_3$ | 4.79 | 18.89 | 29.47 | 96.16 | 120.27 | 128.84 | 98.35 | 106.17 | 112.39 |
| $DyBr_3$ | 4.79 | 18.63 | 28.85 | 96.55 | 120.31 | 128.59 | 98.74 | 106.47 | 112.55 |
| $HoBr_3$ | 4.78 | 18.57 | 28.58 | 96.55 | 120.24 | 128.35 | 98.74 | 106.46 | 112.49 |
| $ErBr_3$ | 4.78 | 18.56 | 28.49 | 96.41 | 120.09 | 128.15 | 98.59 | 106.31 | 111.94 |
| $TmBr_3$ | 4.78 | 18.55 | 28.52 | 95.86 | 119.54 | 127.62 | 98.05 | 105.76 | 111.79 |
| $YbBr_3$ | 4.77 | 18.55 | 28.46 | 94.88 | 118.56 | 126.59 | 97.07 | 104.78 | 110.80 |
| $LuBr_3$ | 4.77 | 18.54 | 28.45 | 90.63 | 114.30 | 122.34 | 92.82 | 100.53 | 106.55 |
| Iodides | | | | | | | | | |
| $LaI_3$ | 5.10 | 18.97 | 28.89 | 98.64 | 122.51 | 130.56 | 100.86 | 108.65 | 114.70 |
| $CeI_3$ | 5.10 | 19.30 | 29.76 | 102.15 | 126.45 | 134.94 | 104.37 | 112.26 | 118.50 |
| $PrI_3$ | 5.10 | 19.33 | 30.02 | 102.83 | 127.18 | 135.85 | 105.05 | 112.95 | 119.23 |
| $NdI_3$ | 5.09 | 19.42 | 30.13 | 102.96 | 127.44 | 136.12 | 105.19 | 113.12 | 119.44 |
| $PmI_3$ | 5.10 | 19.63 | 30.46 | 102.71 | 127.54 | 136.31 | 104.96 | 113.00 | 119.41 |
| $SmI_3$ | 5.11 | 20.01 | 30.95 | 101.83 | 127.28 | 136.16 | 104.13 | 112.39 | 118.93 |
| $EuI_3$ | 5.50 | 21.01 | 31.99 | 100.34 | 127.07 | 135.97 | 102.82 | 111.54 | 118.30 |
| $GdI_3$ | 5.08 | 18.95 | 28.87 | 102.21 | 126.08 | 134.12 | 104.43 | 112.21 | 118.26 |
| $TbI_3$ | 5.08 | 19.26 | 29.86 | 103.03 | 127.32 | 135.90 | 105.25 | 113.13 | 119.38 |
| $DyI_3$ | 5.08 | 19.00 | 29.23 | 103.38 | 127.31 | 135.60 | 105.59 | 113.39 | 119.50 |
| $HoI_3$ | 5.07 | 18.94 | 28.96 | 103.38 | 127.25 | 135.37 | 105.59 | 113.38 | 119.44 |
| $ErI_3$ | 5.07 | 18.93 | 28.88 | 103.16 | 127.03 | 135.10 | 105.38 | 113.16 | 119.22 |
| $TmI_3$ | 5.07 | 18.93 | 28.91 | 102.73 | 126.59 | 134.68 | 104.95 | 112.73 | 118.79 |
| $YbI_3$ | 5.06 | 18.92 | 28.84 | 101.61 | 125.46 | 133.51 | 103.82 | 111.60 | 117.65 |
| $LuI_3$ | 5.06 | 18.92 | 28.84 | 97.46 | 121.32 | 129.37 | 99.68 | 107.46 | 113.51 |

[a] Summary table. Functions tabulated at 100 K increments in the range 298.15-2000 K are given in the supplementary material.

Table III. Estimation of Uncertainties at 2000 K

| | $LnF_3$ | $LnCl_3$ | $LnBr_3$ | $LnI_3$ |
|---|---|---|---|---|
| | $\delta(H°_T - H°_{298.15})$, kcal | | | |
| $d$(Ln–X) ± 0.1 Å | 0 | 0 | 0 | 0 |
| $\nu_1 \pm 20$ cm$^{-1}$ | 0.02 | 0.02 | 0.03 | 0.02 |
| $\nu_2 \pm 10$ cm$^{-1}$ | 0.02 | 0.02 | 0.02 | 0.01 |
| $\nu_3 \pm 20$ cm$^{-1}$ | 0.05 | 0.06 | 0.06 | 0.05 |
| $\nu_4 \pm 10$ cm$^{-1}$ | 0.03 | 0.03 | 0.03 | 0.04 |
| Electronic | 0.20 | 0.20 | 0.20 | 0.20 |
| Total | 0.32 | 0.33 | 0.34 | 0.32 |
| | $\nu S°_T$ (cal mol$^{-1}$ K$^{-1}$) | | | |
| $d$(Ln–X) ± 0.1 Å | 0.25 | 0.23 | 0.20 | 0.20 |
| $\nu_1 \pm 20$ cm$^{-1}$ | 0.07 | 0.12 | 0.15 | 0.20 |
| $\nu_2 \pm 10$ cm$^{-1}$ | 0.22 | 0.35 | 0.47 | 0.59 |
| $\nu_3 \pm 20$ cm$^{-1}$ | 0.14 | 0.24 | 0.30 | 0.38 |
| $\nu_4 \pm 10$ cm$^{-1}$ | 0.31 | 0.49 | 0.62 | 0.87 |
| Electronic | 0.25 | 0.25 | 0.25 | 0.25 |
| Total | 1.24 | 1.68 | 1.99 | 2.49 |
| | $\delta[-(G°_T - H°_{298.15})/T]$, cal mol$^{-1}$ K$^{-1}$ | | | |
| $d$(Ln–X) ± 0.1 Å | 0.26 | 0.22 | 0.20 | 0.20 |
| $\nu_1 \pm 20$ cm$^{-1}$ | 0.06 | 0.11 | 0.14 | 0.20 |
| $\nu_2 \pm 10$ cm$^{-1}$ | 0.22 | 0.35 | 0.47 | 0.59 |
| $\nu_3 \pm 20$ cm$^{-1}$ | 0.12 | 0.23 | 0.29 | 0.37 |
| $\nu_4 \pm 10$ cm$^{-1}$ | 0.31 | 0.51 | 0.62 | 0.87 |
| Electronic | 0.15 | 0.15 | 0.15 | 0.15 |
| Total | 1.12 | 1.57 | 1.87 | 2.38 |

## Electron Levels

Energy level data for $PrI_3$ have been reported in a study of the fluorescence spectrum of matrix-isolated molecules (*3*). The low-lying levels are only about 10% lower in energy than the corresponding levels for the free $Pr^{3+}$ ion or for $Pr^{3+}$ in $LaCl_3$ crystals (*4*), but it is not clear whether levels for other lanthanides should be reduced in the same proportion. Earlier reports (*7*) on $LnBr_3$ and $LnI_3$ (Ln = Pr, Nd, Er, Tm) gaseous molecules gave energy levels very nearly equal to those observed in crystals or free ions. Because of this uncertainty and the advantages of a uniform treatment of all the molecules, the energy levels used in the QEL program (except for $PmX_3$) were the values given by Dieke (*4*) for $Ln^{3+}$ ions in $LaCl_3$ crystals. The levels for $Pm^{3+}$ were taken from Carnall et al. (*2*). Only levels below about 5000 cm$^{-1}$ were included in the calculation since the higher levels have a negligible effect on the thermodynamic functions in the temperature range of interest.

## Results

A summary of the calculated thermodynamic functions of the $LnX_3$ molecules is presented in Table II. A more detailed tabulation is available in the supplementary material. The data for $LaX_3$ molecules are consistently greater than those given earlier by Krasnov and Danilova (*14*). The possibility that the earlier data may be too low has been discussed by Gupta (*8*).

## Uncertainties

In order to assess the effects of uncertainties in the molecular parameters on the results of the calculations, the STRETCH-TDF program was run, changing in turn the internuclear distance by 0.1 Å, the stretching frequencies by 20 cm$^{-1}$, and the bending frequencies by 10 cm$^{-1}$. In addition, the uncertainty in the electronic levels introduces corresponding uncertainties in the thermodynamic functions. All these are summarized at 2000 K in Table III. The uncertainties in electronic levels are most serious at the higher temperatures. If the levels are lower in general in the gaseous molecules than they are in crystals, then the calculated electronic contributions are too small, but this error is compensated, to a degree, in the entropy and free energy function by the slight error introduced in assuming the molecules to be planar.

For temperatures between 1000 and 2000 K, the uncertainties in the tabulated functions may be taken to be those given as $\delta(H°_T - H°_{298.15})$, $\delta S°_T$, and $\delta(-[(G°_T - H°_{298.15})/T])$ in Table III.

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**Supplementary Material Available:** Tables S1-S60, $(H°_T - H°_{298.15})$, $S°_T$, and $-(G°_T - H°_{298.15})/T$ tabulated at 100° intervals to 2000 K for $LnX_3$ (ideal gas) (X = F, Cl, Br, I) (60 pages). Ordering information is given on any current masthead page.

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