Supporting information for:

A comparison of methods for the estimation of the enthalpy of formation of rare earth compounds

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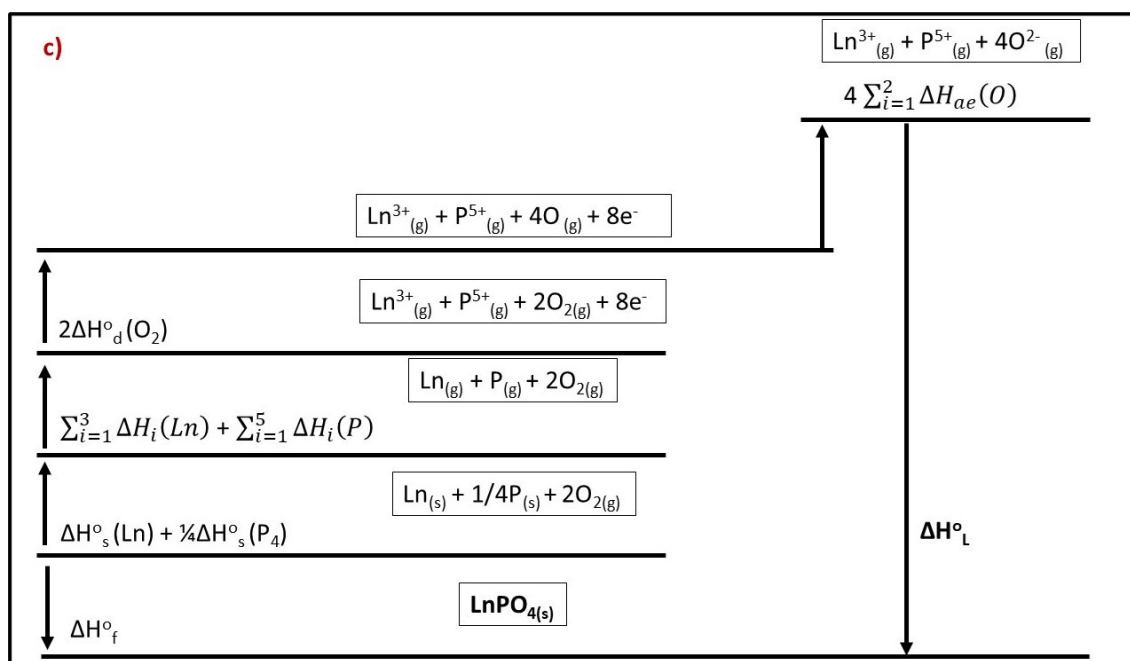E-mail: s.sanchezsegado@leeds.ac.uk sergio.segado@upct.es
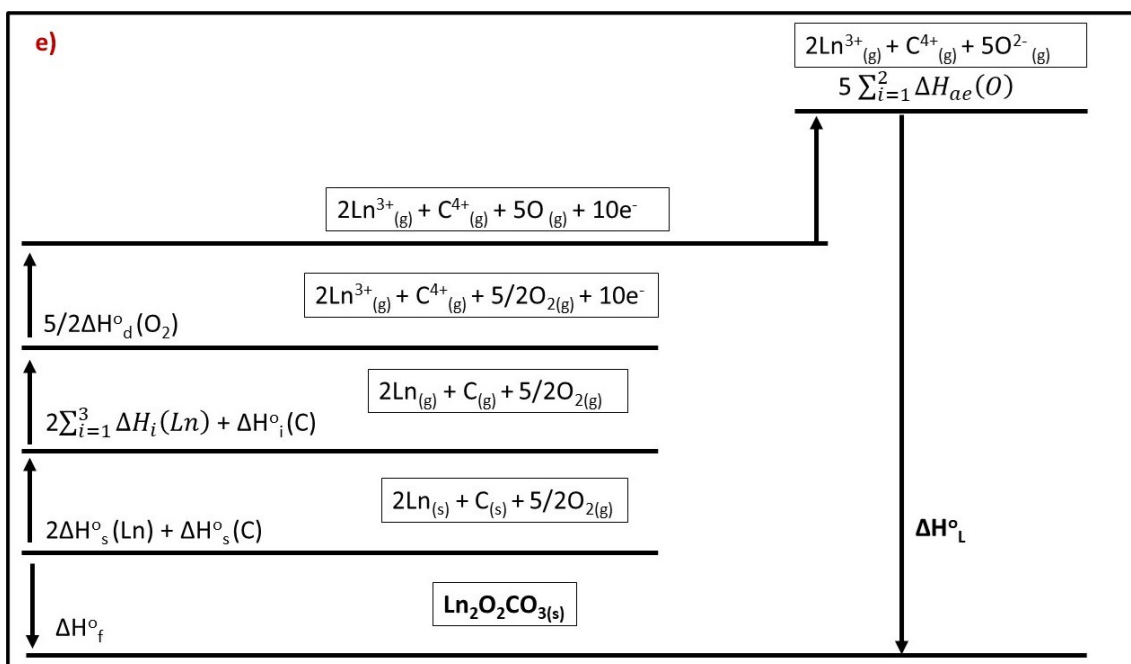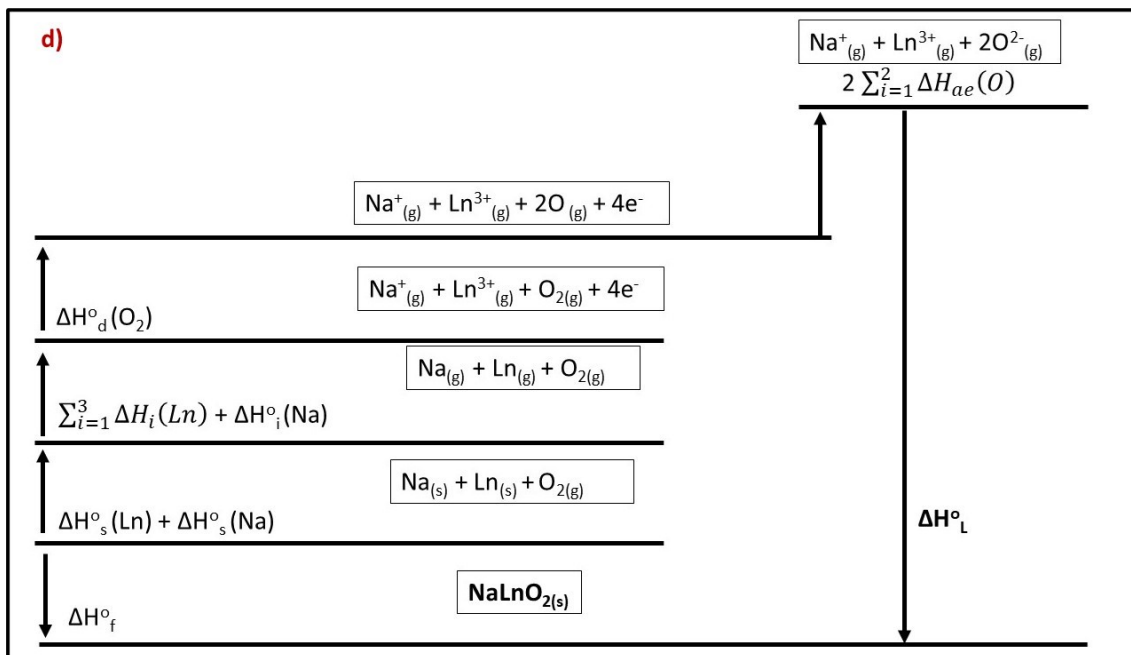
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a)

$Ln^{3+}_{(g)} + 3Cl_{(g)} + 3e^-$

$\frac{3}{2}\Delta H°_d(Cl_2)$

$Ln^{3+}_{(g)} + 3/2Cl_{2(g)} + 3e^-$

$Ln^{3+}_{(g)} + 3Cl^-_{(g)}$

$3\Delta H°_{ae}(Cl)$

$\sum_{i=1}^{3}\Delta H_i(Ln)$

$Ln_{(g)} + 3/2Cl_{2(g)}$

$\Delta H°_s(Ln)$

$Ln_{(s)} + 3/2Cl_{2(g)}$

$\Delta H°_L$

$\Delta H°_f$

$LnCl_{3(s)}$

b)

$Ln^{3+}_{(g)} + O^{2-}_{(g)} + Cl^-_{(g)}$

$\Delta H°_{ae}(Cl) + \sum_{i=1}^{2}\Delta H_{ae}(O)$

$Ln^{3+}_{(g)} + O_{(g)} + Cl_{(g)} + 3e^-$

$\frac{1}{2}\Delta H°_d(Cl_2) + \frac{1}{2}\Delta H°_d(O_2)$

$Ln^{3+}_{(g)} + 1/2O_{2(g)} + 1/2Cl_{2(g)} + 3e^-$

$\sum_{i=1}^{3}\Delta H_i(Ln)$

$Ln_{(g)} + 1/2O_{2(g)} + 1/2Cl_{2(g)}$

$\Delta H°_s(Ln)$

$Ln_{(s)} + 1/2O_{2(g)} + 1/2Cl_{2(g)}$

$\Delta H°_L$

$\Delta H°_f$

$LnOCl_{(s)}$

c)

$Ln^{3+}_{(g)} + P^{5+}_{(g)} + 4O^{2-}_{(g)}$

$4\sum_{i=1}^{2}\Delta H_{ae}(O)$

$Ln^{3+}_{(g)} + P^{5+}_{(g)} + 4O_{(g)} + 8e^-$

$2\Delta H°_d(O_2)$

$Ln^{3+}_{(g)} + P^{5+}_{(g)} + 2O_{2(g)} + 8e^-$

$\sum_{i=1}^{3}\Delta H_i(Ln) + \sum_{i=1}^{5}\Delta H_i(P)$

$Ln_{(g)} + P_{(g)} + 2O_{2(g)}$

$\Delta H°_s(Ln) + \frac{1}{4}\Delta H°_s(P_4)$

$Ln_{(s)} + 1/4P_{(s)} + 2O_{2(g)}$

$\Delta H°_L$

$\Delta H°_f$

$LnPO_{4(s)}$

d)

$Na^{+}_{(g)} + Ln^{3+}_{(g)} + 2O^{2-}_{(g)}$

$2 \sum_{i=1}^{2} \Delta H_{ae}(O)$

$Na^{+}_{(g)} + Ln^{3+}_{(g)} + 2O_{(g)} + 4e^{-}$

$Na^{+}_{(g)} + Ln^{3+}_{(g)} + O_{2(g)} + 4e^{-}$

$\Delta H^{\circ}_{d}(O_2)$

$Na_{(g)} + Ln_{(g)} + O_{2(g)}$

$\sum_{i=1}^{3} \Delta H_{i}(Ln) + \Delta H^{\circ}_{i}(Na)$

$Na_{(s)} + Ln_{(s)} + O_{2(g)}$

$\Delta H^{\circ}_{s}(Ln) + \Delta H^{\circ}_{s}(Na)$

ΔH°_{L}

$NaLnO_{2(s)}$

ΔH°_{f}

e)

$2Ln^{3+}_{(g)} + C^{4+}_{(g)} + 5O^{2-}_{(g)}$

$5 \sum_{i=1}^{2} \Delta H_{ae}(O)$

$2Ln^{3+}_{(g)} + C^{4+}_{(g)} + 5O_{(g)} + 10e^{-}$

$2Ln^{3+}_{(g)} + C^{4+}_{(g)} + 5/2O_{2(g)} + 10e^{-}$

$5/2\Delta H^{\circ}_{d}(O_2)$

$2Ln_{(g)} + C_{(g)} + 5/2O_{2(g)}$

$2\sum_{i=1}^{3} \Delta H_{i}(Ln) + \Delta H^{\circ}_{i}(C)$

$2Ln_{(s)} + C_{(s)} + 5/2O_{2(g)}$

$2\Delta H^{\circ}_{s}(Ln) + \Delta H^{\circ}_{s}(C)$

ΔH°_{L}

$Ln_2O_2CO_{3(s)}$

ΔH°_{f}

f)

$2Ln^{3+}_{(g)} + S^{2-}_{(g)} + 2O^{2-}_{(g)}$

$2\sum_{i=1}^{2}\Delta H_{ae}(O) + \sum_{i=1}^{2}\Delta H_{ae}(S)$

$2Ln^{3+}_{(g)} + S_{(g)} + 2O_{(g)} + 6e^{-}$

$2Ln^{3+}_{(g)} + S_{(g)} + O_{2(g)} + 6e^{-}$

$\Delta H^{\circ}_{d}(O_2)$

$2Ln_{(g)} + S_{(g)} + O_{2(g)}$

$2\sum_{i=1}^{3}\Delta H_i(Ln)$

$2Ln_{(s)} + S_{(s)} + O_{2(g)}$

$2\Delta H^{\circ}_{s}(Ln) + \Delta H^{\circ}_{s}(S)$

ΔH°_{L}

$\mathbf{Ln_2O_2S_{(s)}}$

ΔH°_{f}

Figure S1. Thermodynamic cycles employed to calculate the enthalpy of formation of a) $LnCl_3$, b) $LnOCl$, c) $LnPO_4$, d) $NaLnO_2$, e) $Ln_2O_2CO_3$ and f) Ln_2O_2S. Where ΔH°_{s}, ΔH°_{d}, ΔH°_{i}, ΔH°_{ae} are the standard enthalpies of sublimation, dissociation, ionization and electronic affinity respectively.

Table S1. Madelung Energies calculated using EUGEN code ($E_{Madelung}$), estimated lattice potential energies (U_{POT}), and lattice potential energies (U_{POT}) determined from experimental data taken from ref. 67. All values are in kJ mol^{-1}.

Compound	$E_{Madelung}$ calculated using EUGEN	U_{POT} (this work)	U_{POT} [67]
$LaCl_3$	4343	4343	4263
$CeCl_3$	4373	4373	4348
Li_2S	2830	2405	2464
Rb_2S	2065	1756	1949
Ti_2O_3	17368	14763	14149
Cr_2O_3	17096	14532	14957

Table S2. Estimated values of the enthalpy of formation (ΔH_f^0) (kJ mol^{-1}) for the rare earth compounds considered in this study using Mostafa's group contribution method

Ln	LnCl$_3$	LnOCl	LnPO$_4$	Ln$_2$O$_2$CO$_3$	Ln$_2$O$_2$S	NaLnO$_2$
La	-1050.4±32.3	-986.5±31.1	-1891.6±35.0	-2351.9±67.0	-1626.6±87.2	-1283.0±40.6
Ce	-1072.9±72.6	-1009.0±71.4	-1914.1±75.2	-2396.9±147.5	-1671.6±167.6	-1305.5±80.9
Pr	-1058.4±34.4	-994.4±33.2	-1899.5±37.1	-2367.8±71.2	-1642.5±91.4	-1291.0±42.7
Nd	-1055.8±31.5	-991.8±30.3	-1896.9±34.2	-2362.5±65.4	-1637.2±85.5	-1288.4±39.8
Pm						
Sm	-1038.8±36.1	-974.9±34.9	-1879.9±38.7	-2328.6±74.6	-1603.4±94.7	-1271.4±44.4
Eu	-955.5±36.1	-891.6±34.9	-1796.7±38.7	-2162.1±74.6	-1436.8±94.7	-1188.1±44.4
Gd	-1026.5±35.0	-962.6±33.8	-1867.6±37.6	-2304.0±72.3	-1578.8±92.4	-1259.1±43.3
Tb	-1047.0±37.8	-983.1±36.6	-1888.1±40.4	-2345.0±77.9	-1619.7±98.0	-1279.6±46.1
Dy	-1032.9±36.9	-968.9±35.7	-1874.0±39.5	-2316.8±76.1	-1591.5±96.2	-1265.5±45.2
Ho	-1047.9±36.2	-984.0±35.0	-1889.0±38.8	-2346.8±74.7	-1621.6±94.8	-1280.5±44.5
Er	-1045.4±36.1	-981.4±34.9	-1886.5±38.7	-2341.8±74.6	-1616.5±94.7	-1278.0±44.4
Tm	-1019.2±37.8	-955.3±36.6	-1860.4±40.4	-2289.5±77.9	-1564.2±98.1	-1251.8±46.1
Yb	-1005.6±37.8	-941.6±36.6	-1846.7±40.4	-2262.2±77.9	-1536.9±98.0	-1238.2±46.1
Lu	-1045.0±37.8	-981.0±36.6	-1886.1±40.4	-2341.0±77.9	-1615.7±98.0	-1277.6±46.1

Table S3. Estimated values of the enthalpy of formation (ΔH_f^0) (kJ mol^{-1}) for the rare earth compounds considered in this study using the volume based thermodynamics method

| Ln	LnCl$_3$	LnOCl	LnPO$_4$	Ln$_2$O$_2$CO$_3$	Ln$_2$O$_2$S	NaLnO$_2$
La	-661.8±4.0	-744.3±13.3	-1879.6±81.7	781.4±11.0	-1944.1±14.5	-882.9±4.2
Ce	-642.3±12.9	-748.1±19.5	-1967.7±56.3		-2003.7±29.2	-923.9±11.6
Pr	-599.5±32.4	-754.9±23.0	-2098.4±70.8	682.0±22.5	-2003.1±25.9	-900.7±9.9
Nd	-582.3±41.9	-766.7±47.4	-2209.0±167.6	547.0±86.7		-891.5±42.0
Pm						
Sm	-560.8±37.4	-742.2±44.9	-2334.6±93.3	396.1±77.4		-953.8±37.3
Eu	-434.9±17.5	-623.0±22.5	-2370.0±22.8	701.3±23.5		-847.7±10.4
Gd	-511.3±19.1	-716.3±30.9	-2322.0±60.5	242.8±41.2		-932.6±19.3
Tb		-707.9±27.4	-2162.5±99.2		-2037.2±47.1	-1014.4±20.5
Dy	-125.2±37.6	-719.7±47.8	-2061.2±81.3	414.9±78.1	-2086.1±81.6	-1024.5±37.7
Ho	-106.2±19.9		-2161.1±89.2			-961.7±20.1
Er	-97.8±18.7		-2227.0±90.7	379.4±40.4		-981.8±18.8
Tm	-80.7±18.3		-2282.3±69.4			-960.1±18.4
Yb			-2341.1±45.9			
Lu	-46.4±42.1		-2350.5±70.3			-953.8±42.2

S4. Example calculations for LaPO$_4$

S4.1. Application of Mostafa et al. group contribution method.

Table S4. Contribution of each group to the enthalpy of formation

Group	Contribution kJ mol^{-1}
La^{3+}	-694.1±18.1
PO$_4$$^{3-}$	-1197.5±16.8

Calculation of the enthalpy of formation

LaPO$_4$ → La^{3+} + PO$_4$$^{3-}$ → -694.1±18.1 + (-1197.5) ±16.8 = -1891.6±35.0 kJ mol^{-1}
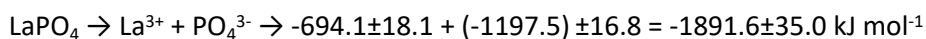
S4.2. Application of the VBT method for $LaPO_4$.

S4.2.1. Calculation of the molecular volume (V_m) (For a more detailed description, please read reference 1)

$$V_m = \frac{V_{cell}}{Z} = \frac{304.76 \ \mathring{A}^3}{4} = 76.2 \ \pm 0.3 \ \mathring{A}^3$$

Where V_{cell} is the crystal unit cell volume and Z is the number of formula units contained within the crystallographic unit cell

S4.2.2. Calculation of the ionic strength factor

$$I = \frac{1}{2}\sum n_i z_i^2 = \frac{1}{2}(3^2 + 5^2 + (4*(-2^2))) = \frac{1}{2}(50) = 25$$

S4.2.3. Calculation of the lattice enthalpy (ΔH_L)

$$U_{POT} = AI\left(\frac{2I}{V_m}\right)^{\frac{1}{3}} = 121.4 * 25 * \left(\frac{2*25}{0.076}\right)^{\frac{1}{3}} = 26315.1 \ kJmol^{-1}$$

$$-\Delta H_L = U_{POT} + \sum_i^{\substack{ions \ in \\ formula \ unit}} s_i\left(\frac{c_i}{2} - 2\right)RT = 26315.1 - 7.5$$
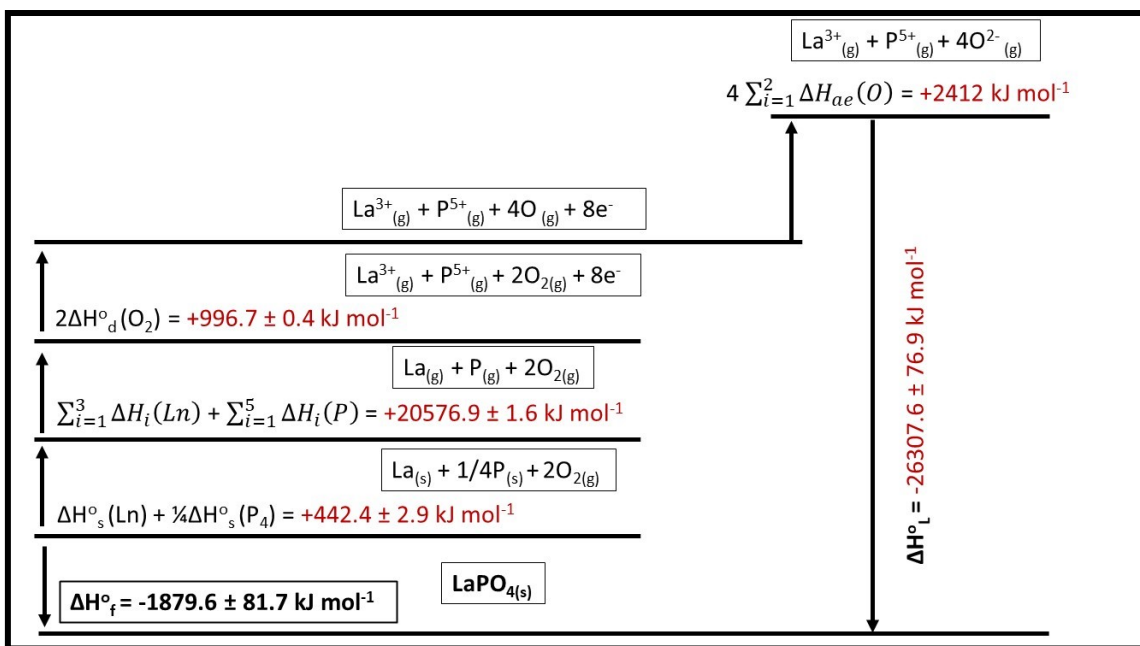
$$\Delta H_L = -26307.6 \ \pm 76.9 \ kJmol^{-1}$$

S4.2.3. Born-Haber-Fajans cycle

Figure S2. Born-Haber-Fajans cycle for LaPO$_4$