REVIEW OF RESEARCH

EMPIRICAL SIMULATION FOR HEATS OF FORMATION TRENDS IN RARE EARTH COMPOUNDS

Shivraj Bhardwaj

Associate Professor, Department of Physics , B.S.A. College Mathura , Dr. B.R. Ambedkar University Agra.

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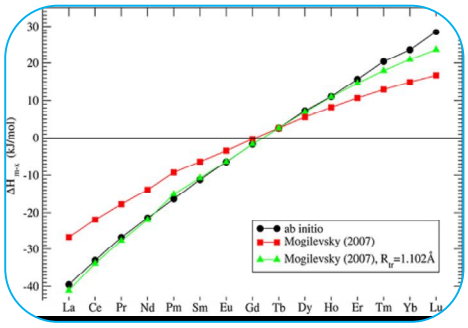

ABSTRACT:

In this paper we have evolved an empirical simulation method for the heats of formation determination for a variety of rare earth Pnictides and sesquioxides. The method proposed for the heats of formation studies is quite simple and applicable for a large number of compounds. The results obtained by applying this simulation method, it is found that there is a very close agreement with the experimental data reported so far.

KEYWORDS: *Heats of formation, electronegativity, Pnictides, sesquioxides.*

INTRODUCTION:

During last two decades there has been a substantial interest in the development and discovery of new energetic compounds which include high explosives and propellants and a new term has assigned to these materials known as high energy density materials (*HEDMs*) [S. Michael et.al. 2016, Konings Rudy JM et al. 2008, Petit L., et al 2016, Grosse Frank, et al 2010]. This class of *HEDMs* categorically include compounds that have detonation pressure greater than or equal to 40.0 GPa, detonation velocities greater than or equal to 9.0 Km/s and densities greater than or equal to 1.9 gm/cm^3. The term has become of greater importance because of increasing environmental concern, call for more effective ways of predicting performance of *HEDMs* is required. The main interest of this research paper is to evolve a more general and relatively rapid method for the prediction / calculation of heats of formation values more accurately and close to the experimental data.

COMPUTATIONAL METHOD

There has been several theoretical / experimental efforts in order to evaluate heats of formation values for different type of materials. It is one of the several important parameter used to assess the performance of energetic materials [Eyring Le Roy et al. 2002, Dere A, 2018, Springer 2001]. In practice most theoretical approaches calculate gas-phase heat of formation values. Solid or liquid phase values are then calculated by subtracting heat of sublimation or heat of vaporization values, respectively, from the gas-phase value. Heats of formation is an important thermo dynamical property of the materials and several researchers [William G. 1978, Rezukhina T.N., 1974, James A., 1977, Sappegin A.M., 1987] have discussed about it in terms of electro-negativity difference of the atoms constituting the system. According to Pauling [Pauling L. 1960] the following relation gives the energy of bond formation between atoms A and B.

$$D_{AB} = 1/2[D(A-A) + D(B-B) + 23\sum_{A\ B}(X - X)] \quad (1.1)$$

Where $D(A-B)$, $D(A-A)$ and $D(B-B)$ are the energies of heteropolar bond $A-B$ and homopolar bond $A-A$ and $B-B$ respectively. X_A and X_B are electro-negativities of atoms A and B.

The second term on the right hand side of the equation (1.1) gives the value of standard heats of formation as given below :

$$\Delta H = 23\sum(X_A - X_B)^2 \quad (1.2)$$

Where $\sum$ is taken over all the bonds in the compound. Phillips [Phillips J.C. 1983, Phillips

J.C. 1984] investigated the heats of formation of few compound semi-conductors and proposed modified relation given as under -

$$\Delta H = 2/3 \times 23 \sum_{A\ B}(X - X)^2 \quad (1.3)$$

According to Pauling the following relation gives the fractional ionic character or ionicity of a heteropolar bond between the atoms A and B.

$$f_i = 1 - \exp\left|-\frac{(X_A - X_B)^2}{4}\right| \quad (1.4)$$

Adolf M. Mulokozi [Mulokozi A.M., 1980] has studied the heats of formation of rare earth compounds and proposed a relation for heats of formation in terms of inter atomic

distance d_{R-X}. According to him, the following relation may express the heats of formation,

$$-\Delta H_f = Ae(\Delta X)^2 / d_{R-X} + C \quad (1.5)$$

In a series of rare earth compounds (Where X does not vary) the partial charge ΔX will be constant (depending upon the electro negativity difference between the atoms R and X), e and A elementary charge, which are Constants. Where C is covalent contribution.

According to Adolf M. Mulokozi the value of $Ae(\Delta X)^2$ and C depends upon cation.

We have drawn curves between heats of formation and lattice parameter, where from it is observed that the heats of formation trends in rare earth compounds increases with decreasing values of lattice parameter.

In the view of above discussion and the trends observed in the curves plotted $-\Delta X_f Vs\ 1/a$, it is quite obvious that the heats of formation of a material is inversely related to lattice parameter. Thus the relation (1.5) can be modified in the following form,

$$-\Delta H_f = C / a \qquad (1.6)$$

Where C is an adjustable parameter. The value of C used in relation (1.6) are presented in following table 1.1 which are evaluated from the curves drawn between heats of formation and lattice constant of rare earth pnictides and sesquioxides.

Table 5.2

Compounds	RE_2O_3	*REN*	*REP*	*REAs*	*RESb*
C	4750	377	433	431	342

(RE = rare - earth metal)

The proposed modified empirical relation has been applied to evaluate heats of formation values for rare earth pnictides (N, P, As, Sb) and rare-earth sesquioxides (RE2O3). The values so obtained are presented in the following table 1.3 and 1.4 and compared with the experimental & theoretical data reported so far.

Table 5.3

Heats of formation of rare earth pnictides

Compound	$a\left(\overset{0}{A}\right)$	$-\Delta H_f$ ref. [Hanks R. 1969]	$-\Delta H_f$ ref. [Zhuze V.P. 1989]	$-\Delta H_f$ this work
Lan	5.305[a]	71.07[d]	72.0[b]	71.07
—	— [c]	— [a]	— [b]	—
PrN	5.165 [c]	73.00[a]	NA	73.00
NdN	5.151[a]	73.20[d]	73.0[b]	73.20
SmN	5.048 [c]	74.69[a]	NA	74.68
GdN	4.999 [a]	75.42[a]	NA	75.42
—	— [c]	— [a]	—	—
DyN	4.903 [c]	76.87[a]	NA	76.86
HoN	4.874 [a]	77.36[a]	NA	77.35
ErN	4.839 [a]	77.92[a]	NA	77.91
TmN	4.809[a]	78.40[d]	NA	78.40
YbN	4.783 [c]	78.79[a]	NA	78.79
—	— [a]	— [a]	— [b]	—
LaP	6.025[e]	NA	72.2[b]	71.90
CeP	5.942 [f]	NA	NA	72.87
PrP	5.903 [f]	NA	NA	73.33
NdP	5.863 [f]	NA	NA	73.85
SmP	5.780[f]	NA	NA	74.91
GdP	5.723[k]	NA	NA	75.66

TbP	5.685 [f]	NA	NA	76.17
HoP	5.627 [f]	NA	NA	76.95
DyP	5.643 [b]	NA	NA	76.73
ErP	5.599 [f]	NA	NA	77.34
TmP	5.572 [f]	NA	NA	77.71
YbP	5.550 [f]	NA	NA	78.02
LaAs	6.158 [c]	64.2	73.0	69.99
CeAs	6.076 [c]	68.4	68.9	70.94
PrAs	6.026 [c]	70.4	73.4	71.52
NdAs	5.987 [c]	71.6	72.7	71.99
SmAs	5.914 [c]	73.6	72.0	72.88
GdAs	5.863 [c]	75.0	74.4	73.51
TbAs	5.821 [c]	76.2	75.0	74.04
DyAs	5.793 [c]	75.4	78.1	74.40
HoAs	5.766 [c]	75.5	72.2	74.75
ErAs	5.741 [c]	75.7	75.6	75.10
TmAs	5.716 [c]	75.8	72.8	75.40
YbAs	5.690 [c]	NA	NA	75.75
LuAs	5.679 [c]	76.0	75.2	75.89
LaSb	6.448 [g]	NA	52.0 [a]	53.04
CeSb	6.412 [g]	NA	NA	53.34
PrSb	6.366 [g]	NA	NA	53.72
NdSb	6.322 [g]	NA	58.8 [g]	54.10
	[e]			
GdSb	6.217 [k]	NA	NA	55.01
TbSb	6.170 [b]	NA	NA	55.42
DySb	6.140 [b]	NA	NA	55.70
HoSb	6.120 [b]	NA	NA	55.88
	[b]			
TmSb	6.080 [b]	NA	NA	56.25
YbSb	6.067 [b]	NA	NA	56.37

(RE = rare - earth metal), (NA = Not Available)

Table 5.3

Heats of formation of rare earth pnictides

Compound	$a\begin{pmatrix}0\\A\end{pmatrix}$	$-\Delta H_f$ ref. [Hanks R. 1969]	$-\Delta H_f$ ref. [Zhuze V.P. 1989]	$-\Delta H_f$ this work
La_2O_3	11.362	427.1	428.57±0.19	418.06
Ce_2O_3	11.163	NA	435.00±6.00	425.51
Pr_2O_3	11.159	NA	436.80±1.60	425.66
Nd_2O_3	11.078	428.5	432.15±0.24	428.78
Sm_2O_3	10.934	432.2	433.89±0.48	434.43
Eu_2O_3	10.867	NA	NA	437.10
Gd_2O_3	10.818	430.9	433.94±0.86	439.08
Tb_2O_3	10.728	NA	436.80±2.00	442.77
Dy_2O_3	10.667	443.1	445.84±0.93	445.30
Ho_2O_3	10.606	447.2	449.55±1.15	447.86
Er_2O_3	10.550	451.6	453.59±0.49	450.24
Tm_2O_3	10.487	448.6	451.40±1.40	452.94
Yb_2O_3	10.434	432.0	433.68±0.53	455.24
Lu_2O_3	10.394	447.3	452.80±3.30	456.99

CONCLUSION

Heats of formation values of a variety of rare earth pnicitides and sesquioxides have been evaluated by using a very simple and generalised relation which depends only on the lattice constant and an adjustable constant C depending upon the crystal structure of the compounds. From the table it is obvious that the values evaluated by the proposed empirical simulation method are in close agreement with the reported experimental data which proves the validity of the approach adopted for the heats of formation determination of a large number of rare earth compounds.

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Shivraj Bhardwaj
Associate Professor, Department of Physics , B.S.A. College Mathura , Dr. B.R. Ambedkar University Agra.