Are High Heats of Atomization for Many Oxides and Fluorides of Z above 37 due to Enhanced Correlation Energy?

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Abstract. Heats of atomization $H_a$ (per atom) are compared for 28 diatomic oxides, 14 diatomic fluorides, 26 solid and 2 polyatomic gaseous oxides, 9 solid and 5 polyatomic gaseous fluorides. There is no universal trend toward lower $H_a$ with increasing $Z$ in a column of the Periodic Table; d-group, post-d-group, and partly filled d-valence orbitals, especially in the begin-ning of the transition groups. The molec-
ular structure of M(II) oxide (melting at 3500 K and boiling above 4700 K) has the highest known value, 8.0 eV. The very large majority of compounds have $H_a$ below 4 eV. Among organic compounds, highly carbon-rich molecules (few 'single' bonds) show higher $H_a$, such as HCCCH4.26 and its trimer benzene 4.77 eV. It was pointed out [1] that only 14 diatomic molecules are known to have $H_a$ above 4 eV (or at least within a narrow interval of experimental uncertainty), that is N2 (4.90), CN (3.99), BF (3.97), and 11 monoxides among those given in the Table. Their order of $H_a$

$$
\text{CO} > \text{N}_2 > \text{ThO} > \text{BO} > \text{HF} > \text{SiO} > \text{LaO} > \text{TaO} > \text{CeO} > \text{ZrO} > \text{NbO} > \text{CN} > \text{BF} > \text{UO}
$$

emphasizes that the chemistry of diatoms studied around 4000 K (in sunspots and in spectra of M- and S-type stars) differs entirely from inorganic chemistry in solids, liquids, and solution. Not a single oxidation state M(II) or B(II) that one might infer from series (I) occurs in non-metallic, non-catenated inorganic solids [2],[3]. The increasing importance of entropy at high T pays a premium for the last step before mononuclearity.

In this note, solid and gaseous binary compounds $M_X$ are selected for comparison of unusually high $H_a$ with some, more typical values. The heat of formation from the elements in their standard state, and $H_a$ of M and X are taken from comprehensive compilations [4],[5]. If the vapour of an element contains large amounts of oligomers (Si, P, Ge, Sn, and even Au and Li), $H_a$ may be considerably larger than the heat of evaporation.

$$
M_X \rightarrow A \text{M}^{\text{stand}} + B \text{X}^{\text{stand}} \rightarrow A \text{M}^0 + B \text{X}^0
$$

(2)

$$
H_a = \{(-\text{heat of formation}) + A \text{H}_a (M) \}
$$

(3)

where $M^0$ and $X^0$ indicate neutral gaseous atoms (in contrast to $L_i^*$ and $F^*$). It is evident that $H_a$ of $M^{\text{stand}}$ and $X^{\text{stand}}$ are not needed, they may be known very imprecisely (or not at all). However, quantum chemistry encouraged this alternative approach. Fortunately, no neutral atoms at sufficient mutual distance decrease their energy by transfer of an electron (not even Cs$^0$ and F$^0$). Most well characterized compounds have negative heat of formation [4] and hence, the first parenthesis of $H_a$ in Eqrn. 2 is usually positive, like the two $H_a$ (M) and $H_a$ (X). One must be aware that even colourless compounds [2] may exist as (LiF)$_2$, (CsI)$_2$, GeO$_2$, W$_2$O$_7$, ..., in vapours [5] (like unexpected ternary compounds such as (ReO$_2$)$_2$Ca, MoO$_2$Ba$_2$, and MoO$_2$Li).

It is a general feeling that both electron-valent bonding and covalency ($c.f.$ $H_a$ > Li$_2$, Na$_2$, or $N_2$ > P$_2$) are stronger in smaller, with a corollary that bond dissociation energies should decrease, when $Z$ increases in a definite column in the Periodic Table. This is not the case in many alkaline-earth compounds. Although hexagonal BeO has $H_a$ 1 eV higher than MgO, the following cubic oxides go through a shallow maximum at CaO and BaO hardly below MgO. The situation is more extreme in rutile-type MgF$_2$ compared to the fluorides CaF$_2$, SrF$_2$, and BaF$_2$, all having $H_a$ 0.4 eV higher. The fluoride-tioxide di-oxides show increasing heats of atomization for increasing unit cell $a_0$ (and concomitant internuclear distances). Although ZrO$_2$ and HfO$_2$ are low-symmetry (monoclinic) compounds, their thermodynamical stability is known to be almost the same as cubic fluorides. Hence, $H_a$ can be arranged in a series terminating roughly where rutile TiO$_2$ is situated. It is also striking that ThF$_2$ > ZrF$_2$ > UF$_2$ show the same order, that UF$_2$ has $H_a$ 70% higher than the other (far less reactive) molecule SF$_6$; that large M$^0$ in La$_2$O$_3$, Nd$_2$O$_3$, and Lu$_2$O$_3$ above Al$_2$O$_3$.

The comparison of solid or gaseous oxides and/or fluorides of a familiar oxidation state (frequently the only known [2],[3]) with high-temperature molecules with oxidation number +2 in MO and +1 in MF is not conceptually evident. However, the trend is that $H_a$ with a given element M are similar in MF and MO (except CF and CO differing by a factor 2). Actually, the diatomic molecules have a plurality of valence orbitals, especially in the beginning of the transition groups. The molecular flame spectra of alkaline-earth MX ($X = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}$) exhibit a groundstate [2] with one electron in a rotationally symmetric orbital (being, e.g. in barium, a mixture of 6s, 6p, 5d, ... in LCAO models), which is filled in the singlet groundstate of MO, and [6] in SeF, YF,
and LaF. Calling this orbital $\sigma$, the $3\Delta$ of TiO is $3d\Delta\sigma$, and $4\Sigma$ of VO $(3d\Delta\sigma)^2$, going through a gradual evolution toward gaseous CuO having a full $3d^9$ but lacking an electron in a $\pi$ orbital localized on oxygen. The situation is more complicated in lanthanide LnO; thus, EuO is a genuine $4f^7$ Ln$^{10}$ oxide, but CeO being $4f^1\sigma^2$, GdO $4f^7\sigma^2$ [7-10] (much like the $\Sigma$ groundstate of MnH, MnF, MnCl, and MnBr being $3d^7\sigma^2$ systems [6]) and (at least) most of the gaseous LnF groundstates $4f^\sigma^2$.

These aspects of diatomics prepare the reader for a surprising demise of 'ligand field' stabilization [11][12]. $H_{S}$ is 0.4 eV lower of solid MnO and NiO than of the isotypic MgO ($a_0 = 443.5, 417.2, 420.3$ pm), almost the same in all three diatomics, and there is a general trend to have the highest $H_{S}$ in the case of no $d$-like electrons (in LCAO models, there is, of course, some $d$-like density [2][12] in the fully occupied, bonding orbitals of appropriate symmetry type), in the 3$d^4$ Ca$^4$, Sc$^{11}$, Ti$^{14}$; 4$d^4$ Sr$^{11}$, Y$^{11}$, Z$^{14}$, before the lanthanides Ba$^{11}$ and La$^{11}$, and in the 5$f$ group Th$^{14}$. This paradox is accentuated by the low $H_{S}$ for Mg$^{11}$ compounds with stronger Madelung potential (due to shorter Mg-X), and forming well-defined aqua ions $[\text{M}[\text{OH}_2]^+\text{r}^2$ similar to Mn$^{11}$, Fe$^{11}$, Co$^{11}$, and Ni$^{11}$.

It is worthwhile to analyze below (what we colloquially and provisionally call) the Barium-Thorium Effect on atomization energies $H_{S}$ Why should the very beginning (if not the penultimate $Z = 56$ and 90) of the 4$f$ and 5$f$ group stabilize compounds against complete atomization? Even the beginning of the 5$d$ group shows indications too in lutetium, hafnium, and tanta- lum (Table). One might think about relativistic effects [13] varying energy-wise roughly as $Z^2$ [17]. It is established [14] that the non-relativistic Hartree-Fock groundstate predicts 1% less binding energy ($600$ eV) than the relativistic wave-function at comparable level of sophistication for $Z = 32$ (germanium) and 10% for $Z = 96$ (curium). The total binding energy of the 90 electrons in the Th-atom is enhanced by $57500$ eV. The relativistic effects [13] are, by far, concentrated on 1s, 2s and 2p$_{1/2}$ inner shells, but a compulsory orthogonalization of valence orbitals acquiring $10^{-5}$ squared amplitude provides more than 0.5 eV each. Pykko [13] argues that the high $H_{S}$ of ThO and UO molecules, and the exclusive behaviour of uranyl chemistry [15-17] hence can be rationalized. Chemi- cally speaking, the most striking result is the difficulty of oxidizing Au$^3$, Ti$^{11}$, Pb$^{11}$, Bi$^{11}$, and Po$^{11}$ which would contain too few electrons as monatomic species.

Our problem is that $H_{S}$ expresses the difference of a novel effect in the compound and in the separated atoms. The metallic elements Mo, Tc, Ru, Rh have $H_{S}$ to 2 eV lower than the homologs W, Re, Os and Ir. This is almost a 'ligand field' tendency [2], octahedral Co$^{11}$, Rh$^{11}$, and Ir$^{11}$ with the same ligands having the anti-bonding tendency $\Delta$ of the two empty, d-like orbitals $[x^2-y^2]$ and $(3z^2-r^2)$ in the ratio 1:1.5:1:8. We know [14][18] that the correlation energy $-E_{corr}$ (indicating the insufficient lowerering of the Hartree-Fock groundstate, where a well-defined electron configuration is presumed) is 1.1 eV in He (and the isoelectronic Li$^+$Be$^{2+}$ ...$2.6$ eV in Be, 1.1 eV in Ne, very close to $20$ eV in Ar, and not far from $40$ eV in Z$^{1+}$ and gaseous Z$^{1+}$ [19]. There is no doubt that $-E_{corr}$, on the average increases by more than the first power of ($Z-1$), and it was $[14][20]$ suggested

$$-E_{corr} = (0.7 \text{ eV}) Z^{1.2}$$
$$E_G = (13.6 \text{ eV}) Z^{2.40}$$

That $-E_{corr}$ is roughly proportional to the square root of the Gáspár expression [21] for the total binding energy $E_T$ of Z electrons in a neutral atom (it runs $3-2\%$ lower than the observed value between $Z = 6$ and 46, and, for relativistic reasons, 6.3-8.3\% too low between $Z = 80$ and 90; if the Rydberg constant is replaced by a free parameter, it might be 14.0 eV). It is not argued [14][18] that $-E_{corr}$ is strictly monotonic with $Z$, but it is likely to be well represented within a factor 1.3.

The correlation energy is very tiny, compared to the total $E_T$ (it is 0.3% for $Z = 10$; 0.09% for $Z = 30$; and 0.04% for $Z = 60$). However, the most interesting aspect for the chemist is the pronounced decrease of the 'squamp' (the squared amplitude of the Hartree-Fock wave-function in the exact non-relativistic Schrödinger solution for the ground state) known [18][19] to be 0.992 in the He-atom, and close to 0.92 in Ne. An (admittedly quite approximate) second-order argument (p. 283 of [20]) equates (1-'squamp') with $-E_{corr}$ ($2I_z$) where $I_z$ is a representative average of the excitation energy $I_z$ of each of the two electrons substituting the ground electron configuration (as shown by Löwdin in 1959 to be the major mechanism of $-E_{corr}$) in a variety of high-energy configurations having optimized squares of the non-diagonal elements of interelectronic repulsion with the Hartree-Fock ground configuration. The estimated 'squamp' values around 0.7 for $Z = 30$ (zinc) and 0.4 for $Z$

<table>
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<tr>
<th>Polyatomic</th>
<th>Diatomic</th>
<th>Polyatomic</th>
<th>Diatomic</th>
<th>Polyatomic</th>
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Table. Heat of Atomization $H_T$ in eV (= 96487 Joule/mol = 23061 cal/mol) for Solid (and a few gaseous) Polyatomic Oxides and Fluorides, and for Similar Gaseous Diatomic MO and MF. Crystalline compounds are marked (c) except the cubic types [NaCl] and [CaF$_2$].
The chemist notes that $-E_{\text{corr}}$ depends mainly on loosely bound orbitals (having one-electron energies far less negative than $E_C$ in Eqn. 4 divided by $Z$) much like chemical bonding occurring in the valence shells. It is not surprising that $-E_{\text{corr}}$ can be strongly enhanced in a compound compared to its constituent atoms. Only recently, precisely $-E_{\text{corr}}$ have become available for molecules with $2-5$ nuclei having one-digit $Z$ values [22][23] such as the isoelectronic $\text{N}_2(5.17)$, $\text{CO}(3.78)$, and $\text{BF}(2.12)$ where the difference between $-E_{\text{corr}}$ of the molecule and the sum over the isolated atoms is given in eV. Said in other words, half of $2H_f \approx 9.80$ eV in $\text{N}_2$ is due to correlation effects. For John Poole,

There is experimental evidence for strong chemical modification of $-E_{\text{corr}}$ from XPES [26][27], e.g. the various inner shells of $\text{Mg}$, $\text{Ca}$, $\text{Sr}$, $\text{Ba}$, and $\text{Hg}$ decrease all ionization energies by a value (for a given $Z$) between 3 and 8 eV by condensation to the metallic element [28]. The ‘barium-thorium effect’ on $H_f$ influences the enthalpy difference between the compound and the separated gaseous atoms. Even if we knew that $-E_{\text{corr}}$ was exactly 80 eV for $\text{Ba}^2$ and 150 eV for $\text{Th}^4$, it would not solve our problem. Since molecular orbitals of the LCAO type occur in a configuration with its ‘squamp’ at most 0.3, and conceivably only 0.2 (extrapolating from $\text{N}_2$ and $\text{CO}$) the atomic orbitals in an optimized LCAO description of electronic density may be modified in the compound, acquiring more $1s$, $2s$, $3s$, ... character than the gaseous atom. Another, more general, situation is ‘chemical polarization’ effects [29]; however, they are synonymous with ‘partly covalent bonding’ to some extent. It should not be neglected that the energies and the positions of the Born-Oppenheimer potential curve minima for a diatomic, or the $(3N-5)$ dimensional surface for $N$ nuclei [18] nuclei are both influenced by relativistic effects (such as $F_2$ dissociating in the Hartree-Fock model).

A quite curious fact is that gaseous $\text{BaF}_2$, $\text{BaCl}_2$, $\text{BaBr}_2$, $\text{SrF}_2$, $\text{SrCl}_2$, and $\text{CaF}_2$ are bent (angle $XMX$ below 180°) but $\text{CaCl}_2$, $\text{CaBr}_2$, $\text{SrBr}_2$, and $\text{SrI}_2$ are linear [30] like $\text{FMF}_2$ for $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$.

For some unknown reason, bending occurs when the ratio $r(M^{+2})/r(X^-)$ is above 0.68. By the way, $\text{ThO}_2$ molecules in a cool Ar matrix has also been reported [31] to be bent (122°) in contrast to the strictly linear uranyl ion $\text{UO}_2^{2+}$ [15][16]. Like several other $\text{Ar}$ complexes [32][33], bent $\text{Co}_2\text{O}_2$ and $\text{Th}_2\text{O}_4$ could be analogous to $\text{Ar}_2\text{Cr}_2(\text{CO})_10$ and $\text{Ar}_2\text{Cr}(\text{NN})_4$. This situation differs from isolated NO and $\text{H}_2\text{O}$, recent precise $E_{\text{corr}}$ have become available.

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[17] R.L. De Kock, E.I. Baerends, P.M. Boer,


