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 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 4f and 5f shells encourage smaller H_a but barium, lanthanum, lutetium, hafnium, tantalum, (to the largest extent thorium), and uranium show unexpected high H_a. This 'Barium-Thorium Effect' can be rationalized by known facts of correlation energy in atoms and (light) compounds, possibly including indirect relativistic effects due to distorted AO in LCAO.

The enthalpies per atom of atomization H_a (*i.e.* sample separated to distant neutral atoms in their groundstate) of diamond and graphite are 7.5 eV and of metallic elements varying from 0.64 eV for mercury, 0.81 eV for caesium, up to 8.0 to 8.2 eV for rhenium and osmium, and 8.8 eV for tungsten. It is worthwhile to consider heats of atomization H_a for compounds, and it seems that solid thorium (IV) oxide (melting at 3500 K and boiling (760 Torr) at 4700 K) has the highest known value, 8.02 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 HCCH 4.26 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 N_2 (4.90), CN (3.99), BF (3.97), and 11 monoxides among those given in the *Table*. Their order of H_a

CO > N_2 > ThO > BO ~ HfO ~ SiO ~ LaO ~ TaO ~ CeO > ZrO ~ NbO ~ CN ~ BF ~ UO (1)
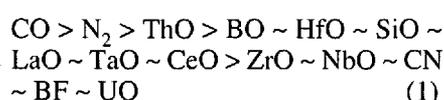
emphasizes that the chemistry of diatomics studied around 4000 K (in sunspots and in spectra of M- and S-type stars) differs entirely from inorganic chemistry in solids, liquids, and solution. Not a single oxidation state M(II) or B(I) that one might infer from series (*1*) occurs in non-metallic, non-catenated inorganic solids [2][3]. The increasing importance of entropy at high T pays a premium for the last step before monatomicity.

In this note, solid and gaseous binary compounds $M_A X_B$ 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.

$$M_A X_B \rightarrow A\ M^{stand} + B\ X^{stand} \rightarrow A\ M^0 + B\ X^0 \quad (2)$$
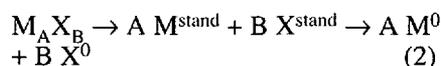
$$H_a = \{(-\text{heat of formation}) + A\ H_a(M) + B\ H_a(X)\}/(A+B)$$

where M^0 and X^0 indicate neutral gaseous atoms (in contrast to Li^+ and F^-). It is evident that *Eqn. 2* has given up the classical advantage that H_a of M^{stand} and X^{stand} are not needed, they may be known very imprecisely (or not at all). However, quan-

tum 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 Cl^0). Most well characterized compounds have negative heat of formation [4] and hence, the first parenthesis of H_a in *Eqn. 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 $(LiF)_2$, $(CsI)_3$, Ge_3O_3, W_4O_{12},... in vapours [5] (like unexpected ternary compounds such as $(ReO_4)_2Ca$, MoO_4Ba_2, and MoO_3Li).

It is a general feeling that both electrovalent bonding and covalency (*cf.* $H_2 \gg Li_2 > Na_2$ or $N_2 \gg P_2$) are stronger in smaller atoms, 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 fluorites CaF_2, SrF_2, and BaF_2 all having H_a 0.4 eV higher. The fluorite-type dioxides 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) baddeleyites, their thermodynamical stability is known to be almost the same as cubic fluorites. Hence, H_a can be arranged in a series terminating roughly where ru-

$$ThO_2 > HfO_2 > ZrO_2 > UO_2 > CeO_2 > PuO_2 \quad (3)$$
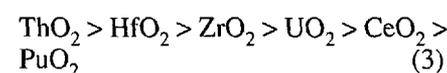
tile TiO_2 is situated. It is also striking that $ThF_4 > ZrF_4 > UF_4$ show the same order; that UF_6 has H_a 70% higher than the other (far less reactive) molecule SF_6; and that large M^{III} in La_2O_3, Nd_2O_3, and Lu_2O_3 above Al_2O_3.

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 = H, F, Cl, Br, I) exhibit a groundstate [2] with one electron in a rotationally symmetric σ 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 ScF, YF,

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and LaF. Calling this orbital σ, the $^3\Delta$ of TiO is $(3d\delta)$ $^1\sigma^1$, and $^4\Sigma$ of VO $(3d\delta)^2\sigma^1$, going through a gradual evolution toward gaseous CuO having a full $3d^{10}$ but lacking an electron in a π orbital localized on oxygen. The situation is more complicated in lanthanide LnO; thus, EuO is a genuine $4f^7$ Ln^{II} oxide, but CeO being $4f^1\sigma^1$, GdO $4f^7\sigma^1$ [7–10] (much like the $^7\Sigma$ groundstate of MnH, MnF, MnCl, and MnBr being $3d^5\sigma^1$ systems [6]) and (at least) most of the gaseous LnF groundstates $4f^q\sigma^2$.

These aspects of diatomics prepare the reader for a surprising demise of 'ligand field' stabilization [11][12]. H_a is 0.4 eV lower of solid MnO and NiO than of the isotypic MgO (a_0=443.5, 417.2, and 420.3 pm), almost the same in all three diatomics, and there is a general trend to have the highest H_a 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 $3d^0$ Ca^{II}, Sc^{III}, Ti^{IV}; $4d^0$ Sr^{II}, Y^{III}, Zr^{IV}; before the lanthanides Ba^{II} and La^{III}; and in the 5f group Th^{IV}. This paradox is accentuated by the low H_a for Mg^{II} compounds with stronger Madelung potential (due to shorter Mg–X), and forming well-defined aqua ions $[M(OH_2)_6]^{+2}$ similar to Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II}.

It is worthwhile to analyze below (what we colloquially and provisionally call) the *Barium-Thorium Effect* on atomization energies H_a. Why should the very beginning (if not the penultimate $Z = 56$ and 90) of the 4f and 5f group stabilize compounds against complete atomization? Even the beginning of the 5d group shows indications too in lutetium, hafnium, and tantalum (*Table*). One might think about relativistic effects [13] varying energy-wise roughly as $Z^4/137$.

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. *Pyykkö* [13] argues that the high H_a of ThO and UO molecules, and the exclusive behaviour of uranyl chemistry [15–17] hence can be rationalized. Chemically speaking, the most striking result is the difficulty of oxidizing Au^{-I}, Tl^I, Pb^{II}, Bi^{III}, and Po^{IV} which would contain two 6s electrons as monatomic species.

Our problem is that H_a express the *difference* between a novel effect in the compound and in the separated atoms. The metallic elements Mo, Tc, Ru, Rh have H_a 1 to 2 eV lower than the homologs W, Re, Os and Ir. This is almost a 'ligand field' tendency [2], octahedral Co^{III}, Rh^{III}, and Ir^{III} with the same ligands having the anti-bonding tendency Δ 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 lowering 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, 11 eV in Ne, very close to 20 eV in Ar, and not far from 40 eV in Zn-atoms and gaseous Zn^{+2} [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

$$-E_{corr} = (0.7 \text{ eV}) Z^{1.2}$$
$$E_G = (13.6 \text{ eV}) Z^{2.40}. \tag{4}$$

That $-E_{corr}$ is roughly proportional to the square root of the *Gáspár* expression [21] for the total binding energy E_G 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_G (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 $-E_{corr}/(2I_k)$ where I_k is a representative average of the excitation energy I_k 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. *Heat of Atomization* H_a *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 [CaF2].

Polyatomic		Diatomic		Polyatomic		Diatomic		Polyatomic		Diatomic	
BeO (c)	6.14	BeO	2.25	BaO [NaCl]	5.11	BaO	2.91	LiF [NaCl]	4.43	HF	2.96
CO2 (g)	5.57	BO	4.18	La2O3 (c)	7.06	LaO	4.14	BF3 (g)	5.01	LiF	3.0
MgO [NaCl]	5.17	CO	5.58	CeO2 [CaF2]	6.93	CeO	4.12	CF4 (g)	4.07	BF	3.97
Al2O3 (c)	6.37	MgO	1.88	Nd2O3 (c)	6.66	NdO	3.65	NaF [NaCl]	3.93	CF	2.86
SiO2 (c)	6.45	AlO	2.65	Lu2O3 (c)	7.22	GdO	3.73	MgF2 (c)	4.93	NaF	2.7
CaO [NaCl]	5.51	SiO	4.14	HfO2 (c)	7.79	ErO	3.19	SiF4 (g)	4.95	MgF	2.39
TiO2 (c)	6.61	ScO	3.53	Ta2O5 (c)	7.20	LuO	3.51	SF6 (g)	2.91	AlF	3.44
MnO [NaCl]	4.75	TiO	3.49	WO3 (c)	6.32	HfO	4.16	CaF2 [CaF2]	5.36	CaF	2.73
NiO [NaCl]	4.77	MnO	2.1	OsO4 (g)	4.42	TaO	4.14	SrF2 [CaF2]	5.32	SrF	2.81
ZnO (c)	3.77	NiO	2.03	PbO (c)	3.44	WO	3.5	ZrF4 (c)	5.78	YF	3.14
SrO [NaCl]	5.20	YO	3.71	ThO2 [CaF2]	8.02	PbO	1.98	BaF2 [CaF2]	5.34	BaF	3.04
ZrO2 (c)	7.63	ZrO	4.02	UO2 [CaF2]	7.32	ThO	4.55	ThF4 (c)	6.23	NdF	2.82
MoO3 (c)	5.57	NbO	4.00	UO3 (c)	6.49	UO	3.94	UF4 (c)	5.75	ErF	2.93
SnO2 (c)	4.77	SnO	2.76	PuO2 [CaF2]	6.54	NpO	3.73	UF6 (g)	4.75	UF	3.42

= 60 (neodymium) decrease roughly linearly as $(1-0.01Z)$. It is not essential that these estimates may be wrong by a factor 1.2 or 0.8; in all scenarios, the *Hartree-Fock* wave-function is not a good approximation to the $3K$-dimensional *Schrödinger* solution [18] for an atom with K higher than 20, that is more electrons than Ca^0 or Fe^{+6}.

The chemist notes that $-E_{corr}$ depends mainly on loosely bound orbitals (having one-electron energies far less negative than E_G in *Eqn. 4* divided by Z) much like chemical bonding occurring in the valence shells. It is not surprising that $-E_{corr}$ can be strongly enhanced in a compound compared to its constituent atoms. Only recently, precise $-E_{corr}$ have become available for molecules with 2–5 nuclei having one-digit Z values [22][23] such as the isoelectronic $N_2(5.17)$, $CO(3.78)$, and $BF(2.12)$ where the difference between $-E_{corr}$ of the molecule and the sum over the isolated atoms is given in eV. Said in other words, half of $2H_a = 9.80$ eV in N_2 is due to correlation effects. The *Hartree-Fock* function of F_2 does not predict bonding, $-E_{corr}$ [22] is 3.64 eV (above 8.87 eV for each of the two F^0), larger than $2H_a = 1.69$ eV. Among the examples [22], linear OCO has the highest additional $-E_{corr} = 6.4$ eV (= 0.38 times the atomization energy 16.7 eV). It is thought-provoking [24] that the elaborate *Gaussian-1* procedure of *Pople* predicts atomization energies (per molecule, all Z below 18, and up to 30 electrons) usually deviating 0.1 eV from the available, accurate experimental heats of atomization. Though this treatment does not imply energy differences between the non-relativistic *Schrödinger* eigen-values for the molecul and for the isolated atoms, it may give some hope for estimates of $-E_{corr}$. *Nesbet* [25] further discussed electron correlation in atoms, molecules and solids in a Festschrift for *John Pople*.

There is experimental evidence for strong chemical modification of $-E_{corr}$ from XPES [26][27], *e.g.* the various inner shells of Mg^0, Ca^0, Sr^0, Ba^0, and Hg^0 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_a influences the enthalpy difference *between* the compound and the separated gaseous atoms. Even if we knew that $-E_{corr}$ was exactly 80 eV for Ba^0 and 150 eV for Th^0, it would not solve our problem. Since molecular orbitals of the LCAO type occur in a configuration with its 'squamp' at most 0.5, and conceivably only 0.2 (extrapolating from N_2 and 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 BaF_2, $BaCl_2$, $BaBr_2$, SrF_2, $SrCl_2$, and CaF_2 are bent (angle XMX below 180°) but $CaCl_2$, $CaBr_2$, $SrBr_2$, and SrI_2 are linear [30] like FMF for M = Mn, Co, Ni, Cu, Zn. For some unknown reason, bending occurs when the ratio $r(M^{+2})/r(X^-)$ between *Goldschmidt* ionic radii is above 0.68. By the way, 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 OUO^{+2} [15][16]. Like several other Ar^0 complexes [32][33], bent CeO_2 and ThO_2 could be $Ar_x CeO_2$ and $Ar_y ThO_2$ in analogy to $ArCr(CO)_5$ and $Ar_2Cr(NN)_4$. This situation differs from isolated NO_2^-, NO_2, O_3^-, and O_3 not being linear (as are OCO, NCO^-, NCN^{-2}, NNN^-, NNO, and ONO^+). It is not easy with quantum chemistry alone to rationalize the tendency of Ba^{II}, La^{III}, to some extent Lu^{III} and Hf^{IV}, and distinctly Th^{IV}, U^{IV}, and U^{VI} compounds to show H_a values at least some 1–2 eV higher (per atom in the compound) than expected for smaller ions in the same oxidation state. The low H_a for Zn^{II}, Sn^{IV}, and Pb^{II} compounds do not suggest a monotonic variation with Z, also since Sr^{II} and Y^{III} already show a weak 'barium-thorium effect'.

The scenario of differential $-E_{corr}$ on forming compounds fits the *low* H_a for compounds containing a partly filled 3d, 4d, 4f, or 5f shell. The oxidation states [2][3] Zr^{IV}, Hf^{IV}, Ta^V, W^{VI}, and Os^{VIII} correspond to d^0 systems. Gaseous atoms with partly filled d or f shells may have enlarged opportunities for two-electron substitutions [19][20] increasing their $-E_{corr}$ (contributing to lower H_a), and compounds at the beginning of transition groups may increase $-E_{corr}$ due to a large number of empty orbitals efficient in the compound. The 'barium-thorium effect' is not much more conspicuous in oxides than in fluorides, rendering electronegativity [18], polarizability [29] and quasi-metallicity [1] less attractive tools of argumentation.

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