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Atom-Based Thermochemistry: Predictions of the Sublimation Enthalpies of Group 12 Chalcogenides and the Formation Enthalpies of their Polonides

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Surprising and useful linear relationships between the atomization enthalpies of molecules and the cohesion enthalpies of crystals are found by shifting the thermochemical reference zero from elements to free atoms. Although the reference shift looks extremely simple, such atom-based thermochemistry (ABT) offers a direct way to calculate and predict the standard atomization enthalpy of molecules, $\Delta_{at}H°(g)$, or solids, $\Delta_{at}H°(s)$, with good accuracy (*J. Am. Chem. Soc.* **2008**, *130*, 5962−5973). It appears that referencing to atoms is able to provide a new unifying perspective. For group 12 metal chalcogenides, ME with M = Zn, Cd, Hg, E = O, S, Se, Te, Po, *diabatic* bond dissociation enthalpies, D^d_{298}, with reference to the $^1D_2$ state of the chalcogen atoms are mandated, in order to analyze the bond strengths properly (*Mol. Phys.* **2007**, *105*, 1139−1155). In this case, ABT implies a 2-fold reference shift (i) from formation enthalpies to atomization enthalpies and (ii) from standard atomization enthalpies to diabatic atomization enthalpies. An excellent linear relationship is found between the D^d_{298}(ME) values and the corresponding diabatic atomization enthalpy of the solids, $\Delta_{at}H^d$(ME, s). The regression line is $\Delta_{at}H^d(\text{ME, s, calc}) = 2.271_7 D^d_{298}(\text{ME}) + 148.1\ \text{kJ mol}^{-1}$ with the correlation coefficient $R = 0.9996$, the standard deviation (SD) = 4.2 kJ mol^{-1} and a mean unsigned deviation (MAD) = 3.7 kJ mol^{-1}. Updated and corrected gas phase standard enthalpies of formation, $\Delta_f H°(g)$, are presented for all 15 group 12 metal chalcogenides, and their lack of correlation with the formation enthalpies of the crystals, $\Delta_f H°(s)$, is documented. The standard sublimation enthalpies, $\Delta_{subl}H°$, are reported for the first time. Recent accurate theoretical D^d_{298} values for the group 12 metal polonides, MPo, are taken to derive the first prediction for the standard atomization, formation, and sublimation enthalpies of their solids.

1. Introduction

Thermodynamics is independent of the existence of atoms and forms a consistent theory without any reference to atoms. By an almost uncontested convention, thermochemical tables are referenced to formation processes from the elements. According to this convention, the standard enthalpy of formation for all elements, A, is defined as zero, $\Delta_f H°(A) \equiv 0$. The convention has been useful historically, as it was easier to obtain pure reference samples of the elements than to generate free atoms. But now the standard atomization enthalpies of the elements, $\Delta_{at}H°(A) \equiv \Delta_f H°(A, g)$, have been established to high accuracy. By choosing the elements as the standard reference, thermochemistry has overlooked interesting and useful relationships between the atomization enthalpies of solids and molecules.[1] In atom-based thermochemistry (ABT), the enthalpy is no longer referenced to the elements but to the free atoms. This shift of the reference frame reveals previously unrecognized linear relationships between the standard atomization enthalpies, $\Delta_{at}H°(g)$, of diatomic and triatomic molecules and the $\Delta_{at}H°(s)$ of corresponding solids for large groups of materials.[1] Although the protocol appears to be almost trivial, ABT offers a direct way to calculate and predict the standard atomization enthalpy of molecules and/or solids with reasonable accuracy. Linear relations between the standard atomization enthalpies of ionic, covalent, polar−covalent, and even metallic solids and the corresponding diatomic or triatomic molecules have been found and predictions have been given.[1] The combined data of 35 alkali and coinage metal halides (AX) and alkali metal hydrides (AH) and 16 triatomic alkaline-earth dihalides (MX_2), altogether 51 materials, obey the relationship

$$\Delta_{at}H°(\text{s, calc}) = 1.2593\Delta_{at}H°(\text{g}) + 119.9\ \text{kJ mol}^{-1} \quad (1)$$

with the correlation coefficient $R = 0.9984$ and the standard deviation (SD) = 18.5 kJ mol^{-1}.

While ref 1 was in print, its prediction that solid gold monofluoride, AuF(s), should be stable at high pressures had received independent computational support, as a new high pressure route toward AuF(s) had been proposed in the meantime.[2] The range of applicability of linear relations between atomization enthalpies furthermore can be extended to the diatoms and solids in the groups 14−14, 13−15, and 2−16. Twenty-five data-pairs for the standard atomization enthalpies of these eight-valence-electron (octet) systems are related by

$$\Delta_{at}H°(\text{s, calc}) = 2.1015\Delta_{at}H°(\text{g}) + 231.9\ \text{kJ mol}^{-1} \quad (2)$$

The fit is characterized by $R = 0.9949$ and SD = 24.0 kJ mol^{-1}. On the basis of eqs 1 and 2, the standard enthalpies of sublimation, $\Delta_{subl}H° = \Delta_{at}H°(s) - \Delta_{at}H°(g)$, have been calculated as a linear function of $\Delta_{at}H°(g)$. Predictions for $\Delta_{at}H°(g)$, $\Delta_{at}H°(s)$, and $\Delta_{subl}H°$ have been given for systems, where these thermodynamic data are not easily accessible by direct experiments and/or quantum mechanical calculations.[1] We have argued frequently that several types of dissociation limits (ionic, atomic, valence-state) are worth being considered, since they complement each other and prove helpful for discussions of bonding.[1,3−7] In particular, $\Delta_{at}H°$ provides an excellent atomistic ordering entity for finding and emphasizing relationships between the enthalpies of molecules and crystals.

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Linear relationships, such as eqs 1 and 2, strengthen and actualize the arguments of Sanderson[8] and subsequently of Spencer et al.[9] for changing the convention of thermochemistry by referencing to atoms instead of elements. Collections of free atoms represent a more uniform thermodynamic reference than the corresponding elements, which may form solids, gases, or even liquids in their standard states.[1] For the definition of chemistry as a subject, atoms are the fundamental building blocks of nature, as they are arranged into compounds forming all materials. In such a context, chemical reactions are rearrangements of atoms leading to the transformation of one material into another.[8,9] However, there is no direct way to relate the conventional standard formation enthalpies, $\Delta_f H°$, to the formation and breaking of bonds in a reaction. Therefore, Sanderson suggested to teach chemistry on the basis of atomization enthalpies whenever possible (ref 8b, pp 30−34). As convincingly demonstrated in many basic examples, there are important didactical and conceptual advantages in teaching thermochemistry on the basis of standard atomization enthalpies and Gibbs free energies of atomization.[8,9]

The linear relationships of ref 1 are perceived in this context, and invite further analysis. The thermochemical correlations under consideration can be expected to generate useful thermochemical data. In order to allow further predictions and/or establish the limits of such rules, the applicability of linear relationships between the atomization enthalpies has to be investigated for other classes of materials.

Here we focus on the compounds of the groups 12−16, generically written as ME. The solid group 12 metal chalcogenides are wide band gap semiconductors and display a variety of crystal structures. Some form important materials in the field of optoelectronics and solar devices.[10] Nanoclusters are particularly interesting: they form a "nonscalable size regime"[11] due to quantum-size effects, and their properties show a strong, nonmonotonic dependence on the cluster size.[12−16]

The diatomic molecules, ME(g), have become the object of intense theoretical interest.[12,17−21] Filatov and Cremer[19] pointed out that the tabulated experimental dissociation enthalpies[22] of most group 12 metal chalcogenides must have been obtained erroneously for mixtures of monomers and much stronger bonded dimers rather than for pure monomers. Thus, the bonding in the monomers is much weaker[12,17−21] than assigned previously. In fact, the standard dissociation enthalpy of zinc oxide $D°_{298}(\mathrm{ZnO}) = 158 \pm 4$ kJ mol^{-1} is considered to date the sole reliable experimental value.[23] Very recently, all 15 group 12 metal chalcogenide molecules have been studied by Peterson et al.[20] in a consistent, accurate theoretical treatment using small-core relativistic Stuttgart pseudopotentials,[24] correlation consistent large basis sets, and highly correlated wave functions. The resulting thermochemical and spectroscopic constants are of uniformly high accuracy, with an estimated uncertainty between ±4 and ±6 kJ mol^{-1} in dissociation enthalpy. They are therefore taken as reference for comparisons with solid state atomization enthalpies.

Within the group 12−16 materials, the polonium chalcogenides constitute the prime example for almost inaccessible and thus poorly documented compounds. Polonium and its compounds are exceedingly rare in nature and most difficult to obtain and detect. Even the atomization enthalpy of elemental polonium cannot be found in the *Handbook of Chemistry and Physics*;[22a] it is, however, available at http://www.webelements.com/[25a] as $\Delta_{at}H°(\mathrm{Po, s}) = 142$ kJ mol^{-1} and from a Russian source[25b] as $\Delta_{at}H°(\mathrm{Po, s}) = 147$ kJ mol^{-1}. Here we use the averaged $\Delta_{at}H°(\mathrm{Po, s}) \equiv \Delta_f H°(\mathrm{Po, g}) = 144{.}_5 \pm 7$ kJ mol^{-1}. It has been argued, however, that the standard atomization enthalpy of solid polonium obtained using the highly radioactive isotope ^{210}Po may be questionable.[25c] The physicochemical measurements may have been uncontrollably influenced by the radioactive decay heat, the decay causing lattice distortion and the accumulation of decay products, such as Pb. According to an unfortunately vaguely documented empirical extrapolation by Eichler,[25c] $\Delta_{at}H°(\mathrm{Po, s})$ could be as high as 200 kJ mol^{-1}. Polonium is the only element crystallizing in the simple cubic (sc) structure at standard conditions.[26] This appears to be connected to its relatively low melting point at 527 K, compared to that of tellurium at 723 K.[25a] Polonium has more isotopes than any other element, all of which are radioactive. It is an extremely toxic and hazardous element: the actual 50% lethal dose, LD$_{50}$, for ^{210}Po is about 1 μg for an 80 kg person.[27] The murderous effects of polonium's radioactivity received extraordinarily wide news coverage in late 2007.[27]

Much less attention has been paid to the thermochemical properties of group 12 metal polonides. They show very strong relativistic effects,[20,28] and the spin−orbit coupling in the ^3P_J states of polonium atom is exceptionally important.[20] Due to the latter effect, the bond dissociation enthalpy with respect to the ground-state atoms is reduced to almost zero.[20] Solid group 12 polonides have been synthesized by different groups in the 1960s and later reviewed by Abakumov.[29] However, there seems to be no published enthalpy or related thermochemical data. Some ground-state structural parameters and the relativistic band structures, including spin−orbit coupling, have been computed and predicted recently.[28] The crystals sublimate at relatively low temperatures between 700 and 800 K.[29]

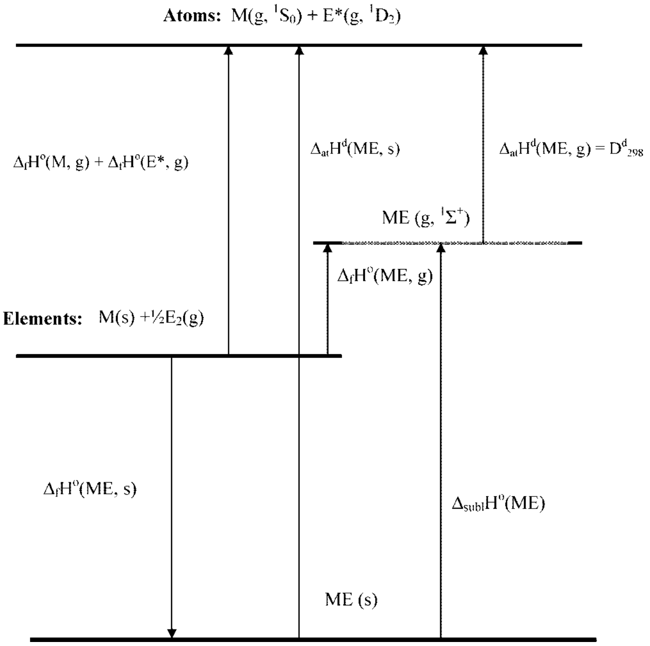
2. Diabatic Atomization Enthalpies, D^d_{298} and $\Delta_{at}H^d$. According to the Wigner−Wittmer rules[30] for the compatibility of symmetries, the $^1\Sigma^+$ ($\Omega = 0^+$) molecular ground-state is to be referenced to the $^1D_2$ state of the chalcogen atoms and not to their $^3P_2$ ground-state.[17,20] The corresponding *intrinsic* dissociation enthalpy is here denoted D^d_{298}. Bauschlicher and Partridge found this reference shift to be essential for the interpretation of the photoelectron spectrum of ZnO$^-$.[17] As emphasized by Peterson et al., referencing the $^1\Sigma^+$ state to the $^1D_2$ atomic level is also needed to analyze the relative bond strengths of the $^1\Sigma^+$ and the lowest $^3\Pi$ states.[20] For the group 12 metal chalcogenides, the equilibrium internuclear distances (r_e), the dipole moments (μ_e), and the spectroscopic constants are more compatible with such *intrinsic* dissociation enthalpies than with the much smaller ground-state dissociation enthalpies $D°_{298}$.[20] This is, of course, in line with Mulliken's classic statement that theoretically more significant *intrinsic* dissociation energies are obtained if the energy is referred to an asymptote in which the atoms are in states suitably prepared for bonding.[31]

Considering *intrinsic* dissociation enthalpies is here equivalent to enforcing a fast, i.e., *diabatic* dissociation process.[32] Thus, diabatic atomization enthalpies, $\Delta_{at}H^d(\mathrm{ME, g}) = D^d_{298}$, with reference to the $^1D_2$ state of the chalcogen atoms are mandated. For consistent comparisons, the equivalent solid state atomization enthalpies, $\Delta_{at}H^d(\mathrm{ME, s})$, are also referenced to chalcogen atoms in the $^1D_2$ state. The latter is defined in eq 3 as the sum of formation enthalpies of the reactant atoms, M(g, $^1S_0$) and E*(g, $^1D_2$), minus the crystal standard enthalpy of formation of solid ME (Scheme 1):

$$\Delta_{at}H^d(\mathrm{ME, s}) = \Delta_f H°(\mathrm{M, g}) + \Delta_f H°(\mathrm{E^*, g}) - \Delta_f H°(\mathrm{ME, s}) \tag{3}$$

The definitions for the diabatic standard atomization, $\Delta_{at}H^d$, standard formation, $\Delta_f H°$, and standard sublimation enthalpies,

SCHEME 1: Thermochemical Enthalpy for Group 12 Metal Chalcogenides, ME[a]



[a] Here, E* symbolizes the chalcogen atom in its excited $^1D_2$ state; $\Delta_{at}H^d$ is the diabatic standard enthalpy of atomization, $\Delta_fH°$ the standard enthalpy of formation, and $\Delta_{subl}H°$ the standard sublimation enthalpy of the bracketed species, respectively.

$\Delta_{subl}H°$, of the group 12 metal chalcogenides are also shown in Scheme 1, together with schematic relations between them.

Note that the terms diabatic and adiabatic are used here according to their quantum mechanical definition, and not in the thermodynamic sense. In thermodynamics, the terms diabatic/adiabatic are used to describe processes with/without the exchange of heat between system and environment. The quantum mechanical definition of diabatic[32] has no direct relation with heat exchange and is closer to a different thermodynamic concept, that of a fast and irreversible process. These two basically different definitions can be the source of much confusion, especially in thermochemical research, when both concepts (heat exchange and sufficiently fast processes) may be present.

The standard atomization enthalpies of the relevant elements, $\Delta_{at}H°(A) \equiv \Delta_fH°(A, g)$, and the $\Delta E(^3P_2 \rightarrow {}^1D_2)$ atom promotion energies[33] for O, S, Se, Te, and Po are listed in Table 1. They are used for converting $\Delta_fH°(ME, s)$ into the diabatic atomization enthalpy of the crystal, $\Delta_{at}H^d(ME, s)$. In case of differing reference data, notably for Se, Te, and Po, averaged values are recommended here, since I did not find independent evidence for preferring a specific value. For polonium, Eichler's upper estimate[25c] is given in brackets.

3. Results and Discussion

3.1. Linear Relation between Diabatic Atomization Enthalpies. Table 2 starts with the diabatic dissociation enthalpy, $D^d_{298} = D^d_0 + 3/2RT_0 = D^d_0 + 3.718$ kJ mol^{-1}, with the D^d_0 values being from Tables 3−7 of ref 20. The solid state data listed in Table 2 contain the stable crystal structures at room temperature (T_0) and atmospheric pressure, the standard enthalpies of formation[34] [$\Delta_fH°$(ME, s)], the standard atomization enthalpies [$\Delta_{at}H°$(ME, s)], and the diabatic atomization enthalpies of the crystals [$\Delta_{at}H^d$(ME, s)], as defined in eq 3. It has been criticized[34b] that the $\Delta_fH°$ data are given by Barin[34a] to an apparent precision of 10^{-3} kJ mol^{-1}, whereas discrepancies on the order of 10 kJ mol^{-1} frequently occur in the original literature.[35] This should be born in mind in evaluating the data in Tables 2 and 3.

TABLE 1: Standard Atomization Enthalpies, $\Delta_{at}H° = \Delta_fH°(A, g)$, for Group 12 Metals (A = M) and the Chalcogenide Elements (A = E), and Chalcogenide Atom Promotion Energies, $\Delta E\ (^3P_2 \rightarrow {}^1D_2)$[a]

M	$\Delta_{at}H°$ (M)[22a]	E	$\Delta_{at}H°$ (E)[22a]	$\Delta_{at}H°$ $(E)_{aver}$[b]	ΔE $(^3P_2 \rightarrow {}^1D_2)$[33]
Zn(s)	130.4 ± 0.4	O_2(g)	249.18 ± 0.10	249.2 ± 0.1	189.9
Cd(s)	111.8 ± 0.2	S(s)	277.17 ± 0.15	277.2 ± 0.2	110.5
Hg(l)	61.38 ± 0.04	Se(s)	227.2 ± 4;[c] 235.4[d]	$231._3$ ± 4	114.6
		Te(s)	196.6 ± 2;[c] 211.7[d]	204 ± 7	126.3
		Po(s)	142 ± 4,[25a] 147 ± 6,[25b] (≤200[25c])	$144._5$ ± 7	259.4

[a] All values in kJ mol^{-1}. [b] this work. [c] Brewer, L.; Rosenblatt, G. M. *Adv. High Temp. Chem.* **1969**, *2*, 1−83. Value recommended in ref 22a. [d] Mills, K. C. *Thermodynamic Data for Inorganic Sulfides, Selenides and Tellurides*; Butterworths: London, 1974. Value recommended in refs 34 and 35a.

While the crystal formation and atomization enthalpies of the group 12 metal polonides are still missing, an excellent linear correlation is found for the other chalcogenides shown in Table 2 and Figure 1

$$\Delta_{at}H^d(\mathrm{s, calc}) = 2.271_7 D^d_{298} + 148.1\ \mathrm{kJ\ mol^{-1}} \qquad (4)$$

The linear relationship is very well satisfied with $R = 0.9996$ and SD = 4.2 kJ mol^{-1}. By propagation of the estimated input errors in D^d_{298} (Table 2) the uncertainty of the calculated diabatic atomization enthalpies, $\Delta_{at}H^d$(s, calc), amounts to $2.271_7 \times 4 \approx 9.1$ (kJ mol^{-1}) and exceeds the statistical SD by a factor of 2.2. The mean unsigned deviation (MAD) amounts to 3.7 kJ mol^{-1}; thus, chemical accuracy has been reached. The relative deviation characterized by its root-mean-square (rms) value amounts to 0.70% only.

Special attention is paid to mercury oxide, HgO(s), as the reported enthalpies of formation differ significantly.[22a,34,35] Fredrickson and Hager[35b] and the recent "HSC Chemistry" database[35c] assign a higher stability to HgO(s) than the one reported earlier.[22a,34,35a] The reference value in Barin[34a] dates from 1953;[34c] thus, the more recent data,[35c] seems preferable. Using $\Delta_fH°(s) = -112.5$ kJ mol^{-1} ,[35c] results in the experimental reference $\Delta_{at}H^d(s) = 613$ kJ mol^{-1} (Table 2). With these data, the deviation of the calculated value, $\Delta_{at}H^d(\mathrm{s, calc}) = 618$ kJ mol^{-1}, amounts to 5 kJ mol^{-1} only.

It is concluded that the applicability and the predictive power of atom-referenced empirical enthalpy relationships extends to the chalcogenides of group 12 elements by applying a further reference shift, which is *intrinsic* to this group of compounds: from standard-state atomization enthalpies to diabatic atomization enthalpies. The linear ABT relationship found for the group 12 metal chalcogenides bridges the gap between molecular and solid state properties, namely, the nonscalable size-regime in clusters, by directly connecting thermochemical properties of solid materials to those of the smallest molecules. Note that no meaningful linear correlation is obtained by referencing the enthalpies to ground-state chalcogen atoms. This finding supports Peterson's analysis in terms of diabatic molecular bond strengths referenced to the $^1D_2$ excited-state chalcogen and the $^1S_0$ ground-state metal atoms. It is also in agreement with the Wigner−Wittmer rules[30] and Mulliken's emphasis on intrinsic dissociation energies.[31]

TABLE 2: Diabatic Dissociation Enthalpies of the Group 12 Metal Chalcogenides, D^{d}_{298}; Standard Atomization Enthalpies, $\Delta_{at}H°(s)$; and Diabatic Atomization Enthalpies, $\Delta_{at}H^{d}(s)$, of Their Crystals[a,b]

ME	D^{d}_{298} (ME)[20] $^{1}\Sigma^{+}$	crystal[c]	$-\Delta_{f}H°(s)$[34]	$\Delta_{at}H°(s)$	$\Delta_{at}H^{d}(s)$ (eq 3)	$\Delta_{at}H^{d}$(s, calc) (eq 4)
ZnO	339 ± 4	W	350.5 ± 0.3	730.1 ± 0.5	920.0 ± 0.5	919 ± 9
CdO	288 ± 4	R	258.3 ± 0.4	619.3 ± 0.5	809.2 ± 0.5	803 ± 9
HgO	207 ± 4	other	112.5;[35bc] (90.8[34])	423.1 ± 0.2; (401.4 ± 0.2)	613.0 ± 0.2; (591.3 ± 0.2)	618 ±9
ZnS	255 ± 4	Sph	$205._{2}$	$612._{8}$ ± 0.5	723	727 ± 9
CdS	222 ± 4	W	$149._{4}$	$538._{3}$ ± 0.3	649	652 ± 9
HgS	155 ± 4	other	$53._{3}$	$391._{8}$ ± 0.3	$502._{3}$ ± 0.3	499 ± 9
ZnSe	224 ± 4	Zb	$177._{6}$	$539._{3}$ ± 4	654 ± 4	658 ± 9
CdSe	198 ± 4	W	$144._{8}$	$487._{9}$ ± 4	$602._{5}$ ± 4	597 ± 9
HgSe	133 ± 4	Zb	$43._{4}$	$336._{1}$ ± 4	$450._{7}$ ± 4	449 ± 9
ZnTe	193 ± 4	R	$119._{2}$	454 ± 7	580 ± 7	586 ± 9
CdTe	175 ± 4	Zb	$101._{8}$	418 ± 7	544 ± 7	544 ± 9
HgTe	119 ± 6	Zb	$31._{8}$	297 ± 7	423 ± 7	417 ± 14
ZnPo	252 ± 6	Zb[28]	na[d]	na	na	Table 4
CdPo	238 ± 6	Zb[28]	na	na	na	Table 4
HgPo	187 ± 6	PbO[28]	na	na	na	Table 4

[a] The uncertainty of the calculated *diabatic* atomization enthalpies, $\Delta_{at}H^{d}$(s, calc), is estimated by error propagation. [b] All values in kJ mol^{-1}. [c] Stable solid structures in the standard state: Zb for zinc-blende; W for wurtzite; R for rock-salt (NaCl); Sph for spharelite. From: Pettifor, D. *Bonding and Structure of Molecules and Solids*; Clarendon Press: Oxford, UK, 1995. [d] na: not available.

TABLE 3: Group 12 Metal Chalcogenides: Adiabatic Dissociation Enthalpy, $D°_{298}$; Sum of Standard Formation Enthalpies of Atoms, $\Delta_{f}H°(M, g) + \Delta_{f}H°(E, g)$; Standard Formation Enthalpies in the Gas Phase, $\Delta_{f}H°(ME, g)$, and the Solid State, $\Delta_{f}H°(ME, s)$; and Standard Sublimation Enthalpies, $\Delta_{subl}H°$, from Eqs 6 and 7b[a]

ME	$D°_{298}$[20] $\Omega = 0^{+}$	$\Delta_{f}H°(M, g) + \Delta_{f}H°(E, g)$ (Table 1)	$\Delta_{f}H°(ME, g)$ (this work)	$\Delta_{f}H°$ (ME, g) ref 34c	$-\Delta_{f}H°$ (ME, s) ref 34	$\Delta_{subl}H°$ (this work, eq 6)	$\Delta_{subl}H°$(calc) (this work, eq 7b)
ZnO	149 ± 4	379.6 ± 0.4	231 ± 4	na[b]	350.5 ± 0.3	581 ± 4	581 ± 5
CdO	98 ± 4	361.0 ± 0.3	263 ± 4	(81.1)	258.3 ± 0.4	521 ± 4	515 ± 5
HgO	25 ± 4	310.6 ± 0.1	286 ± 4	(41.8)	112.5[35b,35c] (90.8[34])	398.5 ± 4 (377 ± 4)	409 ± 5
ZnS	145 ± 4	407.6 ± 0.4	263 ± 4	(202.1)	$205._{2}$	468 ± 4	472 ± 5
CdS	112 ± 4	389.0 ± 0.3	277 ± 4	(188.3)	$149._{5}$	427 ± 4	429 ± 5
HgS	48 ± 4	338.6 ± 0.2	291 ± 4	(127.2)	$54._{5}$	345 ± 4	343 ± 5
ZnSe	111 ± 4	362 ± 4	251 ± 6	237.2	$177._{6}$	429 ± 6	431 ± 5
CdSe	83 ± 4	343 ± 4	260 ± 6	225.9[35a]	$144._{8}$	405 ± 6	399 ± 5
HgSe	18 ± 4	293 ± 4	275 ± 6	(167.4)	$43._{5}$	318 ± 6	314 ± 5
ZnTe	73 ± 4	334 ± 7	261 ± 8	255.2	$119._{2}$	380 ± 8	391 ± 5
CdTe	54 ± 4	316 ± 7	262 ± 8	242.7[35a]	$101._{8}$	364 ± 8	368 ± 5
HgTe	≤0 ± 6	266 ± 7	≥266 ± 9	(184.1)	$31._{8}$	≥298 ± 9	296 ± 5
ZnPo	24 ± 6	275 ± 7 (≤330)	251 ± 9 (≤306)	na	Table 4	Table 4	Table 4
CdPo	14 ± 6	256 ± 7 (≤311)	242 ± 9 (≤297)	na	Table 4	Table 4	Table 4
HgPo	≤0 ± 6	206 ± 7 (≤261)	≥206 ± 9 (≤261)	na	Table 4	Table 4	Table 4

[a] All values in kJ mol^{-1}. [b] na: not available. [c] See the text. The values in parentheses are considered obsolete.

TABLE 4: Predictions for Group 12 Metal Polonides, MPo: Calculated Crystal Atomization Enthalpies, $\Delta_{at}H°$(s, calc); Standard Enthalpies of Sublimation, $\Delta_{subl}H°$(calc); and Standard Enthalpies of Formation, $\Delta_{f}H°$(s, calc)[a]

MPo	D^{d}_{298}[20]	$\Delta_{at}H^{d}$(s, calc) eq (4)[b]	$\Delta_{at}H°$(s, calc) = $\Delta_{at}H^{d}$(s, calc) − 259.4[b]	$\Delta_{subl}H°$(calc) eq (6)[b]	$\Delta_{f}H°$(s,calc) eq (8)[b]
ZnPo	252 ± 6	720 ± 14	461 ±14	437 ± 17	−186 ± 15 (≤−131 ± 15)[c]
CdPo	238 ± 6	689 ± 14	429 ± 14	415 ± 17	−173 ± 15 (≤−118 ± 15)[c]
HgPo	187 ± 6	573 ± 14	313 ± 14	≥313 ± 17	−107 ± 15 (≤− 52 ± 15)[c,b]

[a] All values in kJ mol^{-1}. [b] Uncertainties obtained by error propagation. In order to express the uncertainty by 95% confidence intervals, the present values have to be multiplied by the factor 2. [c] Assuming $\Delta_{at}H°(Po, s) \leq 200$ kJ mol^{-1}; see the text and ref 25c.

It is to be reemphasized that the $\Delta_{f}H°(ME, g)$ and $D°_{0}(ME)$ data normally cited in the literature[22,34−36] have been found to be erroneous for most group 12 chalcogenide molecules.[12,19−21] Therefore, in Table 3, column 4, new data for the gas-phase enthalpies of formation, $\Delta_{f}H°(ME, g)$, are derived from the calculations Peterson et al.[20]

$$\Delta_{f}H°(ME, g) \equiv \Delta_{f}H°(M, g) + \Delta_{f}H°(E, g) - D_{298}° \qquad (5)$$

The adiabatic dissociation enthalpy is $D°_{298} = D°_{0} + 3/2RT_{0} = D°_{0} + 3.718$ kJ mol^{-1}; the $D°_{0}$ values are taken from Tables 3−7 of ref 20. For comparison, the obsolete literature reference values for $\Delta_{f}H°(ME, g)$ have been added to Table 3, column 5. Of the values listed in refs 22, 34−36, only those for ZnSe, ZnTe, CdSe, and CdTe agree with the revised data within reasonable error bars. In fact, all of the revised data are more positive than the earlier reference values. This supports the suggestion in ref[19] that the bonding in the diatomic molecules, ME(g), is generally weaker than assigned previously. The rough agreements for ZnSe, ZnTe, CdSe, and CdTe indicate that in these cases the monomers dominate the gas phase mixture of

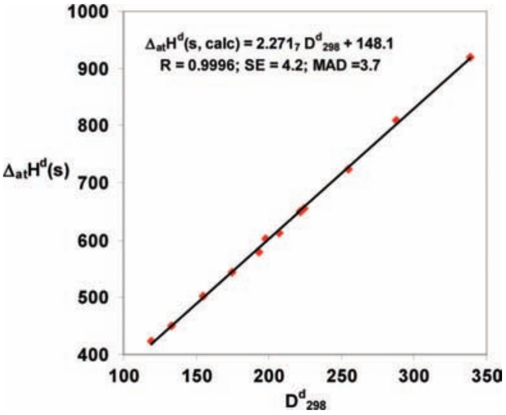


Figure 1. Linear relationship between the diabatic crystal atomization enthalpy, $\Delta_{at}H^d(s)$, and the diabatic molecular atomization enthalpy, D^d_{298}, for group 12 metal chalcogenides. All values in kJ mol^{-1}, from Table 2.

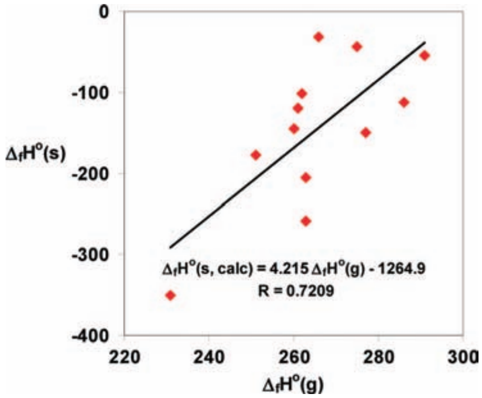


Figure 2. Lack of linear relationship between the standard enthalpies of formation of group 12 metal chalcogenide solids and molecules. Data are from Table 3, in kJ mol^{-1}.

atoms, monomers, dimers, and oligomers at the given experimental conditions. In general, however, additional experiments and the revision of the reference standard enthalpies of formation[22,34−36] are required on the basis of recent accurate calculations[17−21] and the predictions given here. Note that the gas-phase enthalpies of formation of the polonides, $\Delta_fH°$(MPo, g), are reported here for the first time, with the accuracy of the predicted values relying on that of the atomization enthalpy of elemental polonium itself (Table 1). As mentioned in section 2, $\Delta_{at}H°$(Po, s) could be ≤200 kJ mol^{-1}, thus up to 55 kJ mol^{-1} larger than listed in Table 1. Accordingly, the values of $\Delta_fH°$(MPo, g) might have to be increased; see the values in Table 3 in parentheses.

It is key information to note that there are no meaningful linear relations between the standard enthalpies of formation of solids and molecules for the group 12 metal chalcogenides (Figure 2). The gas phase values $\Delta_fH°$(ME, g) (Table 3, column 4) show a rather small spread of approximately ±30 kJ mol^{-1} around an average value of 260 kJ mol^{-1}, while the crystal values $\Delta_fH°$(ME, s) are spread over more than 300 kJ mol^{-1}. The correlation coefficient amounts to $R = 0.7209$ only, similar to the lack of significant linear correlation found between the standard formation enthalpies of molecules and solids of groups' 14−14 compounds.[1] Incidentally, the linear regression of $\Delta_fH°$(ME, s) on the gas phase values $\Delta_fH°$(ME, g) given in refs 34 and 35 results in a complete lack of linear correlation with $R = 0.0084$. A comparison of Figures 1 and 2 highlights the effects of our 2-fold reference shift beyond the thermochemical convention. It is amazing to see to which degree of completeness the widely scattered points in Figure 2 are moved into a single regression line in Figure 1 by shifting the reference frame from elements to atoms.

3.2. Standard Sublimation Enthalpies. The standard sublimation enthalpy, $\Delta_{subl}H°$, is the enthalpy change characterizing the reaction ME(s) → ME(g). It provides a macroscopic measure for the magnitude of intermolecular interactions in solids and is defined as the difference between the standard formation enthalpies of the gas-phase molecule and the solid. By definition, this is equivalent to the standard atomization enthalpy of the solid minus that of the molecule

$$\Delta_{subl}H° = \Delta_fH°(g) - \Delta_fH°(s) = \Delta_{at}H°(s) - \Delta_{at}H°(g) \quad (6)$$

It seems that $\Delta_{subl}H°$ values for group 12 chalcogenides have not been published to date. The application of eq 6 using the obsolete $\Delta_fH°(g)$ or $\Delta_{at}H°(g) = D°_{298}$ values from refs 22 and 34−36 would have led to wrong results indeed; see the discussion in section 3.1. Direct measurements of $\Delta_{subl}H°$(ME) have not been reported, probably because vapors in equilibrium with the condensed phase consist of mixtures of atoms, monomers, dimers, and oligomers in unknown proportions.[19,20,36] Complete experimental information on the standard enthalpy of sublimation is rarely available for inorganic solids. Therefore, it is necessary to accept various approximations described, for instance, in refs 37 and 38. The same is true for quantum mechanical calculations of the standard enthalpy of sublimation, since the temperature dependence of the energy and structure of crystal lattices (including phase transitions) are almost impossible to calculate at present.[39,40] In addition, the presence of a "nonscalable size-regime"[11−16] precludes the extrapolation from the thermochemical data of clusters.

In ref 1 standard sublimation enthalpies were successfully correlated with $\Delta_{at}H°(g)$ data alone, so that the crystal data were not needed anymore. Thus, linear relationships between molecular and solid state atomization enthalpies are helpful in relating $\Delta_{subl}H°$ to more easily accessible thermochemical data, such as, in our case, $D°_{298}$ and D^d_{298}. Scheme 1 indicates that our consistent reference to the $^1D_2$ atomic state of the chalcogen should not affect the enthalpy difference in eq 6. Therefore, the linear relationship between D^d_{298} and $\Delta_{at}H^d(s)$ in eq 4 is transformed to calculate $\Delta_{subl}H°$ values

$$\Delta_{subl}H°(\text{calc}) = aD^d_{298} + b \quad (7a)$$

Combining eqs 4 and 7a, we calculate the standard enthalpy of sublimation for the group 12 chalcogenides by the best linear fit shown in Figure 3.

The linear regression provides a one-to-one correspondence to eq 4

$$\Delta_{subl}H°(\text{calc}) = 1.293D^d_{298} + 140.9 \text{ kJ mol}^{-1} \quad (7b)$$

The correlation coefficient decreases from $R = 0.9996$ (Figure 1) to $R = 0.9972$ in Figure 3. The standard error increases to SE = 6.0 kJ mol^{-1} and the mean unsigned error to MAD = 4.8 kJ mol $^{-1}$. The rms relative error is 1.52%, more than doubled compared to the 0.70% for eq 4. A linear relationship between the diabatic dissociation enthalpy of molecules and the standard sublimation enthalpy of crystals is entirely new and surprising. The agreement of the data calculated via eqs 6 and 7b indicates that for this set of compounds the differing influences of relativity and spin−orbit coupling on the molecules and crystals are absorbed in a linear relationship. The last two columns of Table 3 constitute the first reported data of standard sublimation enthalpies for group 12 metal chalcogenides.

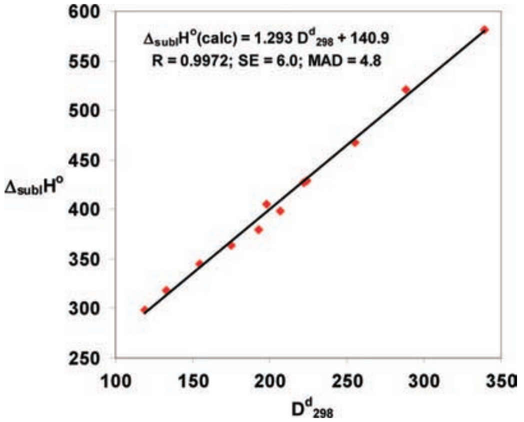


Figure 3. Sublimation enthalpy, $\Delta_{\mathrm{subl}}H°$, of group 12 metal chalcogenides as a linear function of the diabatic molecular atomization enthalpy, D^{d}_{298}. Data are from Table 3, in kJ mol^{-1}.

3.3. Predictions for Group 12 Metal Polonides. The evident success of the ABT reference frame in obtaining highly significant linear relationships encourages the prediction of solid state values $\Delta_{\mathrm{at}}H°(\mathrm{s, calc})$ and $\Delta_{\mathrm{subl}}H°(\mathrm{calc})$ for the group 12 metal polonides. However, three caveats should be discussed, as they could affect some of the predictions of the present approach for the group 12 polonides:

(i) As already mentioned in section 1, $\Delta_{\mathrm{at}}H°(\mathrm{Po, s})$ could be as high as 200 kJ mol^{-1}, thus up to 55 kJ mol^{-1} larger than listed in Table 1. Under such assumptions the bracketed values for $\Delta_f H°(\mathrm{MPo, g})$ in Table 3 would have to be used.

(ii) The D^{d}_{298} dissociation enthalpies of the $^1\Sigma^+$ states taken from ref 20 do not include spin–orbit coupling contributions, presumably because these corrections are of second order only. However, for the polonides, spin–orbit coupling is larger, and a *j*–*j* coupling may be more appropriate than a Russell–Saunders coupling. The adiabatic dissociation enthalpies $D°_{298}$ (Table 3) do contain spin–orbit coupling, but it is not clear how to separate the extra stabilization of the molecular ground-state into adiabatic and spin–orbit contributions.[20] Given the smallness of the calculated $D°_{298}$ (MPo) values, the ground-state stabilization due to adiabatic coupling will reach its maximum at an internuclear distance near the equilibrium bond length of the molecule. For the group 12 metal polonide molecules, the adiabatic stabilization may well exceed the second order effect of spin–orbit splitting. In view of such uncertainties, the consistent use of the diabatic D^{d}_{298} values from ref 20 seems to be the best solution, especially because spin-orbit coupling in the solid state is largely suppressed by the ionic lattice field.

(iii) Relativistic effects become more prominent for the polonides and could affect the validity of predictions. However, according to our experience with gold and lead compounds, ABT type linear relations seem to be robust with respect to the influences of relativistic effects.[1]

Table 4 includes the available D^{d}_{298} data for all three group 12 metal polonide diatoms.[20] The diabatic solid state $\Delta_{\mathrm{at}}H^{d}(\mathrm{s, calc})$ values are predicted via eq 4. The ground-state referenced standard atomization enthalpy $\Delta_{\mathrm{at}}H°(\mathrm{s, calc})$ is defined as $\Delta_{\mathrm{at}}H^{d}(\mathrm{s, calc}) - \Delta E(^3P_2 \rightarrow {}^1D_2)$, with the promotion energy $\Delta E(^3P_2 \rightarrow {}^1D_2)$ for polonium amounting to 259.4 kJ mol^{-1}. The predicted values are given in column 4 of Table 4.

The standard sublimation enthalpies of the polonides are predicted using the basic definition given in eq 6 (Table 4, column 5). In the case of ZnPo and CdPo, the standard atomization enthalpy is predicted to be slightly larger than the standard sublimation enthalpy. This may leave a chance for experimentally observing these molecules in the gas phase. On the other hand, the sublimation enthalpy of HgPo is likely to exceed its atomization enthalpy. Therefore, it is probably not possible to vaporize solid mercury polonide without decomposing it into atoms. In addition, a $^3\Pi_2$ ground state has been calculated for diatomic HgPo, corresponding to a weakly bound van der Waals minimum only.[20]

The equation for calculating the enthalpy of formation, $\Delta_f H°(\mathrm{s, calc})$ from D^{d}_{298} (in kJ mol^{-1}) is

$$\Delta_f H°(\mathrm{s, calc}) = -2.271_7 D^{d}_{298} - 148.1 + \Delta_f H°(\mathrm{M,g}) + \Delta_f H°(\mathrm{E^*, g}) \quad (8)$$

The relevant data for calculating the gas-phase formation enthalpies (Scheme 1) $\Delta_f H°(\mathrm{M, g})$ and $\Delta_f H°(\mathrm{E^*, g})$ are listed in Table 1. Since there seem to be no published enthalpy data on solid group 12 metal polonides, the present extrapolated values in Table 4 are likely to be first predictions.

The polonides of the group 12 metals are predicted to have significantly negative standard enthalpies of formation (Table 4, last column). With respect to the constituent elements, ZnPo is the most stable solid of the group. Solid mercury polonide is predicted to be much less stable than ZnPo and CdPo; this agrees with the trend already established for the group 12 selenides and tellurides. Compared to the corresponding tellurides (Table 3) the $\Delta_f H°(\mathrm{s, calc})$ values of the polonides (Table 4) are more negative by about 70 kJ mol^{-1}. The added stability of the polonides with respect to the elements is due to the relatively low cohesion enthalpy of elemental polonium in its simple cubic structure. The 70 kJ mol^{-1} difference essentially reflects the 60 kJ mol^{-1} difference between the standard atomization enthalpies, i.e., cohesion enthalpies, of the elements Po and Te (Table 1). Alternatively, under the assumption of $\Delta_{\mathrm{at}}H°(\mathrm{Po, s}) \leq 200$ kJ mol^{-1}, the standard enthalpies of formation, $\Delta_f H°(\mathrm{s, calc})$ would be predicted to be less negative by up to 55 kJ mol^{-1}. The standard sublimation enthalpies (column 5) remain unaffected, however, as the gas-phase atomization enthalpy $\Delta_f H°(\mathrm{ME, g})$ in Table 3 would be increased by the same amount.

The standard atomization enthalpies of solid group 12 tellurides (Table 2, column 5) and polonides (Table 4, column 4) are predicted to be rather similar with overlapping error margins. Thus, the bonds also appear to be of comparable strengths. The fact that the few established bond dissociation energies of diatomic molecules with polonium[24a,41] are of the same magnitude as those with tellurium[22a] is seen as independent evidence for strong chemical bonds formed by polonium. Examples for such pairs with comparable bond dissociation energies are (in kJ mol^{-1}) $D_e(\mathrm{PoH}) \geq 220$[41] vs $D°_0(\mathrm{TeH}) \approx 260 \pm 7$,[22a] and $D_e(\mathrm{SiPo}) = 415$[24a] vs $D°_{298}(\mathrm{SiTe}) = 448 \pm 8$.[22a]

4. Summary and Conclusions

We have tested the power of ABT by extending the applicability of heuristic thermochemical relationships to the group 12 metal chalcogenides and predicted the stability of the solid polonides. For the group 12–16 systems, diabatic atomization enthalpies with reference to the $^1D_2$ state of the chalcogen atoms are mandated.[20,30,31] This is tantamount to a 2-fold reference shift, (i) from formation enthalpies to atomization enthalpies and (ii) from standard-state atomization enthalpies to diabatic atomization enthalpies. A corrected list of gas-phase standard enthalpies of formation, $\Delta_f H°(\mathrm{g})$, is presented for all 15 group 12 metal chalcogenides, and their standard sublimation enthalpies, $\Delta_{\mathrm{subl}}H°$, are predicted. We present new evidence that the atomization enthalpy is an excellent atomistic ordering entity for finding and predicting relationships between molecular and crystal enthalpies. A collection of free gas atoms defines a more uniform and, as it increasingly appears, useful thermodynamic reference state than the conventional reference to the elements, which may form solids, gases, or even liquids in their standard states. It appears that referencing to atoms is able to provide a new unifying perspective in thermochemistry.

The ABT interrelations concerning the thermochemistry of molecules and solids were hidden behind the quasi-*paradigmatic* thermochemical convention postulating that the elements are the reference zero of enthalpy. The linear relationships involving atomization and sublimation enthalpies would have become known much earlier, if thermochemical data were not just tabulated with reference to standard-state elements, or ions, but also referenced to atoms with similar emphasis.

The gap between molecular and solid state properties, the nonscalable size-regime in clusters, may be bridged by connecting thermochemical properties of solid materials with those of smallest molecules.[1] The appeal of ABT rests on the straightforwardness in estimating fundamental thermochemical properties from very little experimental data, the accessibility to further testing, and the extendibility to other classes of molecules and solids. Future combinations of the present rules for molecular and crystal atomization enthalpies with universal binding-energy relations, such as reduced potential energy functions, [4,5,7,42−45] should greatly enhance the practical utility and importance of ABT.

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