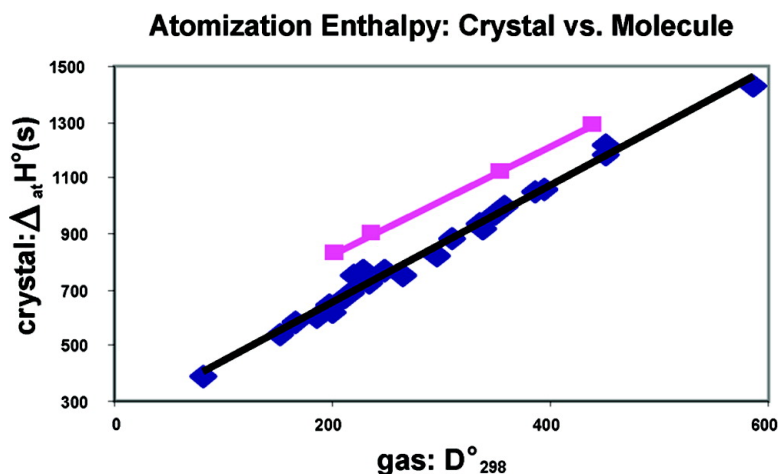## Article

Atom-Based Thermochemistry: Crystal Atomization and Sublimation Enthalpies in Linear Relationships to Molecular Atomization Enthalpy

László von Szentpály

Atomization Enthalpy: Crystal vs. Molecule

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Atom-Based Thermochemistry: Crystal Atomization and Sublimation Enthalpies in Linear Relationships to Molecular Atomization Enthalpy

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Abstract: In atom-based thermochemistry (ABT), state functions are referenced to free atoms, as opposed to the thermochemical convention of referencing to elements in their standard state. The shift of the reference frame reveals previously unrecognized linear relationships between the standard atomization enthalpies $\Delta_{at}H^{o}(g)$ of gas-phase diatomic and triatomic molecules and $\Delta_{at}H^{o}(s)$ of the corresponding solids for large groups of materials. For 35 alkali and coinage-metal halides, as well as alkali metal hydrides, $\Delta_{at}H^{o}(s) = 1.1203 \Delta_{at}H^{o}(g) + 167.0$ kJ mol^{-1} is found; the standard error is SE = 16.0 kJ mol^{-1}, and the correlation coefficient is $R = 0.9946$. The solid coinage-metal monohydrides, CuH(s), AgH(s), and AuH(s), are predicted to be unstable with respect to the formation from the metals and elemental hydrogen by an approximately constant standard enthalpy of formation, $\Delta_{f}H^{o}(s) \approx +80 \pm 20$ kJ mol^{-1}. Solid AuF is predicted to be marginally stable, having $\Delta_{f}H^{o}(s) = -60 \pm 50$ kJ mol^{-1} and standard a Gibbs energy of formation $\Delta_{f}G^{o}(s) \approx -40 \pm 50$ kJ mol^{-1}. Triatomic alkaline-earth dihalides MX$_2$ obey a similar linear relationship. The combined data of altogether 51 materials obey the relationship $\Delta_{at}H^{o}(s) = 1.2593 \Delta_{at}H^{o}(g) + 119.9$ kJ mol^{-1} with $R = 0.9984$ and SE = 18.5 kJ mol^{-1}. The atomization enthalpies per atom of 25 data pairs of diatoms and solids in the groups 14–14, 13–15, and 2–16 are related as $\Delta_{at}H^{o}(s) = 2.1015 \Delta_{at}H^{o}(g) + 231.9$ kJ mol^{-1} with $R = 0.9949$ and SE = 24.0 kJ mol^{-1}. Predictions are made for the GeC, GaSb, Hf$_2$, TlN, BeS, MgSe, and MgTe molecules and for the solids SiPb, GePb, SnPb, and the thallium pnictides. Exceptions to the rule, such as SrO and BaO, are rationalized. Standard enthalpies of sublimation, $\Delta_{subl}H^{o} = \Delta_{at}H^{o}(s) - \Delta_{at}H^{o}(g)$, are calculated as a linear function of $\Delta_{at}H^{o}(g)$ profiting from the above linear relationships, and predictions for the $\Delta_{subl}H^{o}$ of the thallium pnictides are given. The validity of the new empirical relationships is limited to substances where at least one of the constituent elements is solid in its standard state. Reasons for the late discovery of such relationships are given, and a meaningful ABT is recommended by using $\Delta_{at}H^{o}$ as an important ordering and reference state function.
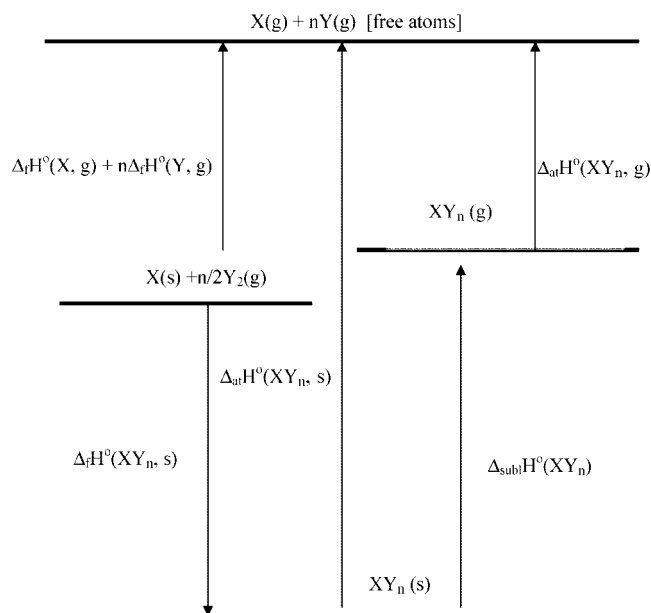
1. Introduction

One would expect to easily locate them in the literature, but the relationships presented in the abstract appear not to have been discovered up to now. We find excellent linear relations between the gas-phase standard atomization enthalpy, $\Delta_{at}H^{o}(XY_n,g)$, and the crystal standard atomization enthalpy, $\Delta_{at}H^{o}(XY_n,s)$, for the alkali and coinage-metal halides and hydrides, the alkaline-earth dihalides, and compounds formed between elements of the groups 14–14, 13–15, and 2–16. The standard atomization enthalpy of a molecule, $XY_n(g)$, and a crystal, $XY_n(s)$ are defined as the sum of enthalpies of formation of the component gaseous atoms minus the formation enthalpy of the compound, $\Delta_{at}H^{o}(XY_n) = \Delta_{f}H^{o}(X,g) + n\Delta_{f}H^{o}(Y,g) - \Delta_{f}H^{o}(XY_n)$ and characterize the reactions $XY_n(g) \rightarrow X(g) + nY(g)$ and $XY_n(s) \rightarrow X(g) + nY(g)$, respectively (Scheme 1).

A very close linear relation between D_{VS}, the valence-state dissociation energy of diatomic molecules,[1] and the lattice energy of binary solids, U_{POT}, has been published recently.[2] During the preparation of the manuscript of ref 2, it appeared as if there were no reports on relations between molecular and solid-state atomization energies. The present work has been triggered by this impression. A more detailed literature search revealed some interesting early investigations into the matter.[3] Verhaegen, Goldfinger, et al.[3a,b] related the atomization enthalpy of metallic elements, M, to the dissociation enthalpy of the corresponding homonuclear diatoms, M$_2$, and obtained approximately constant ratios, $\alpha = \Delta_{at}H^{o}(M,s)/\Delta_{at}H^{o}(M_2)$, within each family of metals, for example, $\alpha \approx 1.5$ for the alkali metals

(1) (a) von Szentpály, L. *Chem. Phys. Lett.* **1995**, *245*, 209–214. (b) von Szentpály, L. *J. Phys. Chem. A* **1998**, *102*, 10912–10915. (c) Gardner, D. O. N.; von Szentpály, L. *J. Phys. Chem. A* **1999**, *103*, 9313–9322. (d) von Szentpály, L.; Gardner, D. O. N. *J. Phys. Chem. A* **2001**, *105*, 9467–9477. (e) Donald, K. J.; Mulder, W. H.; von Szentpály, L. *J. Phys. Chem. A* **2004**, *108*, 595–606.

(2) Glasser, L.; von Szentpály, L. *J. Am. Chem. Soc.* **2006**, *128*, 12314–12321.

(3) (a) Verhaegen, G.; Strafford, F. E.; Goldfinger, P.; Ackerman, M. *Trans. Faraday Soc.* **1962**, *58*, 1926–1938. (b) Colin, R.; Goldfinger, P. In *Condensation and Evaporation of Solids*, Rutner, E., Goldfinger, P., Hirth, J. P., Eds.; Gordon and Breach: New York, 1964, pp 165–179; (c) Miedema, A. R.; Gingerich, K. A. *J. Phys. B* **1979**, *12*, 2081–2095. (d) Miedema, A. R. *Faraday Symp. Chem. Soc.* **1980**, *14*, 137–148. (e) Miedema, A. R. *Faraday Symp. Chem. Soc.* **1980**, *14*, 240.

(4) (a) Kim, C. K.; Won, J.; Kim, H. S.; Kang, Y. S.; Li, H. G.; Kim, C. J. *Comput. Chem.* **2001**, *22*, 827–834. (b) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 3308–3311.

Scheme 1. Thermochemical Enthalpy Scheme[a]

X(g) + nY(g) [free atoms]

$\Delta_f H°(X, g) + n\Delta_f H°(Y, g)$

$\Delta_{at} H°(XY_n, g)$

XY_n (g)

X(s) + n/2Y$_2$(g)

$\Delta_{at} H°(XY_n, s)$

$\Delta_f H°(XY_n, s)$

$\Delta_{subl} H°(XY_n)$

XY_n (s)

[a] $\Delta_{at} H°$ is the standard enthalpy of atomization, $\Delta_f H°$ the standard enthalpy of formation, and $\Delta_{subl} H°$ the standard sublimation enthalpy of the bracketed species.

and $\alpha \approx 1.8$ for the coinage metals. However, more recent experimental results on atomization enthalpies of other metals yielded widely varying α values; thus, the correlations were judged to be of little value for predicting data.[3c] Miedema and Gingerich discussed exceptions encountered with the Verhaegen α-parameter method and restricted the correlations to certain related groups of metals.[3d] This allowed the remarkable prediction of the stability of Be$_2$ molecule by Miedema.[3e] In general, however, $\Delta_{at} H°$ was not perceived as an important ordering entity, and even other types of relationships between molecular and solid-state properties have been rarely probed.[2,4a] Semi-empirical methods postulating transferable bond energy increments between molecules and solids are Pauling's resonating valence bond model for metals[5] and Sanderson's coordinated polymeric model for solids.[6]

For many of the solids discussed in this article, attention has traditionally been focused on energy relations involving the free-ion limit as reference energy, for example, ionic lattice energy, U_{POT}, versus heterolytic bond dissociation energy[4a] and U_{POT} versus nearest internuclear distance, R_0.[4b] Hisham and Benson additionally examined the enthalpies of atomization of the alkali-metal halides and hydrides as a function of R_0 and concluded that "no simple, general covalent model will describe the entire group."[4b] Thus, searching for relationships involving atomization enthalpies seemed to be of little interest. We have, however, obtained significant insight into the type of bonding in the group 12 dihalide molecules (ZnX$_2$, CdX$_2$, and HgX$_2$) by considering the ground-state atoms' dissociation limit instead of the conventional free ions' asymptotic energy.[7] It was found that the polarized ion model is completely unable to rationalize

bonding in the group 12 dihalides, whereas it is a reasonable model for the group 2 dihalides.[7] In general, several types of dissociation limits seem worth being considered and compared for discussing bonding.[1,2,7] This article presents a new empirical rule, a linear relationship between the solid-state and molecular atomization enthalpies, also for classes of compounds where one tends to think in terms of Born–Haber–Fajans cycles with fully ionic dissociation products. We will show that $\Delta_{at} H°$ provides an excellent atomistic ordering entity for finding and highlighting linear relationships between molecular and crystal enthalpies, including sublimation enthalpies. A predictive power will be attributed to the newly found rules. This is of special importance because attempts to obtain crystal atomization enthalpies by extrapolating those of small clusters, or vice-versa, have not been successful.[8] Molecular clusters are often in a non-scalable size regime, where most properties do not scale with size, are highly nonmonotonic, and cannot be extrapolated to or from the solid state.[8c] We bridge the gap by directly connecting thermochemical properties of solid materials with those of the smallest molecules.

The results to be presented will strengthen and actualize Sanderson's plea for changing the convention in thermochemistry.[6] Sanderson suggested teaching thermochemistry by using atomization enthalpies of elements and compounds whenever possible (ref 6, pp 30−34). According to Sanderson, the reference zero energy should be shifted from the elements in their standard state to the free atoms. In order to understand the origin and meaning of the reaction enthalpy, it should be taught as the difference between the total atomization enthalpies of the reactants and that of the products. As convincingly demonstrated in several basic examples, there is a distinct didactical advantage in teaching thermochemistry on the basis of standard atomization enthalpies and, of course, Gibbs enthalpies of atomization.[6] This is equivalent to establishing an atom-based thermochemistry (ABT).

The article is organized a follows: section 2.1 establishes a linear $\Delta_{at} H°$ relationship for 35 alkali and coinage-metal halides and hydrides; in section 2.2, the validity is extended to alkaline-earth dihalides, and a single linear equation is presented for 51 compounds; in section 2.3, covalent, polar, and metallic systems of the groups 14, 13−15, and 2−16 are investigated; section 2.4 highlights the linear dependence of the standard sublimation enthalpy, $\Delta_{subl} H°$, on the molecular bond dissociation enthalpy, D_{298}^0. Section 3 is reserved for conclusions and perspectives of the study.

2. Results and Discussion

2.1. Alkali and Coinage-Metal Halides and Hydrides. We consider different classes of compounds and document the close linear proportionality between the atomization enthalpies of ionic, covalent, polar-covalent, and even metallic solids and the corresponding diatomic or triatomic molecules. We start with the materials investigated in ref 2. Table 1 contains the experimental $D_{298}^0 = \Delta_{at} H°(g)$ data for gas-phase diatomic alkali and coinage-metal halides and hydrides taken from Section 9 of the *Handbook of Chemistry and Physics*[9a] (with some corrections, as indicated) and the corresponding solid-state

(5) (a) Pauling, L. *Phys. Rev.* **1938**, *54*, 899–904. (b) Pauling, L. *Nature* **1948**, *161*, 1019–1020. (c) Pauling, L. *Phys. Rev. Lett.* **1969**, *23*, 480. (d) Pauling, L. *J. Solid State Chem.* **1984**, *54*, 297–307.
(6) Sanderson, R. T. *Polar Covalence*; Academic Press: New York, 1983.
(7) Donald, K. J.; Mulder, W. H.; von Szentpály, L. *J. Chem. Phys.* **2003**, *119*, 5423–36.

(8) (a) Matxain, J. M.; Mercero, J. M.; Fowler, J. E.; Ugalde, J. M. *J. Phys. Chem. A* **2003**, *107*, 9918–9923. (b) Matxain, J. M.; Mercero, J. M.; Fowler, J. E.; Ugalde, J. M. *J. Phys. Chem. A* **2004**, *108*, 10502–10508. (c) Jena, P.; Castleman, A. W., Jr *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10560–10569. (d) Srnec, M.; Zahradník, R. *Eur. J. Inorg. Chem.* **2007**, 1529–1543.

Table 1. Experimental Diatomic and Crystal Atomization Enthalpies, D°_{298} and $\Delta_{at}H^{\circ}(s)$, Calculated $\Delta_{at}H^{\circ}(s,calc)$ with eq 1, and Difference $\Delta\Delta_{at}H^{\circ}(s) = \Delta_{at}H^{\circ}(s,calc) - \Delta_{at}H^{\circ}(s)^a$

	D°_{298} (kJ mol^{-1}, ref 9)	$\Delta_{at}H^{\circ}(s)$ (kJ mol^{-1}, ref 9)	$\Delta_{at}H^{\circ}(s,calc)$ (kJ mol^{-1}, eq 1)	$\Delta\Delta_{at}H^{\circ}(s)$ (kJ mol^{-1})
LiH	238	468	434	−34
NaH	186	382	376	−6
KH	177 ± 5	365	366 ± 6	−1
RbH	167 ± 21	351	354 ± 23	+3
CsH	175	349	363	+15
LiF^b	591 ± 5^b	854	829 ± 6	−25
LiCl	469 ± 13	690	693 ± 14	+3
LiBr	419 ± 4	622	637 ± 5	+15
LiI	345 ± 4	537	554 ± 5	+17
NaF	519 ± 3	760	749 ± 3	−11
NaCl	413 ± 8	640	630 ± 9	−10
NaBr	367 ± 1	580	579 ± 1	−1
NaI	304 ± 2	502	508 ± 2	+6
KF	498 ± 3	735	725 ± 3	−10
KCl	433 ± 8	647	652 ± 9	+5
KBr	380 ± 1	595	593	−2
KI	325 ± 1	524	531	+7
RbF	494 ± 21	718	721 ± 23	+3
RbCl	428 ± 8	638	647 ± 9	+9
RbBr	381 ± 4	588	594 ± 5	+6
RbI	319 ± 2	529	525 ± 2	−4
CsF^c	500 ± 2^c	709	727 ± 2	+18
CsCl	445 ± 8	641	666 ± 9	+25
CsBr	389 ± 4	598	603 ± 5	+5
CsI	337 ± 2	529	545 ± 2	+16
CuCl^c	383 ± 3^c	599	596 ± 3	−3
CuBr^c	335 ± 15^c	557	543 ± 17	−14
CuI^c	≤314 ± 20^c	512	≤519 ± 22	≤+7
AgF	354 ± 16	569	564 ± 18	−5
AgCl	315 ± 10	533	520 ± 12	−13
AgBr	293 ± 29	497	496 ± 33	−1
AgI^c	254 ± 10^c	453	452 ± 12	−1
AuCl^d	304 ± 10^d	522	508 ± 12	−14
AuBr^d	289 ± 10^d	492	491 ± 12	−1
AuI^d	278 ± 10^d	473	479 ± 12	+6

^{a} Experimental data for alkali and coinage-metal halides and hydrides including error margins from ref 9, except if indicated in footnotes. ^{b} Bond dissociation enthalpy of LiF from Partridge, H.; Bauschlicher, C. W.; Langhoff, S. R. *Chem. Phys. Lett.* **1984**, *109*, 446–449. ^{c} Bond dissociation enthalpies of CsF, CuCl, CuBr, CuI, and AgI from ref 11. ^{d} Bond dissociation enthalpies of AuCl, AuBr, and AuI from Reynard, L. M.; Evans, C. J.; Gerry, M. C. L. *J. Mol. Spectrosc.* **2001**, *205*, 344–346.

$\Delta_{at}H^{\circ}(s)$ derived from their standard thermodynamic properties collected in Section 5 of ref 9a, wherein other well-known compendia have been incorporated.[9] Note that some of the $\Delta_{at}H^{\circ}(g) = D^{\circ}_{298}$ values in ref,[9] for example, CuI (from 1968), AuBr, and AuCl, are outdated or unreliable and have to be replaced. If only D°_0 is listed in the literature, the standard relation for diatomic bond dissociation enthalpy $D^{\circ}_{298} = D^{\circ}_0 + 3.72$ kJ mol^{-1} is used.[9]

The experimental uncertainties listed in column 2 of Table 1 are taken from ref 9, and those given in column 4 are the results of error combination. The data for the alkali metal halides and hydrides and the coinage-metal monohalides obey the relation shown in Figure 1.

$$\Delta_{at}H^{\circ}(s,calc) = 1.1203 D^{\circ}_{298} + 167.0 \text{kJmol}^{-1} \qquad (1)$$

(9) (a) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 83rd Ed., CRC Press: Boca Raton, FL ,2003; Sections 5.1 ff and 12.22 ff. (b) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*, Hemisphere Publ. Corp.: New York, 1989. (c) Chase, M. W. *J. Phys. Chem. Ref. Data, Monogr.* **1998**, *9*, NIST-JANAF Thermochemical Tables (4th ed.)
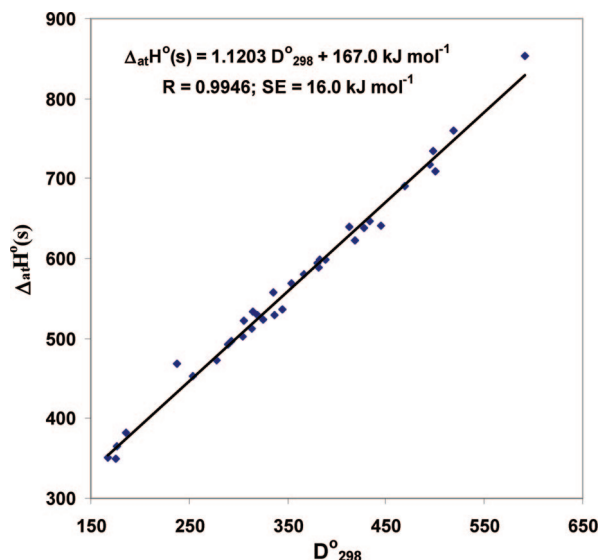
Figure 1. Linear relationship between crystalline atomization enthalpy, $\Delta_{at}H^{\circ}(s)$, and diatomic bond dissociation enthalpy, D°_{298}. Data for 35 alkali and coinage-metal halides and hydrides in kJ mol^{-1}.

The linear correlation coefficient for the sample of 35 materials is $R = 0.9946$, and the standard deviation is SE = 16.0 kJ mol^{-1}, corresponding to the root mean square (rms) relative error of 2.20% only. The experimental uncertainty of the input data, D°_{298}, is frequently comparable to the standard deviation of the output. The linear correlation may be further improved by replacing D°_{298} by the spectroscopic dissociation energy, $D_e = D^{\circ}_0 + $ ZPE, because the vibrational zero-point energy (ZPE) is particularly important for hydrides and lithium salts. The corresponding solid-state phonon ZPEs seem, however, not to be available for all of the compounds considered in this article.

Evidently, the particular choice of the free atoms as the reference zero of enthalpy is essential for the relationship. This kind of linear relationship is new but might not be surprising for ionic halides and group 1 hydrides, because the atoms in molecules and the atoms in solids show only small differences in their electron configurations. In addition, Manby et al. have recently found that the correlation contribution to the cohesive energy of solid LiH is almost matched by the correlation energy (approximately 100 kJ mol^{-1}) present in the LiH molecule.[10] However, the similarity in electron configuration is not a necessary condition for linear enthalpy relationships; examples to the contrary are given in section 2.3 below. Pauling[5] and Sanderson[6] assumed some kind of linear relationships between the bond strengths in molecules and crystals; this forms part of the empirical, heuristic input in their respective models and cannot be considered as theoretically understood. For metals and their diatomic molecules, some explanation was given by Miedema and Gingerich.[3c] It appears that at least one of the constituting elements has to be a solid at standard temperature and pressure. No linear relationships have been reported between the corresponding enthalpies of formation, $\Delta_f H^{\circ}(s)$ and $\Delta_f H^{\circ}(g)$, which are referenced to the elements in their standard state. This evidences that a collection of ideal-gas atoms is conceptually a more uniform thermodynamic reference than the corresponding

(10) Manby, F. R.; Alfè, D.; Gillan, M. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5178–5180.

Table 2. Coinage-Metal Hydrides and Fluorides: Predicted Crystal Atomization Enthalpies, $\Delta_{at}H°$(s,calc), and Enthalpies of Formation, $\Delta_f H°$(s,calc), Based on Experimental Bond Dissociation Enthalpies, D_{298}^0, and Eq 1[a]

XY	D_{298}^0 (kJ mol^{-1})	ref	$\Delta_{at}H°$(s,calc) = 1.1203 D_{298}^0 + 167.0 (SE = 16.0 kJ mol^{-1})	$\Delta_{at}H°$(s,obs) (kJ mol^{-1})	$\Delta_f H°$(s,calc) (kJ mol^{-1})
CuH	267 ± 6	11	467 ± 17	n. a.[b]	+87 ± 17
AgH	223 ± 10	11	417 ± 19	n. a.	+86 ± 19
	215 ± 9[c]		408 ± 18		+95 ± 18
AuH	314 ± 10	11	519 ± 19	n. a.	+67 ± 19
	303 ± 13	9	507 ± 22		+79 ± 22
CuF	413 ± 13	9	630 ± 22	646[2]	−213 ± 22
AuF	310 ± 40	19a	510 ± 50	n. a.	−60 ± 50

[a] Uncertainty of predictions estimated from error propagation: $[SE^2 + (1.120\,\Delta D_{298}^0)^2]^{1/2}$. [b] Not available. [c] Kant, A.; Moon, K. A. *High Temp. Sci.* **1979**, *11*, 55–62.

elements, which may form solids, real gases, or even liquids at the standard state.

Equation 1 allows predictions if only one quantity, either D_{298}^0 or $\Delta_{at}H°$(s), is known. This is the case for the coinage-metal monohydrides and some monohalides, specifically, CuF and AuF, for which only D_{298}^0 values are known to a sufficient accuracy[1,6,9,11] (Table 2). At standard conditions, the solid coinage-metal monohydrides, CuH(s), AgH(s), and AuH(s), are known to be unstable with respect to their elements, that is, H_2 and the coinage metal.[12,13] Metastable solid CuH(s) has been synthesized and forms the wurtzite structure.[14] Some estimates for the activation barriers to such dissociation were reported.[13b] We shall use the linear eq 1 in order to quantify the amount of instability, which seems not to have been reported so far.

On the basis of the tabulated molecular bond dissociation enthalpy, D_{298}^0, the atomization enthalpy of the solid coinage-metal hydrides, CuH(s), AgH(s), and AuH(s), is assessed in Table 2. All of the coinage-metal hydride crystals are, of course, stable with respect to their atoms but definitely unstable with respect to the standard states of the elements, gaseous H_2 and the coinage metals. Interestingly, the instability is here predicted as nearly constant: $\Delta_f H° \approx +80 \pm 20$ kJ mol^{-1}.

The accepted rationales for the instability of the coinage-metal monohydrides are as follows. (i) As a result of small electronegativity differences, the Madelung energy is less important in these solids than in the more ionic alkali metal hydrides.[2] (ii) A significant part of the metal's cohesive energy is lost when the metal lattice is expanded into the arrangement of metal ions in the metal hydride lattice.[13c] This picture is completed in the present work by a molecular connection. The new argument emphasizes that bonding for the coinage-metal monohydrides is exceptionally weak both in the molecular ground state and in the solid state. Let us compare the experimental bond dissociation energy, D_{298}^0, of molecular CuH with its textbook-expectation value based on Pauling's empirical geometric-mean rule.

$$D_{298}^0(\text{CuH}) = [D_{298}^0(\text{Cu}_2)D_{298}^0(\text{H}_2)]^{1/2} + c\Delta\chi^2 \quad (2)$$

where $\Delta\chi$ is the Pauling electronegativity difference and $c \approx$ 30 kcal mol$^{-1} \approx 125$ kJ mol^{-1}. Comparing the data listed by Huber and Herzberg,[11] the observed $D_{298}^0(\text{CuH}) = 267$ kJ mol^{-1} is significantly ($\sim 13\%$) smaller than the sum on the right-hand side of eq 2: $[D_{298}^0(\text{Cu}_2)\,D_{298}^0(\text{H}_2)]^{1/2} + c\Delta\chi^2 = \{(200 \times 436)^{1/2} +12\}$ kJ mol$^{-1} = 307$ kJ mol^{-1}. The simplest measure for thermodynamic stability, the arithmetic average, yields a much too high $0.5(200 + 436) = 318$ kJ mol^{-1} on the right-hand side of eq 2. Thus, the molecular case parallels the solid state case: bonding in CuH is exceptionally weak for the molecule and the solid. Under the right conditions for collision, two CuH molecules will form Cu_2 and H_2. The kinetic stabilization is, however, much more efficient for gas-phase molecules than for the solid. The solid is unstable with respect to elements; whereas the diatomic molecule is stable with respect to atoms but not with respect to the formation of homonuclear molecules. The same reasoning is valid for AgH and AuH.

The obvious question is why did Pauling fail to incorporate these facts on the coinage-metal hydrides while generating eq 2? First, Pauling assumed that Cu_2 was triple-bonded and based on the electron configuration 3d^{9}4s4p for each of the two atoms;[15] in fact, he refused to accept the increasing evidence[16] for the 4s−4s single σ bond in Cu−Cu until very late.[15] Second, the Pauling rule is applicable to polar single bonds but not to multiple bonds. Thus, Pauling did not expect the CuH bond energy to be an average of the Cu_2 and H_2 bond energies. Had he accepted that Cu_2 is single-bonded, he would have probably chosen a harmonic-mean rule for his definition of electronegativity instead of the arithmetic-mean and, subsequently, the geometric-mean rule. Thus, history of the textbook chemistry might have changed somewhat, and the introduction of the harmonic-mean rule would not have been left to T. L. Allen[17a] and R. T. Sanderson.[17b] One could even speculate whether Pauling's resistance to accepting single-bonded Cu_2 was guided by his quest of maintaining his definition of the electronegativity for atoms in molecules as it was introduced in the first place.

Gold monofluoride, AuF, is unknown as a solid, but the diatomic molecule AuF has been predicted theoretically[18] and characterized experimentally.[19] Taking the best experimental estimate for the molecule,[19a] $D_{298}^0 \approx 310 \pm 40$ kJ mol^{-1}, solid AuF is predicted to have an enthalpy of atomization $\Delta_{at}H°$ (s,calc) $\approx 510 \pm 50$ kJ mol^{-1}, corresponding to an enthalpy of formation $\Delta_f H°$(s,calc) $\approx -60 \pm 50$ kJ mol^{-1} (Table 2). An eventual reduction of the experimental uncertainty will reduce the estimated error of our prediction. Within the error bars, this value is in agreement with recent solid-state density functional theory results[20c] on the sublimation energy at 0 K, $\Delta_{subl}E \approx$ 182 kJ mol^{-1}, leading to $\Delta_f H°$(s) $\approx -40 \pm 40$ kJ mol^{-1} and our recent valence-state-based result,[2] $\Delta_f H°$(s) $\approx -100 \pm 50$ kJ mol^{-1}, but in strong disagreement with Waddington's 1959

(11) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* Van Nostrand Reinhold: New York, 1979.

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prediction of a positive enthalpy of formation $\Delta_f H^\circ(s) \approx +170$ kJ mol^{-1}.[21] Waddington further estimated the entropy contributions $\Delta_f S^\circ(s)$ by Latimer's method[22] and obtained $T_o \Delta_f S^\circ(s) \approx -20$ kJ mol^{-1} at $T_o = 298.15$ K. By using this value, the standard free enthalpy of formation is here predicted to be $\Delta_f G^\circ(s) = \Delta_f H^\circ(s) - T_o \Delta_f S^\circ(s) \approx -40 \pm 50$ kJ mol^{-1}; thus, solid AuF might be only slightly stable under standard conditions. However, it is expected and predicted that AuF forms a stable solid at high pressures.

The reasons for the very large ($\sim$230 kJ mol^{-1}) discrepancies between Waddington's estimate for AuF and the more recent predictions have been recently discussed for the coinage-metal monohalides in general.[2] For gold monohalides in particular, relativistic effects reduce the bond ionicity by up to 50%.[1e,2,20b] Different methods agree in assigning relativistic partial charges of $\delta \approx 0.52$ to both molecular AuF and its cubic crystal.[1e,2,20b] Therefore, significant covalent bonding must be attributed to the coinage-metal monohalides and especially the gold monohalides. Quite to the opposite, Waddington's approach[21] is a simplistic point-charge model, which is unable to account for covalent effects. For the coinage-metal monohalides, such Coulombic models systematically underestimate the Born–Haber–Fajans lattice energy, U_{POT}, by up to 36%.[2] Solid AuF, however, was excluded from the quantitative comparison in ref 2 because of lack of reliable experimental data. On the basis of the other coinage-metal halides listed in Table 1 of ref 2, the best estimate for the ionic $U_{POT}(AuF)$ will be 25–35% above that of a Waddington-type calculation. Because Waddington estimated $U_{POT}(AuF) \approx 800$ kJ mol^{-1}, the approximate correction yields scaled values.

$$U_{POT}(AuF) \approx 800(1.30 \pm 0.05) \text{kJmol}^{-1} \approx 1040 \pm 40 \text{kJmol}^{-1} \quad (3)$$

Thus, via a Born–Haber–Fajans cycle and with $\Delta H_L = U_{POT} + RT$ for the lattice enthalpy with reference to monatomic ions, we obtain

$$\Delta_f H^\circ(s)_{scaled}(AuF) \approx \Delta_f H^\circ(Au^+) + \Delta_f H^\circ(F^-) - U_{POT,scaled}(AuF) \approx -30 \pm 40 \text{kJmol}^{-1} \quad (4)$$

The latter value is not any more at variance with the recent calculations and agrees in characterizing AuF as a marginally stable solid.

Neither the lattice energy, nor the enthalpy of formation of solid copper monofluoride, CuF(s), are given in ref 9; therefore, it is included in Table 2. The Born–Haber–Fajans lattice energy[2] allows us to back calculate the standard enthalpy of atomization. The two independently obtained $\Delta_{at} H^\circ(s)$ values, 630 ± 25 and 646 kJ mol^{-1}, agree within the limits of error bars (Table 2). Solid copper fluoride, CuF$_2$, is listed with $\Delta_f H^\circ(s) = -542.7$ kJ mol^{-1};[9] thus, the reaction 2 CuF(s) → CuF$_2$(s) + Cu(s) is here calculated to be exothermic by approximately 120 $\pm$ 44 kJ mol^{-1}.

2.2. Extension to Alkaline-Earth Dihalides. Is the new type of linear relationship in ABT limited to crystals of diatomic

Table 3. Alkaline-Earth Dihalides, Molecular and Crystal Atomization Enthalpies: Coordination Number (CN), Experimental $\Delta_{at} H^\circ(g)$ and $\Delta_{at} H^\circ(s)$, Calculated $\Delta_{at} H^\circ(s,calc)$, and Difference $\Delta\Delta_{at} H^\circ(s) = \Delta_{at} H^\circ(s,calc) - \Delta_{at} H^\circ(s)$

MX$_2$	CN[a]	$\Delta_{at} H^\circ(g)$[b]	$\Delta_{at} H^\circ(s)$[c]	$\Delta_{at} H^\circ(s,calc)$	$\Delta\Delta_{at} H^\circ(s)$
					eq 5a
MgF$_2$	6	1025 ± 17	1430	1421 ± 22	−9
MgCl$_2$	6	777 ± 13	1095	1100 ± 17	+5
MgBr$_2$	6	671 ± 10	959	963 ± 13	+4
MgI$_2$	6	518 ± 10	788; (742)	765 ± 13	−23; (+23)
CaF$_2$	8	1111 ± 13	1559	1532 ± 17	−27
CaCl$_2$	6	883 ± 13	1220	1237 ± 17	+17
CaBr$_2$	6	785 ± 10	1087	1110 ± 13	+23
CaI$_2$	6	649 ± 17	940	934 ± 22	−6
SrF$_2$	8	1097 ± 17	1538	1514 ± 22	−24
SrCl$_2$	8	873 ± 13	1236	1224 ± 17	−12
SrBr$_2$	7 + 2	792 ± 17	1108	1119 ± 22	+11
SrI$_2$	7	650 ± 8	938	936 ± 10	−2
BaF$_2$	8	1143 ± 17	1545	1573 ± 22	+28
BaCl$_2$	8	916 ± 13	1277	1280 ± 17	+3
BaBr$_2$	7 + 2	824 ± 17	1154	1161 ± 22	+7
BaI$_2$	7 + 2	692 ± 23	989	990 ± 30	+1
					eq 5b
BeF$_2$	4	1276 ± 1[6,d]	1509	1495 ± 1	−14
BeCl$_2$	4	920 ± 25	1060	1081 ± 28	+21
BeBr$_2$	4	780 ± 25	903	917 ± 28	14
BeI$_2$	4	600 ± 40	731	709 ± 46	−22

[a] Reference 27. [b] Data from ref 28. [c] Data from refs 6 and 9. [d] Karton A.; Martin, J. M. L. *J. Phys. Chem. A* **2007**, *111*, 5936–5944.

molecules? The triatomic alkaline-earth dihalides, MX$_2$, constitute a well-investigated class of significantly ionic materials, for which the existence of linear atomization enthalpy relationships may be tested. Because of their unexpected bent structures, the heavy alkaline-earth dihalide molecules (M = Ca, Sr, Ba) have been long in the focus of interest.[7,23–27] The consensus has been reached that both the polarization of the metal ion by the anions and the d-orbital participation in the covalent part of bonding are significant; they indeed form the two sides of the same coin.[23–26] Recently, Donald and Hoffmann established an interesting link between the structural preferences in the monomer, dimer, and solid-state structures of the alkaline-earth dihalides.[27] It appears that the dimers (M$_2$X$_4$) and even the solids remember the structural peculiarities of the building blocks.[27] The alkaline-earth dihalides form a set of 20 materials with coordination numbers, CN, ranging from 4 to 8 (Table 3). The beryllium dihalides show CN = 4, whereas the remaining 16 MX$_2$ (containing M = Mg, Ca, Sr, Ba) have CN = 6, 7, or 8.[27] The latter 16 compounds show an excellent linear proportionality between $\Delta_{at} H^\circ(s)$ and $\Delta_{at} H^\circ(g)$ (Table 3 and Figure 2).

$$\Delta_{at} H^\circ(s,calc) = 1.2936 \Delta_{at} H^\circ(g) + 94.9 \text{kJmol}^{-1} \quad (5a)$$

The correlation coefficient is $R = 0.9977$, and the standard error is SE = 16.1 kJ mol^{-1}, comparable to that of the gas-phase input data. The experimental atomization enthalpies are taken from refs 6, 9, and 28. As might be anticipated for the smaller coordination number, the 4-fold coordinated BeX$_2$ follows a linear relation different from that in eq 5a, and for a given molecular atomization enthalpy, their crystal atomization enthalpies are smaller than those of other MX$_2$ solids. The difference is documented in the smaller slope and the much reduced, in fact, practically zero, intercept in eq 5b.

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$$\Delta_{at}H^o(s,calc) = 1.1625\Delta_{at}H^o(g) + 11.7 kJmol^{-1} \quad (5b)$$

with $R = 0.9980$ and SE $= 21.0$ kJ mol^{-1}.

In order to explore the size of the data domain for which linear atomization enthalpy relationships may hold, the standard atomization enthalpies in Table 1 are combined with those in Table 3. The combined data set of the 51 diatomic and triatomic halides and hydrides fits surprisingly well into a single linear relationship (Figure 3).

$$\Delta_{at}H^o(s,calc) = 1.2593\Delta_{at}H^o(g) + 119.6 kJmol^{-1} \quad (6)$$

The slope and intercept of eq 6 are intermediate to those of eqs 1 and 5. The fit is quantified by $R = 0.9984$ and further characterized by SE $= 18.5$ kJ mol^{-1}, and the corresponding rms relative error is 2.00%. The range of validity is significantly extended in going from two smaller sets to the combined data set; still, the standard error remains low, and the correlation coefficients are excellent throughout. It is remarkable and promising to find groups of diatomic and triatomic compounds connected by a common linear relation between their molecular and crystal atomization enthalpies. In contrast, different slopes and intercepts are recommended for the linear relations estimating the Born−Haber−Fajans lattice energies of MX and MX$_2$ crystals, because the correlation coefficients drop significantly if the same slope and a single intercept are used for the combined data set of MX and MX$_2$ solids.[29]

The alkaline-earth dihydrides form stable orthorhombic or rutile-type crystals.[9] The stability of their molecules is, however, open to discussion. Solid alkaline-earth dihydrides decompose into their elements at high temperatures.[28] Although free BeH$_2$ and MgH$_2$ molecules were first observed recently, a thorough experimental search for the free gas-phase hydrides CaH$_2$, SrH$_2$, and BaH$_2$ proved unsuccessful, as none of these species were found so far in the gas phase.[30a] They were identified, however, in solid rare gas matrices,[30b] and the available infrared spectra with supporting density functional calculations indicate decreasing obtuse valence angles in the sequence CaH$_2$, SrH$_2$, and BaH$_2$. Thus, the angular bending of alkaline-earth dihydrides obeys the same hard-bends-soft rule as the alkaline-earth dihalides.[26] Post-Hartree-Fock-type calculations to gain insight into the matter of stability and structure are under way in this laboratory, also in order to test linear relationships between their molecular and solid enthalpies of atomization. Work is in progress to investigate possible linear enthalpy relationships for the group 13 trihalides (MX$_3$) and ternary compounds (XYZ).

2.3. From Covalent to Metallic Bonds: Compounds of Groups 14−14, 4−4, 13−15, and 2−16. So far, we have been concerned with significantly, indeed often predominantly, ionic molecules and salts. Does this mean that the relationships work only for significantly ionic materials? Evidently, the question of generality for other classes of materials, for example, covalent or metallic, is to be answered in order to establish the limits of linear relationships in general. Starting from predominantly covalent systems formed by group 14 elements and proceeding
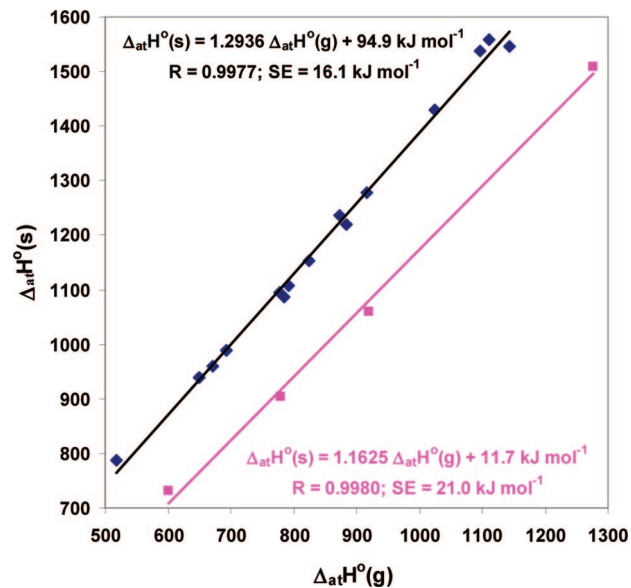
Figure 2. Linear relationships, eq 5, between the atomization enthalpies of solid and molecular alkaline-earth dihalides. MgX$_2$ to BaX$_2$ (black line), BeX$_2$ (pink line). Units in kJ mol^{-1}.
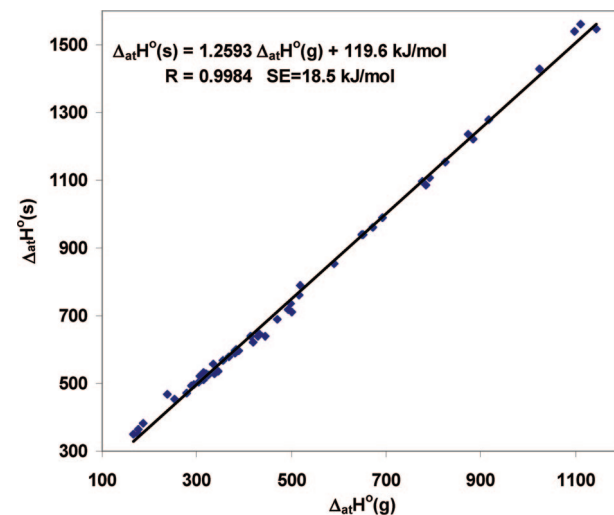
Figure 3. Combined linear regression on 51 halides and hydrides of groups 1, 2, and 11 metals. Crystalline atomization enthalpy, $\Delta_{at}H^o(s)$, versus molecular atomization enthalpy, $\Delta_{at}H^o(g)$. See eq 6. Units in kJ mol^{-1}.

to groups 4, 13−15, and 2−16 materials, it is possible to further assess the range of applicability of linear enthalpy relations similar to eq 1. In this section, isoelectronic eight-valence-electron (octet) systems are considered, as listed, for example, in the Periodic Table of Diatomic Molecules.[31] For a consistent comparison of the atomization enthalpy of a homonuclear diatomic molecule, X$_2$, with that of its element, the atomization enthalpy per two moles of the element X is taken as reference.[2,4b] Recent updates for $\Delta_{at}H^o(X)$ of the elements are placed on the web.[33] Note that many of the molecular or crystal enthalpy data given in Table 4 are either not listed in ref 9 or need corrections and updating therein.

Materials investigated by Colin and Goldfinger[3b] or Miedema and Gingerich[3c,d] are revisited, the data are updated, and the range of compounds is expanded. We note that the characteriza-

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Table 4. Structures and Atomization Enthalpies of 47 Compounds Formed by the Groups 14−14, 4−4, 13−15, and 2−16 Elements[a]

XY	crystal[b]	D^o_{298}	$\Delta_f H^o(s)$	$\Delta_{at} H^o(s)$	$\Delta_{at} H^o(s,calc)^a$
			14−14		
C_2 ($a^3\Pi$); C(s)	graphite	587^{11}	0	2×716.7^{33}	2×732.5
Si_2; Si(s)	D	310 ± 8	0	2×440^{33}	2×441.5
SiC	Zb	452 ± 5	-64 ± 2	1220 ± 2	1182
Ge_2; Ge(s)	D	264 ± 7	0	$2 \times (377 \pm 3)^{33}$	2×393
GeC	(Zb)	$(456^{34a})\ 386^{34b}$	+32	1054^{34c}	1043
GeSi	(Zb)	296 ± 20	$+5^{35b}$	820^{35b}	854 ± 42
Sn_2; Sn(s)	D	187	0	$2 \times (302 \pm 1.5)^{33}$	2×312.5
SnGe	Zb	234 ± 14^{35a}	$\sim -54^{35b}$	$\sim 726^{35b}$	724 ± 30
Pb_2; Pb(s)	fcc	$81 \pm 6^{11,c}$	0	$2 \times (195.2 \pm 1)$	2×201
SiPb	n. a.	169 ± 7^{37}	n .a.	see text	Table 5
GePb	n. a.	144.5^{37}	n. a.	see text	Table 5
SnPb	n. a.	126 ± 4^{37}	n. a.	see text	Table 5
			4−4		
Ti_2 ($^3\Delta_g$); Ti(s)	hex	152^{38}	0	$2 \times 473 \pm 3$	see text
Zr_2($^3\Delta_g$); Zr(s)	hex	298.2 ± 0.2	0	$2 \times 610 \pm 9$	see text
Hf_2($^3\Delta_g$); Hf(s)	hex	(328 ± 58)	0	$2 \times 618 \pm 7$	see text
			13−15		
BN	graphite	438 ± 12^{d}	-252 ± 6^{40}	1287 ± 8^{40}	eq 8: 1283 ± 23
BP	other	$348^{11,e}$	-93 ± 4^{40}	974 ± 7^{40}	963
AlN	W	356 ± 42	-318 ± 8^{40}	1122 ± 12^{40}	eq 8: 1125 ± 80
AlP	Zb	228^{41}	-118 ± 14^{f}	764 ± 28^{f}	711
AlAs	Zb	220^{41}	-117 ± 2^{f}	748 ± 32^{f}	694
AlSb	Zb	216 ± 6	-96 ± 10^{f}	692 ± 2^{f}	686
GaN	W	238^{41}	-157 ± 4^{40}	900 ± 6^{40}	eq 8: 898 ± 2
GaP	Zb	217^{41}	-100 ± 4^{40}	690 ± 6^{40}	688
GaAs	Zb	211^{41}	-80 ± 2^{40}	674 ± 4^{40}	675
GaSb	Zb	$192 \pm 13;^{42a}\ 165 \pm 10^{42b}$	-42 ± 2^{40}	578 ± 4^{40}	$(634 \pm 27);\ 578$
GaBi	n. a.	158 ± 16	n. a.	see text	Table 5
InN	W	202^{41}	-112 ± 6^{40}	828 ± 8^{40}	eq 8: 829 ± 2
InP	Zb	198 ± 8	-88	648	648
InAs	Zb	200 ± 10	-58 ± 2^{40}	618 ± 4^{40}	652
InSb	Zb	152 ± 12	-31 ± 0.6^{40}	538 ± 6^{40}	551 ± 26
TlN	W	Table 5	-80 ± 6^{44}	732 ± 6^{44}	see text
TlP	n. a.	209 ± 14	n. a.	See text	Table 5
TlAs	n. a.	198 ± 14	n. a.	See text	Table 5
TlSb	n. a.	126 ± 10	n. a.	See text	Table 5
TlBi	n. a.	120 ± 12	n. a.	See text	Table 5
			2−16		
BeO	W	452 ± 10^{31}	-609.4 ± 2.5^{9b}	1185 ± 6	1182
MgO	R	358 ± 7	-601.6 ± 0.3^{9b}	998	984
CaO	R	394^{g}	-634.9 ± 0.9^{9b}	1062	1060
SrO	R	426 ± 6	-592	1006 ± 2	see text
BaO	R	562 ± 13	-548	976 ± 6	see text
BeS	Zb	$338 \pm 64^{h};\ 372 \pm 59$	-234 ± 2.5	838 ± 7	see text
MgS	R, W	248^{I}	-346	770	753
CaS	R	335 ± 21	-482	938	936 ± 45
SrS	R	338 ± 17	-472	914	942 ± 36
BaS	R	400 ± 19	-460	916 ± 6	see text
MgSe	R	Table 5	-292.8^{45}	667^{45}	see text
MgTe	R, W	Table 5	-209.2^{45}	553^{45}	see text

[a] Observed $\Delta_{at}H^o(g)$, $\Delta_f H^o(s)$, and $\Delta_{at}H^o(s)$ data from ref 9, except when noted otherwise; calculated $\Delta_{at}H^o(s,calc)$ from eq 10. Propagated uncertainties of the input data (e. g., 2.102 D^o_{298}) are indicated only if in excess of the calculated SE = 24.0 kJ mol^{-1} of eq 10. Units kJ mol^{-1}. [b] Stable solid structures in standard state. D, diamond; Zb, zinc-blende; W, wurtzite; R, rock-salt (NaCl); fcc, face-centered cubic; hex, hexagonal structures. From Pettifor, D. *Bonding and Structure of Molecules and Solids.* Clarendon Press: Oxford, **1995**. [c] Gingerich, K. A.; Cocke, D. L.; Miller, F. *J. Chem. Phys.* **1976**, *64*, 4027−4033. [d] Peterson, K. A. *J. Chem. Phys.* **1995**, *102*, 262−277. [e] Gingerich, K. A. *J. Chem. Phys.* **1972**, *56*, 4239. [f] De Maria, G.; Gingerich, K. A.; Piacente, V. *J. Chem. Phys.* **1968**, *49*, 4705−4710. [g] See discussion in footnote (a) of ref 11; also Fuentealba, P.; Savin A. *J. Phys. Chem. A* **2000** *104*, 10882−10886. [h] Chase, M. W., Jr.; Davies, C.A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N., JANAF Thermochemical Tables, 3rd ed., J. Phys. Chem. ref. Data, Suppl. 1, **1985**, *14*, 1. [I] From ref 8d but referenced to ground-state atoms.

tion of a group of materials by the ratio $\alpha = \frac{1}{2}\Delta_{at}H^o(XY,s)/D^o_{298}(XY)$ imposes the intercept zero for the linear relation between the $\Delta_{at}H^o(s)$ and D^o_{298} values.[3] This, however, is equivalent to restrictive and unlikely assumptions on the enthalpy of sublimation (Scheme 1 and section 3). The standard sublimation enthalpy, $\Delta_{subl}H^o$, is a macroscopic measure for the magnitude of intermolecular interactions in solids. According to the first law of thermodynamics, the equation $\Delta_{at}H^o(s) = \Delta_{subl}H^o + D^o_{298}$ is exact; thus, the parameter α could be constant

within a group of materials only if $\Delta_{subl}H^o/D^o_{298}$ were constant for the whole group, thus, if the intermolecular interactions were directly proportional to the interatomic interactions. This is more than unlikely to be a reasonable approximation. A comparison of α parameters shows that they are far from being constant for the group 14−14 compounds but increase from α(C) = 1.22 to α(Sn) = 1.62 and α(Pb) = 2.25. The

(32) Harris, J.; Jones, R. O. *Phys. Rev. A* **1978**, *18*, 2159.

restriction is lifted by allowing for nonzero intercept in $\Delta_{at}H^o(XY, s) = aD^o_{298}(XY) + b$.

Table 4 lists a wide range of insulators, semiconductors, and metals varying between covalent and predominantly ionic materials. As noticed in ref 2, linear energy relations may apply to very different materials without inferring that the types of bonding in insulators and metals are closely related. This set is even more remarkable than the ones discussed in sections 2.1 and 2.2., because multiple bonds between two atoms differ very much from bonds in solids, and thus, the electron configurations of the atoms in molecules and atoms in solids differ widely. Furthermore, solids range from insulators through some of the best known semiconductors to metals such as tin and lead. Even the molecular ground states, for example, of C_2, SiC, and Si_2 differ in symmetry ($^1\Sigma_g^+$, $^3\Pi_i$, and $^3\Sigma^-$, respectively). We achieve some unification for the group 14 diatoms by considering triplet states only, thus referring to the first triplet state, $^3\Pi_u$, of C_2, which is barely 8 kJ mol^{-1} above the $^1\Sigma_g^+$ ground state. The ground states of molecules containing carbon differ from those of the other homonuclear diatoms within the 14−14 groups, which all show $^3\Sigma^-$ symmetry. The reason has been given by Harris and Jones: the π_u^4 electron configuration in C_2 is stabilized because of the absence of a p-core in carbon atom and the compactness of the 2p orbitals as compared to the 2s orbitals.[32] For the remaining diatoms, the np orbitals are more extended than the corresponding ns orbitals; therefore, the σ bond is stabilized. The available experimental diatomic dissociation and crystal atomization enthalpies are collected in Table 4. For some compounds, for example, BeS, less reliable values with large error margins are given in the literature. In consequence, they are of little use for the present comparisons and postponed for later consideration, as explained below. Strontium oxide and barium chalcogenides will be omitted from the correlation because the highly polarizable cations and d-orbital participation in bonding are affecting the diatoms and the solids in very different ways (see further discussion below).

We start by investigating the homonuclear or slightly polar diatoms and solids, as formed by group 14 atoms, and then widen the range by including increasingly more polar compounds formed by atoms of the groups 13−15 and 2−16. The subset of 12 pairs of group 14 diatoms and crystals covers a wide range of values from lead to graphite (Table 4). The data for GeC, SiPb, GePb, and SnPb seem to be uncertain or incomplete and will be discussed below. For the remaining eight

compounds, an excellent linear relationship is found; the regression line ($R = 0.9970$) is

$$\Delta_{at}H^o(s,calc) = 2.130D^o_{298} + 215.6 \, kJ \, mol^{-1} \qquad (7)$$

The rms error is SE = 23.4 kJ mol^{-1}. The largest single deviation $\Delta_{at}H^o(s,calc) - \Delta_{at}H^o(s) = -42$ kJ mol$^{-1} \approx -2$ SE is found for SiC. Most of the materials with some ionic character from group 14, that is, SiC, GeC, GeSi, and SnGe, are man-made and unusual.[35] Our results shed a new light on the unsettled controversy over the bond dissociation enthalpy of the GeC molecule. The experimental[9,34a] $D^o_{298} = 455.7 \pm 11$ kJ mol^{-1} and theoretical[34b] $D^o_{298} = 386$ kJ mol^{-1} results differ by 70 kJ mol^{-1}. A detailed comparative discussion of the experimental and computational methods hints to the likelihood of a contamination by traces of $^{12}C_7$ carbon clusters in the experimental sample.[34b] Sekkal and Zaoui presented a predictive study of solid GeC, which is expected to have important photovoltaic properties.[34c] Accordingly, solid zinc-blende-type germanium carbide should be thermodynamically unstable against decomposition into its elements by $\Delta_fH^o(GeC,s) = +32$ kJ mol^{-1}, equivalent to $\Delta_{at}H^o(GeC,s) = 1054$ kJ mol^{-1}.[34c] According to eq 7, this solid-state value is at variance with $D^o_{298} = 455.7 \pm 11$ kJ mol^{-1} but in good agreement with the calculated $D^o_{298} = 386$ kJ mol^{-1}; $\Delta_{at}H^o(GeC,s,calc) = 1038$ kJ g-at$^{-1} = 2.130 \times 386 + 215.6$ kJ mol^{-1}. As discussed in section 2.1, our rule appears to work for both stable and unstable solid materials. Thus, germanium carbide will be included in the extended correlations below, thereby raising the class-based subset to nine compounds. The $\Delta_{at}H^o(s,calc)$ values calculated for this subset from eq 7 are, however, not the ones listed in Table 4, this being reserved for the combined set also containing compounds between elements of the groups 13−15 and 2−16.

We emphasize the fact that the linear enthalpy relationship combines homonuclear diatomic molecules, such as C_2, Si_2, Sn_2, and Pb_2, with their crystals, that is, covalent graphite or silicon, and metals, that is, the tetragonal metallic white-tin and the 12-fold coordinated fcc lead. Apparently, the linear relationships are not affected by whether the valence electrons can be localized, as in most molecules and covalent crystals, or cannot be localized, as in metals. This observation is consistent with the statement by Phillips and Van Vechten that "the valence electrons in covalent crystals are itinerant, in much the same way as in metals like Na or Al."[36] Thus, even if metallic bond is a category sui generis, this does not necessarily mean that all properties of metals must differ from those of insulators.

Equation 7 cannot be transferred to the transition metal elements of the group 4 (Ti, Zr, Hf), where the bonding patterns are different. Solid elemental titanium, for example, is listed with $\Delta_{at}H^o(s) = 473 \pm 3$ kJ g-at^{-1}, a value comparable to that of silicon (440 ± 8 kJ g-at^{-1}).[33] The molecular bond, however, is much weaker for Ti_2 than Si_2; the relativistic multireference configuration interaction calculations by Hübner et al.[38] result in a $^3\Delta_g$ ground state with $D^o_{298}(Ti_2) = 152$ kJ mol^{-1}, and the Leroy-Bernstein-Lam analysis of Raman progressions gives 118

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kJ mol^{-1} only.[9] In either case, the calculated $\Delta_{at}H°$ according to eq 7 as $\Delta_{at}H°$(Ti,s) = 2.143 × $0.5D°_{298}$ + 103.0 kJ mol^{-1} ≤ 266 kJ mol^{-1} falls way below the solid's value of 473 ± 3 kJ mol^{-1}. Incidentally, the standard atomization enthalpies of zirconium, $\Delta_{at}H°$(Zr,s) = 610 ± 9 kJ g-at^{-1}, and hafnium, $\Delta_{at}H°$(Hf,s) = 618 ± 7 kJ g-at^{-1}, agree within their indicated error bars.[9] However, the very large uncertainty listed for $D°_{298}$ (Hf$_2$) = 328 ± 58 kJ mol^{-1} prevents including the tabulated value[9] into a linear regression with reasonable confidence. This $D°_{298}$ (Hf$_2$) value has been regarded as suspect and lacks direct experimental evidence.[39] In view of the almost identical solid-state atomization enthalpies of Zr and Hf, it seems acceptable to venture the guess that $D°_{298}$ (Hf$_2$) ≈ $D°_{298}$ (Zr$_2$) ≈ 300 kJ mol^{-1}.

The next class listed in Table 4 consists of 21 pairs of the groups' 13−15 family and contains some of the best-known zinc-blende-type semiconductors, such as GaAs. An essential difference between homopolar, diamond-like group 14 semiconductors and heteropolar, zinc-blende-like groups 13−15 semiconductors is due to perturbations by a long-range dipole potential. Thus, the diamond-like group 14 solids and the zinc-blende-like group 13 phosphides, arsenides, and antimonides may be expected to follow a common energetic trend. The stable form of boron nitride, BN, is a 3-fold coordinated graphite-like structure. The other boron pnictides are difficult to study, and the data seem unreliable.[40] The nitrides of aluminum, gallium, and thallium exhibit covalent-ionic binding and form the hexagonal wurtzite structure, which is favored by larger charge transfer to nitrogen as the more electronegative constituent. An excellent recent review of the solid-state energetics is given by Vasil'ev and Gachon.[40] The dissociation enthalpies for most group 13−15 diatoms have been calculated by Costales et al.[41] Two different $D°_{298}$ values are listed for gallium antimonide, GaSb (Table 4): the old experimental result[9,42a] of 192 ± 13 kJ mol^{-1} and a more recent MRD-CI (Multi Reference Doubles−Configuration Interaction) value of 165 ± 10 kJ mol^{-1}.[42b] The extrapolated contribution due to d-electron correlation, 30 ± 10 kJ mol^{-1}, is included in the latter value.[42b] As shown above for GeC, the new linear relationships may help clarify such situations.

Because some atomization enthalpies of 13−15 compounds remain unavailable, a secure subset of 14 will be considered first, totaling 23 compounds together with the nine compounds from group 14. Altogether, the group 13 nitrides show anomalous features in several respects[5c,43] and have been excluded from the extensive Born−Haber−Fajans lattice energy tables in section 12 of ref 9. Their directional polar-covalent bonds are stronger than those in zinc-blende-type materials, a fact also reflected in the pressure-dependent phonon properties.[43c] Thus, the group 13 nitrides form outliers, their $\Delta_{at}H°$(s) values being systematically above the overall regression line. If considered as a separate subgroup, however, the molecular and crystal atomization enthalpies of BN, AlN, GaN, and InN are found to be very closely correlated (Figure 4).

$$\Delta_{at}H°(s,calc) = 1.9232 D°_{298} + 440.2 \text{ kJ mol}^{-1} \qquad (8)$$

with R = 0.99995 and SE = 2.4 kJ mol^{-1} only. The intercepts in eqs 7 and 8 differ by 225 kJ mol^{-1}. Quantitative enthalpy data seem to be lacking for molecular and crystalline TlN, which is known in thin films; however, Gordienko and Fenochka[44] estimate $\Delta_{at}H°$(TlN,s) ≈ 732 kJ mol^{-1}. The excellent linear relationship, eq 8, allows the prediction of the dissociation enthalpy for the TlN diatom. By reversing eq 8, we obtain
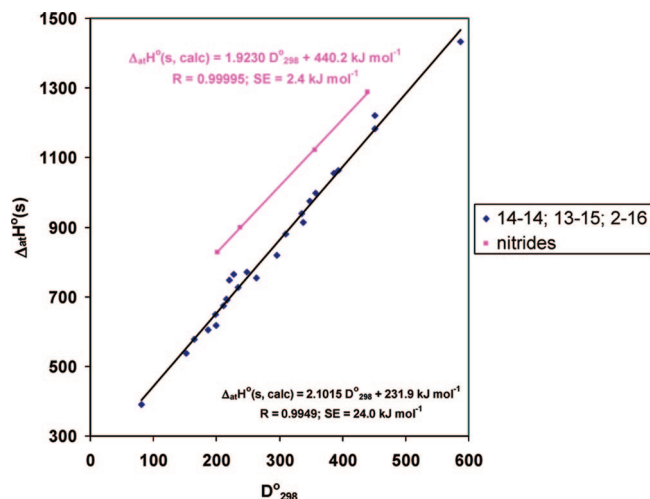

Figure 4. Linear relationships eqs 8 and 10 between the molecular, $\Delta_{at}H°$(s), and crystal, $\Delta_{at}H°$(s), atomization enthalpies of 29 group 14−14, 13−15, and 2−16 compounds. Group 13 nitrides are shown as a separate subgroup (pink line).

$D°_{298}$(TlN,calc) ≈ 152 kJ mol^{-1}. The accuracy of the predicted value depends on that of the estimate for the solid state of $\Delta_{at}H°$(s) ≈ 732 kJ mol^{-1} given in ref 44.

Extending the group 14−14 sample (including GeC) by adding the selected groups 13−15 compounds yields a highly correlated linear relationship for 19 compounds, R = 0.9942 and SE = 25.0 kJ mol^{-1}

$$\Delta_{at}H°(s,calc) = 2.104 D°_{298} + 230.9 \text{ kJmol}^{-1} \qquad (9)$$

The largest single deviations belong to AlP and AlAs, with −52 kJ mol^{-1} each. These deviations do not exceed the standard deviation by more than a factor of 2. According to eq 9, the theoretical MRD-CI result[42b] for GaSb of $D°_{298}$(GaSb) = 165 ± 10 kJ mol^{-1} appears to be the recommended value.

We now turn to the group 2 metal chalcogenides, ME, for which experimental data are unfortunately less abundant. The solids in this subset display mainly two structures (Table 4): the magnesium, calcium, strontium, and barium salts are stable in the rock-salt structure, whereas the less ionic beryllium chalcogenides are in the 4-fold coordinated wurtzite or zinc-blende structures. The ground state of the corresponding diatomic molecules is generally of $^1\Sigma^+$ symmetry. The bond dissociation enthalpy shows a significant dip from BeE to MgE and increases from the CaE to the BaE diatoms. However, the increase in $D°_{298}$ contrasts to a decrease in the crystal atomization enthalpy of the corresponding solids (Table 4). For all of the compounds discussed so far, $\Delta_{at}H°$(s) and $D°_{298}$ were directly proportional, but the trend is here broken and even reversed. A limit to the applicability of the present type of linear relationships is thus established. The reasons are that highly polarizable ions and d-orbital participation in bonding affect the diatoms and the solids in very different ways. The important role of ion polarization for the energy and geometry of alkali metal and alkaline-earth halides and hydrides has been discussed in the literature.[1e,7,23–27] In the case of the diatomic alkaline-earth chalcogenides, both the bond polarity and the cation polarizability increase significantly down the group. Thereby, the bond energy increases. This is not the case for the solid state, because the polarizing electric field is vectorially canceled by symmetry so that polarization does not significantly contribute to the

Table 5. Predicted Crystal Atomization Enthalpies, $\Delta_{at}H^{\circ}$(s,calc), and Enthalpies of Formation, $\Delta_f H^{\circ}$(s,calc), Based on Bond Dissociation Enthalpies, D°_{298}, and eq 10[a]

XY	input $D^{\circ}_{298} \pm \Delta D^{\circ}_{298}$	prediction	
		$\Delta_{at}H^{\circ}$(s,calc)	$\Delta_f H^{\circ}$(s,calc)
SiPb	169 ± 7[37]	587 ± 28	+48 ± 29
GePb	144.5 ± 7[37]	535 ± 28	+31 ± 29
SnPb	126 ± 4[37]	497 ± 26	0 ± 26
GaBi	158 ± 6[9]	564 ± 27	−82 ± 28
TlP	209 ± 14[9]	671 ± 38	−172 ± 38
TlAs	198 ± 14[9]	648 ± 38	−163 ± 38
TlSb	126 ± 10[9]	497 ± 33	−50 ± 33
TlBi	120 ± 12[9]	484 ± 35	−91 ± 35

XY	input $\Delta_{at}H^{\circ}$(s)	prediction D°_{298}(calc) = 0.476 $\Delta_{at}H^{\circ}$(s) − 110.3
TlN	732 ± 6	152 (eq 8, reversed)
BeS	838 ± 7	289 ± 24
MgSe	667[45]	207 ± 24
MgTe	553[45]	153 ± 24

[a] Uncertainty of predictions estimated from error propagation, for example, $(24^2 + 2.102 \Delta D^{\circ2}_{298})^{1/2}$. Units in kJ mol^{-1}.

cohesion energy. Strontium oxide and the barium chalcogenides are therefore omitted from further consideration. As mentioned at the beginning of this subsection, the bond dissociation enthalpy of beryllium sulfide is rather uncertain; thus, BeS will be included at a later stage of data evaluation (see Table 5).

The statistical evaluation is shown in Figure 4 on data of 25 different binary compounds, consisting of three subsets containing 9, 10, and 6 items formed from groups 14−14, 13−15, and 2−16 atoms, respectively. The linear relationship is very well satisfied, and the standard deviation is SE = 24.0 kJ mol^{-1}. The relative error is characterized by its rms value of 3.06%.

$$\Delta_{at}H^{\circ}(s,calc) = 2.1015 D^{\circ}_{298} + 231.9 \, kJ\,mol^{-1} \qquad (10)$$

The slope and the intercept of the best line are practically identical to those in eq 9. The correlation coefficient $R = 0.9949$ almost reaches that of the group 14−14 compound subset alone ($R = 0.9974$). The crystal atomization enthalpies calculated from eq 10 are listed in Table 4. The largest deviations $\Delta_{at}H^{\circ}$(s,calc) − $\Delta_{at}H^{\circ}$(s) are again ∼53 kJ mol^{-1} and thus about 2SE. It is safe to state that the range of application and the good performance of atom-based empirical relationships extend from homonuclear materials through the polar-covalent 13−15 compounds to ionic oxides of group 2 elements.

It is particularly gratifying that the present atom-referenced thermochemical approach does not need any assumptions on the stability of doubly, or even triply, charged anions in crystals. This marks a contrast to discussing solid metal chalcogenides and pnictides in terms of ionic lattices, Born−Haber−Fajans cycles,[9] and volume-based thermodynamics,[29] which are all known to be hampered by the necessity of ad hoc assumptions on the energy of highly charged anions (O^{2-}, N^{3-}, etc.) in solids. Here, the advantage and simplicity of ABT is evident.

In Table 4, the atomization enthalpies are incomplete for some of the compounds, and reference is made to Table 5. The linear relationships in eqs 8 and 10 allow a number of predictions to be made. Table 5 lists available D°_{298}, or $\Delta_{at}H^{\circ}$(s) data, and predicted $\Delta_{at}H^{\circ}$(s,calc), or D°_{298}(calc). The last column in Table 5 indicates predicted standard enthalpies of formation, according to $\Delta_f H^{\circ}$(XY,s) = $\Delta_f H^{\circ}$(X,g) + $\Delta_f H^{\circ}$(Y,g) − $\Delta_{at}H^{\circ}$(XY,s). The gas-phase dissociation enthalpies of SiPb, GePb, and SnPb have been measured recently.[37] The corresponding solids, SiPb(s),

GePb(s), and SnPb(s), are not expected in the form of ordered crystals but could exist as random alloys or amorphous thin films.[37] The bond dissociation enthalpy,[37] D°_{298}(SnPb) = 126 ± 4 kJ mol^{-1}, serves here as example for predicting the solid-state atomization enthalpy as $\Delta_{at}H^{\circ}$(SnPb,s,calc) = 497 ± 26 kJ mol^{-1} according to eq 10. It is calculated to be almost unstable against dissociation into the elements, Sn and Pb, by $\Delta_f H^{\circ}$(SnPb,s,calc) ≈ 0 ± 26 kJ mol^{-1}. Note that eq 7 derived from the group 14 subset alone yields a slightly smaller value of $\Delta_{at}H^{\circ}$(SnPb,s,calc) = 484 ± 26 kJ mol^{-1} and thus $\Delta_f H^{\circ}$ (SnPb,s,calc) ≈ +12 ± 26 kJ mol^{-1}. The difference is within the error bars.

Incidentally, the bond dissociation enthalpies of TlSb and SnPb are equal, D°_{298}(TlSb) = 126 ± 10 kJ mol^{-1}. Although the crystal atomization enthalpies are predicted to be 497 kJ mol^{-1} for both systems, the predicted enthalpies of formation differ by 50 kJ mol^{-1} because of the differences in enthalpies of formation of the gaseous atoms. Similarly, the standard enthalpy of formation of solid TlBi is predicted to be more negative than that of solid TlSb. This reflects the more than 50 kJ mol^{-1} difference in the enthalpies of formation of the gaseous atoms Bi and Sb.[9,33]

For MgSe and MgTe, the diatomic dissociation enthalpy seems missing, and it is very uncertain for BeS (Table 4). The available crystal values $\Delta_{at}H^{\circ}$(s) allow us to make predictions for the gas-phase molecules BeS, MgSe, and MgTe by reversing eq 10 into D°_{298}(calc) = 0.476 $\Delta_{at}H^{\circ}$(s) − 110.3 kJ mol^{-1} (Table 5). The equivalent procedure has been described above in obtaining D°_{298}(TlN,calc) ≈ 152 kJ mol^{-1} from eq 8.

2.4. Standard Sublimation Enthalpies. We continue with a general implication of the linear relations between $\Delta_{at}H^{\circ}$(g) and $\Delta_{at}H^{\circ}$(s). The standard sublimation enthalpy, $\Delta_{subl}H^{\circ}$, characterizes the reaction XY(s) → XY(g) and provides a macroscopic measure for the magnitude of intermolecular interactions in solids. It is defined by the following relations (Scheme 1).

$$\Delta_{subl}H^{\circ} = \Delta_f H^{\circ}(g) − \Delta_f H^{\circ}(s) = \Delta_{at}H^{\circ}(s) − \Delta_{at}H^{\circ}(g)$$

(11)

Direct measurements[46] are scarce and difficult to interpret for inorganic solids because their vapors in equilibrium with the condensed phases consist of mixtures of monomers, dimers, oligomers, and atoms,[28] but a variety of indirect measurements, estimates, and empirical correlations have been reported.[47,48] Unfortunately the experimental values are mostly given to an estimated accuracy of ± 15 kJ mol^{-1} only. Some data lack any indication of the reference temperature, other are given for 0 or 900 K, instead of 298.15 K. It remains very difficult, however, to correct for the effects of temperature and possible phase transitions in order to obtain the standard enthalpy of sublimation.[46e,48] Complete experimental information of this kind is rarely available, and it is therefore necessary to rely on various approximations. The same is true for quantum mechanical calculations of the standard enthalpy of sublimation, because

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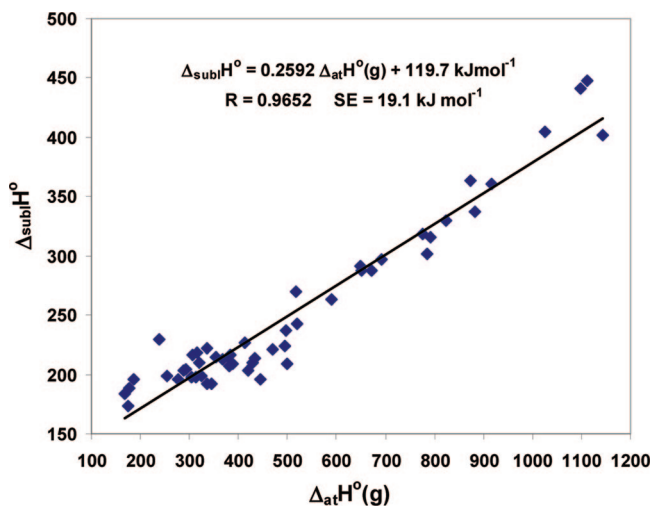
Figure 5. Linear relationship between the standard sublimation enthalpy, $\Delta_{subl}H^\circ$, of 51 solid diatomic and triatomic halides and hydrides of the groups 1, 2, and 11 and the corresponding molecular atomization enthalpy, $\Delta_{at}H^\circ(g)$. Data are in kJ mol^{-1}. Correlation coefficient $R = 0.9652$.

the temperature dependence of the energy and structure of crystal lattices (including phase transitions) are almost impossible to calculate at present.[4a,20c] Thus, the novel linear relationships between molecular and solid-state standard atomization enthalpies may be helpful in relating $\Delta_{subl}H^\circ$ to more easily accessible thermochemical data.

Combining eqs 6 and 11, we calculate $\Delta_{subl}H^\circ$ for the set of 51 diatomic and triatomic halides and hydrides of the groups 1, 2, and 11 by the best linear fit shown in Figure 6. The combined errors for the relatively small differences $\Delta_{subl}H^\circ = \Delta_{at}H^\circ(s) - \Delta_{at}H^\circ(g)$ of larger enthalpies of atomization are bound to increase, for both relative and absolute errors by propagation of the individual input errors. The linear regression equation

$$\Delta_{subl}H^\circ(calc) = 0.2592\Delta_{at}H^\circ(g) + 119.7 \text{kJmol}^{-1} \quad (12)$$

provides a one-to-one correspondence to eq 6, because the slope drops by one unit, and the intercept remains constant. The correlation coefficient decreases from $R = 0.9983$ in Figure 3 to $R = 0.9652$ in Figure 5. The standard error increases only marginally from 18.9 kJ mol^{-1} in eq 6 to 19.1 kJ mol^{-1} here. However, the average unsigned relative error increases to 5.25%, and the rms relative error is 8.00%, compared to 2.00% for eq 6. The limits of calculating sublimation enthalpy from molecular atomization enthalpy become evident in the lower left part of Figure 5.

Combining eqs 10 and 11, we now calculate $\Delta_{subl}H^\circ$ for the set of 25 compounds from the groups 14−14, 13−15, and 2−16 and the special subset of four group 13 nitrides. For comparing the standard sublimation enthalpies of diatomic solids, XY, and solid elements, X, with the corresponding molecular atomization enthalpies, D°_{298}, the sublimation enthalpy of two moles of the element X into one mole of X_2 is taken as reference. This is, of course, in analogy to the protocol followed in section 2.3 and in refs 2 and 4b. The best linear fit to D°_{298} is shown in Figure 6.

$$\Delta_{subl}H^\circ(calc) = 1.1106D^\circ_{298} + 227.66 \text{ kJmol}^{-1} \quad (13)$$

A comparison with eq 10 shows that the slope drops by one unit, and the intercepts are very similar in both equations. The correlation coefficient $R = 0.9816$ is reduced compared to $R =$
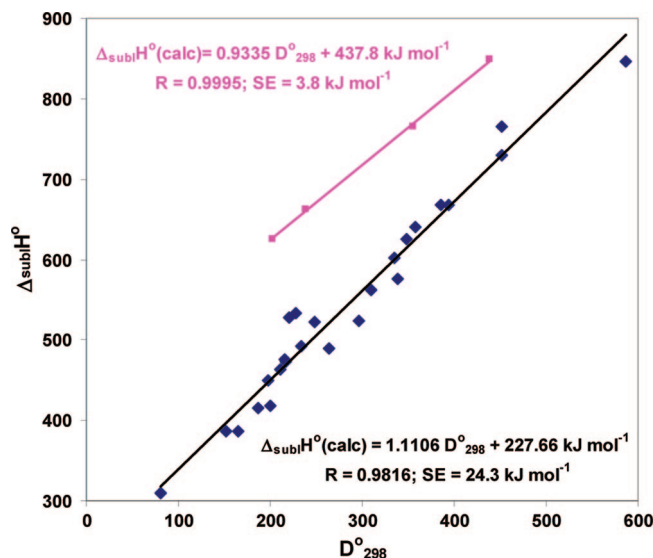
Figure 6. Linear relationship between the standard sublimation enthalpy, $\Delta_{subl}H^\circ$, of 29 group 14−14, 13−15, and 2−16 compounds (group 13 nitrides shown as separate subgroup) and the corresponding molecular bond dissociation enthalpy, D°_{298}. Data are in kJ mol^{-1}.

0.9948 in eq 10. The group 13 nitrides again form a separate highly correlated subset with the linear relationship shown in Figure 6.

$$\Delta_{subl}H^\circ(calc) = 0.9335D^\circ_{298} + 437.8 \text{kJmol}^{-1} \quad (14)$$

The difference in intercepts is similar to that found in eqs 7 and 8. The close linear relationships between the sublimation enthalpy of solids and the atomization enthalpy of molecules (shown in Figures 5 and 6) are remarkable and unexpected in view of the different bonding situations in solids and molecules. The linear relations can be used to predict the standard enthalpy of sublimation even for cases where either the molecular or the crystal atomization enthalpies are unknown; the knowledge of just one of these data will be sufficient. The thallium pnictides serve as examples here. We use eq 13 and the D°_{298} data given in Table 4 in order to predict the standard sublimation enthalpy of TlP in kJ mol^{-1} as $\Delta_{subl}H^\circ(\text{TlP,calc}) = 1.1106 (104.5 \pm 7) + 227.4 = 344 \pm 16$. Other thallium pnictides are predicted to have $\Delta_{subl}H^\circ(\text{TlAs,calc}) = 444 \pm 16$, $\Delta_{subl}H^\circ(\text{TlSb,calc}) = 364 \pm 12$, and $\Delta_{subl}H^\circ(\text{TlBi,calc}) = 356 \pm 14$ kJ mol^{-1}. The sublimation enthalpy of thallium nitride is predictable in two ways. We have the reverse situation, knowing only $\Delta_{at}H^\circ(s) \approx 732$ kJ mol^{-1} estimated in ref 42, and TlN belongs to the small subgroup of nitrides (Table 4). By reversing and extrapolating eq 8, the value $D^\circ_{298}(\text{TlN,calc}) \approx 152$ kJ mol^{-1} has been given in Table 5. Equation 14 yields the sublimation enthalpy $\Delta_{subl}H^\circ(\text{TlN,calc}) = 0.9335 D^\circ_{298}(\text{TlN,calc}) + 437.8 = 580$ kJ mol^{-1}, a value, of course, consistent with the one obtained by inserting the predicted $D^\circ_{298}(\text{TlN,calc})$ into eq 11.

3. Summary and Outlook

ABT reveals unrecognized linear relationships between molecular and crystal atomization enthalpies for a wide variety of compound classes. Out of the presented 107 data pairs, $\Delta_{at}H^\circ(g)$ and $\Delta_{at}H^\circ(s)$, of corresponding molecules and solids, 76 are connected by just two linear relationships, that is, eqs 6 and 10, whereas the four group 13 nitrides form a separate, but particularly well correlated subgroup with eq 8. Predictions are given for another 18 systems, and only three data pairs (SrO,

BaO, and BaS) are found to be exceptions to the rule. ABT offers very simple protocols to obtain, among other, the following information.

(i) Quantitative data on the instability of solid coinage-metal monohydrides and the marginal stability of solid AuF.

(ii) Estimates for the diatomic dissociation enthalpy of germanium carbide, GeC, gallium antimonide, GaSb, hafnium dimer, Hf_2, thallium nitride, TlN, beryllium sulfide, BeS, and two magnesium chalcogenides, that is, MgSe and MgTe.

(iii) Quantitative predictions of the crystal atomization enthalpies of SiPb, GePb, SnPb, and the thallium pnictides.

(iv) A new approach to calculating standard enthalpies of sublimation for systems where such thermodynamic data are not easily accessible by direct experiments and/or quantum mechanical calculations. The standard sublimation enthalpies of the thallium pnictides are predicted.

We bridge the gap between molecular and solid-state properties, that is, the nonscalable size regime in clusters, by connecting thermochemical properties of solid materials with those of the smallest molecules. The appeal rests on the straightforwardness in estimating fundamental thermochemical properties from very little experimental data, the accessibility to further test, and extendibility to other classes of molecules and solids. In ABT, there is no need for any assumptions on the stability of doubly or even triply charged anions in crystals. It is hoped that the present paper provides some stimulus for further experimental and theoretical work. Notwithstanding the links to Pauling's resonating valence bond model[5] and Sanderson's coordinated polymeric model[6] of solids, there is the open question about the underlying theoretical validity of empirical correlations. Relationships between molecular and solid-state properties may well come into the focus of interest and offer a chance to explore hitherto uncharted chemical territories.

Why did such simple empirical relationships between molecular and solid-state atomization enthalpies remain hidden for so long? Why was $\Delta_{at}H°$ not emphasized as an important atomistic ordering and reference entity? This is due to the convention basing thermochemical tables on the standard enthalpies of formation from the elements, as opposed to formation from atoms. Historically, the standard practice had the advantage that no knowledge of the atomization enthalpies of the elements was required. But now, the atomization enthalpies of the elements are well established. It is also a fact that thermodynamics, as one of the three pillars of theoretical chemistry, is independent of the existence of atoms and is a consistent theory without any reference to atoms. Nevertheless, thermochemistry seems to have overlooked a number of interesting and useful energy relationships between solids and molecules by exclusively using the convention of referencing to elements in their standard states. A collection of ideal-gas atoms is definitely a more uniform thermodynamic reference than the corresponding elements, which may form solids, real gases, or even liquids in their standard states.

Efforts to establishing meaningful relations between the standard enthalpies of formation of solids and molecules are discouraging; for example, the $\Delta_f H°(s)$ and $\Delta_f H°(g)$ of the group 14 materials listed in Table 4 correlate extremely poorly, with a very wide scatter from the best line and $R \approx 0.45$ only. This is the case because by convention, $\Delta_f H°(s) \equiv 0$ for the elements, whereas the gas phase $\Delta_f H°(g)$ values for the corresponding homonuclear diatoms cover the wide range between 300 and 850 kJ mol^{-1}. The present relations in atomization enthalpies would have become known much earlier if thermochemical data were tabulated in terms of atomization enthalpies, that is, in terms of ABT. Admittedly, I cannot complain, because otherwise I would have lost all the joy and fun in exploring the relationships. It will be interesting to explore how many more such relationships are valid.