Born−Haber−Fajans Cycle Generalized: Linear Energy Relation between Molecules, Crystals, and Metals

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Abstract: Classical procedures to calculate ion-based lattice potential energies (U_{POT}) assume formal integral charges on the structural units; consequently, poor results are anticipated when significant covalency is present. To generalize the procedures beyond strictly ionic solids, a method is needed for calculating (i) physically reasonable partial charges, δ, and (ii) well-defined and consistent asymptotic reference energies corresponding to the separated structural components. The problem is here treated for groups 1 and 11 monohalides and monohydrides, and for the alkali metal elements (with their metallic bonds), by using the valence-state atoms-in-molecules (VSAM) model of von Szentpály et al. (*J. Phys. Chem. A* **2001**, *105*, 9467). In this model, the Born−Haber−Fajans reference energy, U_{POT}, of free ions, M^+ and Y^-, is replaced by the energy of charged dissociation products, $M^{\delta+}$ and $Y^{\delta-}$, of equalized electronegativity. The partial atomic charge is obtained via the iso-electronegativity principle, and the asymptotic energy reference of separated free ions is lowered by the "ion demotion energy", $IDE = -^1/_2(1 - \delta_{VS})(I_{VS,M} - A_{VS,Y})$, where δ_{VS} is the valence-state partial charge and $(I_{VS,M} - A_{VS,Y})$ is the difference between the valence-state ionization potential and electron affinity of the M and Y atoms producing the charged species. A very close linear relation ($R = 0.994$) is found between the molecular valence-state dissociation energy, D_{VS}, of the VSAM model, and our valence-state-based lattice potential energy, $U_{VS} = U_{POT} - ^1/_2(1 - \delta_{VS})(I_{VS,M} - A_{VS,Y}) = 1.230D_{VS} + 86.4$ kJ mol^{-1}. Predictions are given for the lattice energy of AuF, the coinage metal monohydrides, and the molecular dissociation energy, D_e, of AuI. The coinage metals (Cu, Ag, and Au) do not fit into this linear regression because d orbitals are strongly involved in their metallic bonding, while s orbitals dominate their homonuclear molecular bonding.

1. Introduction

The lattice potential energy, U_{POT}, of an ionic salt, M^+Y^-, measures the energy required to convert a solid ionic material into its independent gaseous ions (Scheme 1).[1]

U_{POT} is primarily defined for materials assumed to be completely ionic and is not directly measurable experimentally, even for such materials, because salts generally dissociate either into neutral atoms or neutral atom groups in the gas phase. While the true dissociation process is rather complicated, the "simplification" of "constrained dissociation" into gaseous free ions operates by maintaining the Coulombic interactions between all structural components of the solid at all internuclear distances, R. The beauty and simplicity of the model is matched by its success in describing ionic crystals. For solid polar covalent materials, $M^{\delta+}Y^{\delta-}$(s), the "lattice energy" is defined again with reference to gaseous ions, M^+(g) + Y^-(g); in such cases, the initial partial charges of the solid ($\pm\delta$) do not remain constant, but must be increased to become the

Scheme 1. Born−Haber−Fajans Thermochemical Energy Cycle for a Strictly Ionic Solid Material, M^+Y^-(s)^a
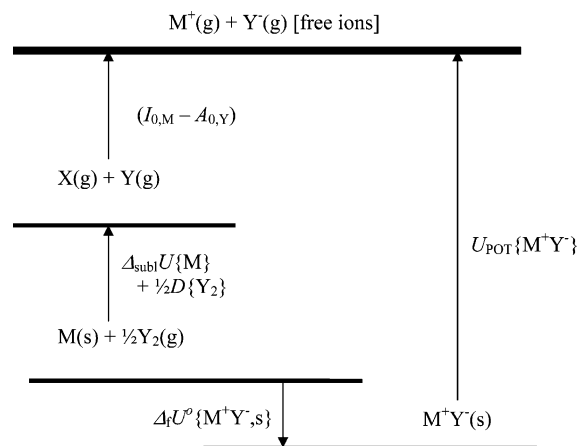
^{a} $\Delta_f U^\circ$ is the standard energy of formation of the bracketed species, $\Delta_{subl}U$ the sublimation energy, and D the bond dissociation energy; g refers to gaseous, s to solid states. $I_{0,M}$, $A_{0,Y}$ are respectively the ground-state ionization potential and electron affinity of the gaseous atoms forming the free ions. The reference state is that of gaseous "free ions" (heavy horizontal line).

integer formal charges of the gaseous products during the dissociation process so defined. These complicated shifts in the

interaction modes destroy the great simplicity of the model for this case.

In both the scenarios described, the so-called "experimental" U_{POT}^{BHF} can generally be evaluated from a Born−Haber−Fajans thermochemical cycle,[1] using tabulated values[2] of the standard enthalpies of formation, $\Delta_f H°$, of the relevant materials and their component ions. In each case, the starting material is the condensed-phase compound (covalent or ionic), and the products are the fully charged gaseous ions. Note that the discussion which follows is entirely in terms of energies, rather than enthalpies. The adjustments involved[3] are small and hardly significant for present purposes.

Over the past few years, one of us and colleagues have developed simple, yet reliable, procedures for evaluating U_{POT} for strictly ionic materials of essentially any complexity.[4] These procedures require knowledge of only the chemical formula and integer charge distribution of the material, together with its formula unit volume (obtained from routine X-ray crystallography or from density[5a] or even estimated by summing tabulated ion volumes[5b−d]). Further thermodynamic functions (e.g., standard entropy,[6] etc.) have been found to depend on volume,[4] and a number of previously undiscovered, but quite general, thermodynamic relationships (e.g., the thermodynamic "difference" rule,[7] the isomegethic rule,[8] etc.) have been reported and have been extended into an approach we now term "volume-based thermodynamics", VBT.[4] These procedures and relationships owe their success to the almost overwhelming predominance of the Coulombic forces between the ions, balanced against repulsive forces, with relatively minor contributions from other interactions. When covalent contributions become significant, however, these ionic-based procedures become less reliable, as Yoder and Flora have recently demonstrated.[9]

As will be observed in Figure 1 (data in Table 1), U_{POT}^{BHF} for the monohalides is generally larger, for the hydrides smaller, than is predicted by our simplistic Coulombic VBT procedure, which assumes integer charges for the separated gaseous species. The differences increase as the covalency or core repulsion grows, and as the differences in electronegativity decrease.

Two other points are worth mentioning here:

(i) The required ion data for evaluations such as these are not always available. Particular cases in question are gaseous multiply charged anions, such as O^{2-} or N^{3-}, which do not exist as stable species.[10] In such cases, U_{POT} has generally been estimated, as an average value, by reference to experimental data for ionic solids or, alternatively, may be calculated using specialized and computationally costly, quantum theoretical methods.[11]
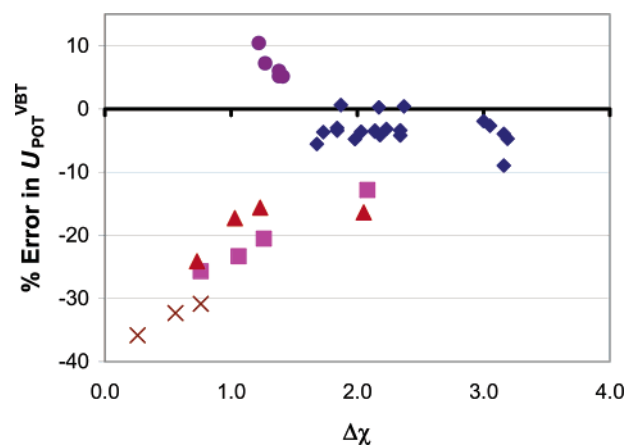
(2) (a) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 83rd ed.; CRC Press: Boca Raton, London, New York, Washington, D.C., 2002−2003; sections 5-1 ff and 12-22 ff. (b) Marcus, Y. *Ion Properties;* Marcel Dekker: New York, 1997.
(3) Jenkins, H. D. B. *J. Chem. Educ.* **2005**, *82*, 950−952.
(4) Glasser, L.; Jenkins, H. D. B. *Chem. Soc. Rev.* **2005**, *10*, 866−874.
(5) (a) Jenkins, H. D. B.; Tudela, D.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 2364−2367. (b) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 4378−4388. (c) Marcus, Y.; Jenkins, H. D. B.; Glasser, L. *J. Chem. Soc., Dalton Trans.* **2002**, 3795−3798. (d) Jenkins, H. D. B.; Liebman, J. F. *Inorg. Chem.* **2005**, *44*, 6369−6372.
(6) (a) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2003**, *42*, 8702−8708. (b) Glasser, L.; Jenkins, H. D. B. *Thermochim. Acta* **2004**, *414*, 125−130.
(7) Jenkins, H. D. B.; Glasser, L. *J. Am. Chem. Soc.* **2004**, *126*, 15809−15817.
(8) Jenkins, H. D. B.; Glasser, L.; Klapötke, T. M.; Crawford, M.-J.; Bhasin, K. K.; Lee, J.; Schrobilgen, G. J.; Sunderlin, L. S.; Liebman, J. F. *Inorg. Chem.* **2004**, *43*, 6238−6248.
(9) Yoder, C. H.; Flora, N. J. *Am. Mineral.* **2005**, *90*, 488−496.

Figure 1. Percent error in our VBT-based U_{POT} [$= 100(U_{POT}^{VBT} - U_{POT}^{BHF})/U_{POT}^{BHF}$] versus Pauling electronegativity difference, $\Delta\chi$, for 31 monohalides and 5 hydrides. Distinguished by symbols from the remainder are the coinage metal monohalides (except AuF) [Cu (■), Ag (▲), and Au (×)] and the alkali metal hydrides [●] all of which are generally regarded as polar covalent. Data appear in Table 1.

Table 1. Comparison of VBT-Based Lattice Energy and Born−Haber−Fajans Lattice Energy[a]

	$\Delta\chi$	V_m/nm^3	U_{POT}^{VBT}/kJ mol^{-1}	U_{POT}^{BHF}	% error
LiH	1.22	0.0171	1014	918	10.4
NaH	1.27	0.0292	865	807	7.2
KH	1.38	0.0466	756	713	6.0
RbH	1.38	0.0553	719	684	5.2
CsH	1.41	0.0652	687	653	5.2
LiF	3.00	0.0163	1029	1049	−1.9
LiCl	2.18	0.0340	828	864	−4.2
LiBr	1.98	0.0416	781	820	−4.8
LiI	1.68	0.0547	722	764	−5.5
NaF	3.05	0.0251	905	930	−2.7
NaCl	2.23	0.0447	765	790	−3.2
NaBr	2.03	0.0534	727	754	−3.6
NaI	1.73	0.0678	679	705	−3.7
KF	3.16	0.0389	796	829	−4.0
KCl	2.34	0.0623	696	720	−3.4
KBr	2.14	0.0721	667	691	−3.4
KI	1.84	0.0884	631	650	−3.0
RbF	3.16	0.0542	724	795	−9.0
RbCl	2.34	0.0727	666	695	−4.2
RbBr	2.14	0.0820	644	668	−3.6
RbI	1.84	0.0993	610	632	−3.4
CsF	3.19	0.0544	723	759	−4.7
CsCl	2.37	0.0701	673	670	0.4
CsBr	2.17	0.0798	649	647	0.3
CsI	1.87	0.0956	617	613	0.6
CuF	2.08	0.0194	977	1121	−12.8
CuCl	1.26	0.0397	791	996	−20.5
CuBr	1.06	0.0478	750	978	−23.3
CuI	0.76	0.0558	718	966	−25.7
AgF	2.05	0.0360	814	974	−16.4
AgCl	1.23	0.0428	774	918	−15.6
AgBr	1.03	0.0482	748	905	−17.3
AgI	0.73	0.0686	677	892	−24.1
AuCl	0.76	0.0508	737	1066	−30.8
AuBr	0.56	0.0561	717	1059	−32.3
AuI	0.26	0.0652	687	1070	−35.8

[a] Pauling electronegativity difference, $\Delta\chi$; formula unit volume, V_m; volume-based lattice potential energy, U_{POT}^{VBT}; Born−Haber−Fajans cycle-based lattice potential energy, U_{POT}^{BHF}; and % error in VBT-based U_{POT} [$= 100(U_{POT}^{VBT} - U_{POT}^{BHF})/U_{POT}^{BHF}$].

(ii) Quantitative Born−Landé type relations between the lattice energy and the near-neighbor distance, R_0, of cubic crystals are valid well beyond the group of ionic metal halides.[12] Quite unexpectedly, the assumption of ionic bonding by point

charge attraction yields a good correlation between U_{POT} and $1/R_0$ even for the series of alkali metals.[12b] As O'Keefe[12a] and Grodzicki[12c] have pointed out, such quantitative agreements do not necessarily prove the physical reality of the assumptions; in particular, partial covalent bonding cannot be separated from the ionic Madelung energy around the equilibrium distance.[12c] In addition, important finite-ion-size corrections to the conventional Madelung number are required in many studies of lattice energies, even for ionic crystals.[13]

The present contribution provides a generalization of the thermochemical cycle for obtaining U_{POT} by incorporating the essential ingredients of the valence-state atoms-in-molecules (VSAM) model of bonding developed by one of us and colleagues.[14,15] This is a method of constructing a universal potential energy curve (PEC) applicable to all diatomic molecules, from covalent to polar, even to those of high ionicity.

The bonding model involves the optionally polarizable[15] VSAM "ansatz" which describes the electron-pair bond in the gaseous M−Y molecules by superposing the ionic M^+Y^- and M^-Y^+ configurations with the covalent M:Y structure, as "weighted" contributions whose "weights" are determined by electronegativity (EN) equalization, as described below.[14] An important starting point was Mulliken's statement that the potential well depth, D_e, is a good practical measure of the diatomic bond energy; however, a theoretically more significant "intrinsic dissociation energy", the valence-state dissociation energy, D_{VS}, is obtained by measuring the energy from the asymptote in which the atoms are in suitable valence states, VS.[16] The VSAM model has been applied to a series of covalent and polar diatomic molecules, including the alkali metal dimers, to yield D_{VS} and the partial charge, δ, for each molecule. The resulting higher spectroscopic constants (vibration−rotation coupling and anharmonicity) and the overall accuracy of the PECs are substantially improved[14,15] relative to those of other

parametrized PECs, such as the Morse potential. It is found that D_{VS} is a parameter with high information content, e.g., R_e/D_{VS} (where R_e represents the equilibrium bond distance in the molecule) acts as the linear scaling factor for the harmonic force constant, k_e, in generating transferable force constant increments, $k_e R_e/D_{VS}$, which cannot be achieved using D_e or D_{ion}, the ionic dissociation energy.[14c]

In the present paper we investigate the relations between D_{VS} and U_{POT}, noting that general relations between D_e and the atomization energy, $\Delta_{at}U$, have not been reported, as far as we know. We show that measuring the energy from the partially charged gaseous VS atoms, as the separated structural units of crystals, is able to achieve the required generalization.

One purpose of this work is to enable us to generate thermodynamic cycles for materials for which the necessary data are presently unavailable, or unreliable. Examples of materials for which current data are unsuitable are oxides of the transition metals and nitrides in general, since the multiply charged gaseous anions are unstable species, as earlier noted. Development of procedures by which to reliably examine the energetics of these materials would form a valuable addition to this area of chemistry, and these are planned for the future.

2. Theory

2.1. The Valence-State Energy of a Crystal. In searching for a model of the structural components in the crystal and the corresponding asymptotic reference energies, we are led to the valence-state concept of molecular bond analysis. We adapt, and here apply to crystals, Ruedenberg's most general definition of valence-state atoms:[17] that atoms in the valence-state corresponding to a given molecule are generated by a constrained dissociation that maintains ("freezes") the interference-free portions of the electron populations and intra-atomic electron-pair populations at their molecular values. Ruedenberg's definition separates the wave-mechanical interference from the other steps in the bond formation (e.g. the ionic attraction after charge transfer) and characterizes partially charged atoms-in-molecules. Since electron pairs are shared in bonds, there is always an energetically repulsive "sharing-penetration" present in molecules, which increases the electron-pair population of the atoms-in-the-molecule beyond that of free atoms, or appropriate hybridized atoms Thus, the sharing-penetration energy promotes the valence-state atoms above their ground or hybridized state.[17]

By analogy, we define the valence-state atoms corresponding to a given crystal by separating the crystal into its gaseous structural components while keeping their partial charges and intra-atomic electron-pair populations frozen during this process. Two problems had to be addressed before application of these ideas to the relation between molecules and crystals:

(i) Ruedenberg's definition normally requires sophisticated calculations of the interference-free one-electron and electron-pair densities and their integrated populations for the atoms-in-the-molecule. This will, of course, also apply for a corresponding Ruedenberg analysis of a crystal.

(ii) The populations, in particular the electron-pair populations, depend on the theoretical modeling; thus, the amount of sharing-penetration and, consequently, the asymptotic VS reference energy differ according to the model used, e.g. valence bond or SCF-MO.[17]

(10) (a) Spence, D.; Chupka, W. A.; Stevens, C. M. *Phys. Rev. A* **1982**, *26*, 654−657. (b) Harding, J. H.; Pyper, N. C. *Philos. Mag. Lett.* **1995**, *71*, 113−121. (c) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F., III. *Chem. Rev.* **2002**, *102*, 231−282. (d) Even though ions such as O^{2-} are not "bound" states and their energies cannot be satisfactorily computed using ab initio methods, nonetheless thermochemical cycles *can* be drawn incorporating them because the thermodynamic property corresponding to enthalpy (or energy) change is a *state function*, and a cycle is thus valid provided that initial and final states defined for two enthalpy changes are *identical*, even if not realizable. Thus, we can incorporate "hypothetical" states of this kind into cycles. So, for example, a value for $\Delta_f H°(O^{2-},g)$, averaged over different oxides, can be estimated. See for example Dasent, W. E. *Inorganic Energetics*, 2nd ed.; Cambridge: Cambridge University Press: 1973.

(11) (a) Pisani, C., Ed. *Quantum-Mechanical ab Initio Calculation of the Properties of Crystalline Materials*; Springer: Berlin, 1996. (b) Doll, K.; Stoll, H. *Phys. Rev. B* **1997**, *56*, 10121−10127. (c) Smithson, H.; Marianetti, C. A.; Morgan, D.; Van der Ven, A.; Predith, A.; Ceder, G. *Phys. Rev. B* **2002**, *66*, Art. 144107. (d) Pisani, C.; Busso, M.; Capecchi, G.; Cassara, S.; Dovesi, R.; Maschio, L.; Zicovich-Wilson, C.; Schütz, M. *J. Chem. Phys.* **2005**, *122*, Art. 094113.

(12) (a) O'Keefe, M. In *Structure and Bonding in Solids*; O'Keefe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. 1, p 299. (b) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1989**, *93*, 3308−3311. (c) Grodzicki, M. In *Theoretical Models of Chemical Bonding*, Part 2, Maksić, Z. B., Ed.; Springer-Verlag: Berlin, Germany, 1990; pp 417−452.

(13) Wilson, J. W.; Heinbockel J. H.; Outlaw, R. A. *J. Chem. Phys.* **1986**, *84*, 543−544.

(14) (a) von Szentpály, L. *J. Mol. Struct. (THEOCHEM)* **1991**, *233*, 71−81. (b) von Szentpály, L. *Chem. Phys. Lett.* **1995**, *245*, 209−214. (c) von Szentpály, L. *J. Phys. Chem. A* **1998**, *102*, 10912−10915. (d) Gardner, D. O. N.; von Szentpály, L. *J. Phys. Chem. A* **1999**, *103*, 9313−9322. (e) von Szentpály, L.; Gardner, D. O. N. *J. Phys. Chem. A* **2001**, *105*, 9467−9477.

(15) Donald, K. J.; Mulder, W. H.; von Szentpály, L. *J. Phys. Chem. A* **2004**, *108*, 595−606.

(16) (a) Mulliken, R. In *Quantum Theory of Atoms, Molecules and the Solid State*; Löwdin, P.-O., Ed.; Academic Press: New York. 1966; p 231. (b) Mulliken, R. J. *Phys. Chem.* **1952**, *56*, 295−311.

(17) Ruedenberg, K. *Rev. Mod. Phys.* **1962**, *34*, 326−376.

In our VSAM model, we bypass the calculations of densities and pair densities, and obtain orbital populations and pair populations by calculating the partial charges and the sharing-penetration energy on minimizing the sum of VS energies by charge transfer, a procedure equivalent to VS electronegativity (VSEN) equalization.[14a,b] Since the VSAM model has been published, only its salient features are given here, and the reader is referred to the literature for further details.[14,15]

The sharing-penetration energy in a bonding atomic orbital (AO) of occupation number n_j is proportional to $(n_j/2)^2$, and the energy of the VS atom, M, is a parabolic function of n_j

$$E_{VS}(M,n_j) = E_{VS}(M,0) - n_j I_{VS,j} + (n_j/2)^2 (I_{VS,j} - A_{VS,j}) \quad (1)$$

where $0 \leq n_j \leq 2$, $I_{VS,j}$ is the valence-state ionization energy, and $A_{VS,j}$, the valence-state electron affinity of M. The negative gradient, $-\partial E_{VS}(M,n_j)/\partial n_j$, defines the VSEN function, which is thus characterized by a straight line of slope $-\frac{1}{2}(I_{VS,j} - A_{VS,j})$ connecting the two ionic electronegativity (EN) values, viz., I_j and A_j

$$\chi_{VS}(n_j) = I_{VS,j} - \frac{1}{2}n_j(I_{VS,j} - A_{VS,j}) = $$
$$\frac{1}{2}[I_{VS,j} + A_{VS,j} + (I_{VS,j} - A_{VS,j})\delta_j] = \chi_j^0 + \eta_j\delta_j \quad (2)$$

where $\chi_j^0 = \frac{1}{2}(I_{VS,j} + A_{VS,j})$ is Mulliken's EN, $\eta_j = \frac{1}{2}(I_{VS,j} - A_{VS,j})$ is the valence-orbital hardness, and $\delta_j = 1 - n_j$ is the partial charge. To determine the electron-pair distribution in polar bonds by charge-dependent electronegativity alone we must, of course, correctly reproduce the electronegativity of the ions, which is found by several methods to be $\chi\{M^+\} = I_{VS,j}$ and $\chi\{M^-\} = A_{VS,j}$.[18]

How then is VS promotion energy to be calculated for polar molecules and solids when integer charges are not justified? To assess the charge-transfer interaction between VS atoms, we consider the gaseous diatomic molecule MY formed between a monovalent metal atom, M, and a halogen, Y. The atoms interact at a distance comparable to the classical ionic–covalent crossover radius, $R_c = e^2/4\pi\epsilon_0(I_{VS,M} - A_{VS,Y})$, minimizing the sum of their VS energies, $E_{VS}\{M^{\delta+}\} + E_{VS}\{Y^{\delta-}\}$, by charge transfer. The minimum energy is reached for $\partial E_{VS}\{M^{\delta+}\}/\partial\delta = \partial E_{VS}\{Y^{\delta-}\}/\partial\delta$, i.e., when the VSENs become equalized.[14a] When resolved for the partial charge, VSEN equalization across the bond results in

$$\delta_{VS;j}\{M\} = \frac{[\chi_i^0\{Y\} - \chi_j^0\{M\}]}{[\eta_i\{Y\} + \eta_j\{M\}]} = \frac{|\Delta\chi^0|}{\sum\eta} \quad (3)$$

D_{VS} is defined as the difference between the minimum of the PEC and the VS energy at infinite internuclear separation. We need a charge-dependent relation between D_{VS} and the ionic dissociation energy, D_{ion}, to which the former converges for $|\delta_{VS}| \to 1$

$$D_{ion}\{MY\} = D_e\{MY\} + (I_{0,M} - A_{0,Y}) \quad (4)$$

$I_{0,M}$ and $A_{0,Y}$ are respectively the ground-state ionization energy and the ground-state electron affinity of Y. For our

example molecule, MY, the expression from ref 14c for the sum of sharing-penetration energies is expanded to yield

$$D_{VS}\{MY\} = D_e\{MY\} + \sum E_{hyb} + \frac{1}{2}[\sum\eta - (\Delta\chi)^2/\sum\eta]$$
$$= D_e\{MY\} + \sum E_{hyb} + \frac{1}{2}(1 - \delta_{VS,M}^2)\sum\eta$$
$$= D_e\{MY\} + \sum E_{hyb} +$$
$$\frac{1}{2}(1 + \delta_{VS,M})(I_{VS,M} - A_{VS,Y}) \quad (5)$$

where $I_{VS,M}$ and $A_{VS,Y}$ are respectively the valence-state ionization potential and electron affinity of the cation- and anion-forming atoms and $\sum E_{hyb}$ is the hybridization and deformational promotion energy, including averaging over the spin–orbit split states of the given electron configuration.[14,15]

The contributions of $A_{VS,M}$ and $I_{VS,Y}$, as explicitly present in $\sum\eta$, become absorbed in $\delta_{VS,M}$; thus, eq 5 highlights the direct relation of D_{VS} with the ionic promotion energy, $(I_{VS,M} - A_{VS,Y})$. The promotion energy due to sharing-penetration depends linearly on the partial charge and is smaller than the energy needed to generate free ions.

For the other extreme of vanishing bond polarity we consider a singly bonded homonuclear diatomic molecule, M_2, with the one-center electron-pair repulsion energy in the bonding atomic orbital j being J_M. According to the restricted Hartree–Fock (RHF) theory, the energy $1/4J_M$ per atom is the leading term in the VS promotion energy; thus, it becomes $\frac{1}{2}J_M$ for M_2.[17] On the RHF-PEC of the homonuclear molecule, the valence-state energy asymptote is reached proportionally to $1/R$, and we get $D_{VS} = D_e + \frac{1}{2}J_M$. This common feature for ionic MY and covalent M_2 molecules has been a principal reason for adopting the Coulombic "ansatz" for a universal VS PEC.[14b] Many tests on a large set of diatomic molecules have shown that the Coulombic $1/R$ attraction correctly describes, with reference to the VS energy, the interactions of the atoms as they are bonded in the molecules.[14,15]

Accordingly, the VS energy of a crystal is the reference point from which all of the interactions can be modeled as Coulombic in nature. Instead of promoting the separated atoms by $(I_{0,M} - A_{0,Y})$ into free ions, as in the Born–Haber–Fajans cycle, we use the promotion energy $\frac{1}{2}(1 + \delta_{VS})(I_{VS,M} - A_{VS,Y}) + \sum E_{hyb}$ to form VS atoms of partial charge, $\pm\delta_{VS}$. Thus, the reference energy of the crystal will differ from that of the free ions by an amount which we will denote IDE. From the point of view of the BHF cycle, this may be regarded as the "ion demotion energy" since EN equalization energetically demotes free ions into entities of smaller charge; indeed, Mulliken introduced the term "demotional resonance energy" in a similar context.[16b] This ion demotion energy, IDE, corresponds to the energy change on converting free ions into charged VS atoms, all in the gas phase:

$$IDE = D_{VS} - D_{ion} = \frac{1}{2}(1+\delta_{VS})(I_{VS,M} - A_{VS,Y}) + $$
$$\sum E_{hyb} - (I_{0,M} - A_{0,Y}) \quad (6a)$$

(18) (a) Janak, J. F. *Phys. Rev. B* **1978**, *18*, 7165−7168. (b) Gopinathan, M. S.; Whitehead, M. A. *Isr. J. Chem.* **1980**, *19*, 209−214. (c) Perdew, J. P.; Parr R. G.; Levy, M.; Balduz, J. *Phys. Rev. Lett.* **1982**, *49*, 1691−1694. (d) Phillips, P.; Davidson, E. R. *Int. J. Quantum Chem.* **1983**, *23*, 185−194.

Scheme 2. Thermochemical Energy Cycle for a Polar Covalent Material, Using VSAM Parameters[a]
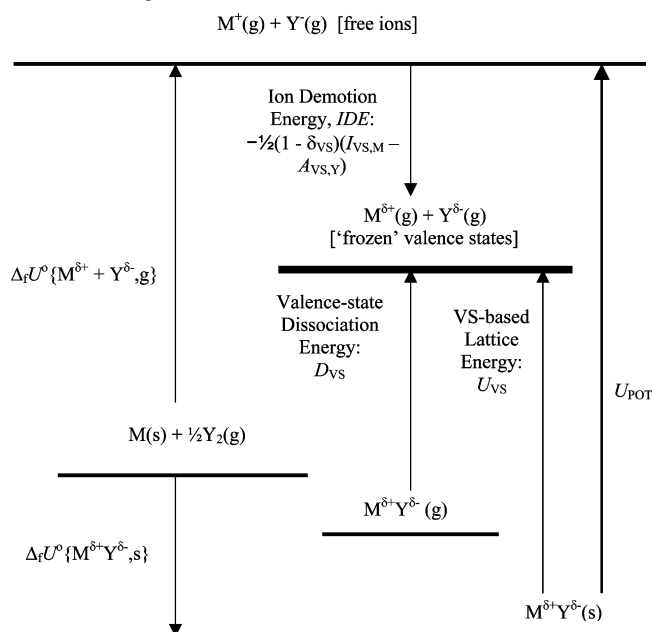
[a] Valence-state dissociation energy of the molecule, D_{VS}; partial charge, δ_{VS}; and ion demotion energy, IDE $= -\frac{1}{2}(1 - \delta_{VS})(I_{VS,M} - A_{VS,Y})$. The reference is "frozen" valence states (heavy horizontal line). $U_{VS} = U_{POT} +$ IDE.

For our set of materials, $\sum E_{hyb}$ is the sum of the atomic promotion energies, P^0, as given by Bratsch:[19]

$$\sum E_{hyb} = P_M{}^0 + P_Y{}^0 = (I_{0,M} - I_{VS,M}) + (A_{VS,Y} - A_{0,Y}) \quad (6b)$$

thus

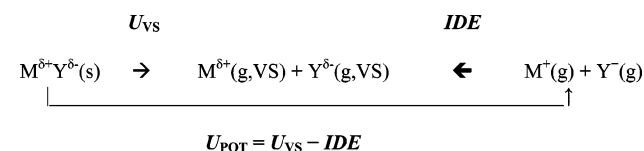$$\sum E_{hyb} - (I_{0,M} - A_{0,Y}) = -(I_{VS,M} - A_{VS,Y})$$

gives

$$\text{IDE} = -\tfrac{1}{2}(1 - \delta_{VS})(I_{VS,M} - A_{VS,Y}) \quad (6c)$$

When δ_{VS} is equal to one, the valence state is already the free-ion state, $M^+(g) + Y^-(g)$, so that the demotion step is redundant in this situation; that is, IDE $= 0$.

2.2. Crystal Lattice Formation. We model the process of lattice formation, when taking account of covalency, as shown in Scheme 2.

Thus, the process considered corresponds to:

$$\begin{array}{ccccc} & U_{VS} & & IDE & \\ M^{\delta+}Y^{\delta-}(s) & \rightarrow & M^{\delta+}(g,VS) + Y^{\delta-}(g,VS) & \leftarrow & M^+(g) + Y^-(g) \end{array}$$

$$U_{POT} = U_{VS} - IDE$$

We seek relations between the molecular valence-state dissociation energy, D_{VS}, the valence-state-based lattice energy, U_{VS}, and the ion-based lattice energy U_{POT}.

2.3. Alkali Metal Lattice Energy. Hisham and Benson[12b] considered the alkali metals as forming ionic lattices of the 1:1 (M^+M^-) salt type, and found a good correlation between U_{POT} and $1/R_0$. Accordingly, an electron is transferred between two

(19) Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 34−41.

separated gaseous atoms, each with sublimation energy $\Delta_{subl}U$, and the resulting free ions, $M^+(g)$ and $M^-(g)$, are the ultimate products for the steps determining the lattice energy:
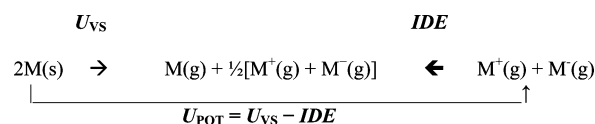
$$\begin{array}{ccccc} & 2\Delta_{subl}U & & (I_0 - A_0) & \\ 2M(s) & \rightarrow & 2M(g) & \rightarrow & M^+(g) + M^-(g) \end{array}$$
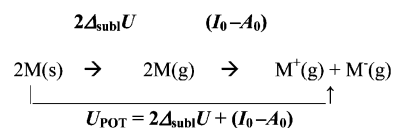
$$U_{POT} = 2\Delta_{subl}U + (I_0 - A_0)$$

To test whether these metals can be included in the present work, we have determined values of U_{POT}, following Hisham and Benson[12b] together with the enthalpy-to-energy correction,[3] as:

$$U_{POT} = 2\Delta_{subl}U + (I_0 - A_0) =$$
$$2(\Delta_{subl}H - RT) + (I_0 - A_0) \quad (7)$$

since two atoms of the metal are required to sublime to their gaseous ground states in forming the diatomic species, and charges are produced by releasing an electron from the "cation" (with ground-state ionization potential of the atom, I_0) and attaching it to the "anion" (ground-state electron affinity of the atom, A_0).

Szentpály and Gardner,[14e] and Donald et al.,[15] included the alkali and coinage metal diatoms, M_2, in their analyses. When the diatomic molecule is homonuclear, δ is zero, so that IDE $= -\frac{1}{2}(I_{VS} - A_{VS})$. For the alkali and coinage metal atoms, $I_{VS} = I_0$, and $A_{VS} = A_0$. In the restricted Hartree−Fock limit, $D_{VS} = D_e + \frac{1}{2}(I_{VS} - A_{VS})$. The thermochemical cycle below for alkali and coinage metals refers to two moles of the metal and corresponds to the process

$$\begin{array}{ccccc} & U_{VS} & & IDE & \\ 2M(s) & \rightarrow & M(g) + \frac{1}{2}[M^+(g) + M^-(g)] & \leftarrow & M^+(g) + M^-(g) \end{array}$$

$$U_{POT} = U_{VS} - IDE$$

The end state of the cycle represents the contributions from the covalent and ionic configurations to the VSAM model. A relation is sought between D_{VS}, U_{VS}, and U_{POT} for these metals as well.

3. Results and Discussion

3.1. Heteronuclear Systems. The atomic ionization potentials, electron affinities, and partial charges for the set of 43 diatomic molecules considered in this work are listed in Tables 2 and 3; the partial charges, δ_{VS}, are taken from refs 14a and 15, the VS dissociation energies, D_{VS}, are from ref 15. Note that, for the alkali halides, the VS charges are very close to current charge estimates[20] for the solid state, e.g. for CsCl, we get $|\delta_{VS}| = 0.968$. For the gold halides, the ionicity is strongly (up to 50%) reduced by relativistic effects.[20c] A comparison of VS charges and relativistic Mulliken population analyses[20c] for the gold monohalides demonstrates the extent to which our VSEN equalization successfully reproduces the strong relativistic reduction of bond polarity. For molecular AuF and its cubic

(20) (a) Levine, B. F. *J. Chem. Phys.* **1973**, *59*, 1463−1486. (b) Liu, D.; Zhang, S.; and Wu, Z. *Inorg. Chem.* **2003**, *42*, 2465−2469. (c) Söhnel, T.; Hermann, H.; Schwerdtfeger, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4381−4385.

Table 2. Ionization Potentials, $I_0 = I_{VS}$, and Ground- and Valence-State Electron Affinities, A_0 and A_{VS}, respectively, for the Elements Considered in this Paper (all in kJ mol^{-1})[a]

element (orbital)	$I_0 = I_{VS}$	A_0	A_{VS}	$\Delta_i U\{ion,g\}$
		Cations		
Li(s)	520	60	60	683
Na(s)	496	53	53	607
K (s)	419	48	48	512
Rb(s)	403	47	47	488
Cs(s)	376	46	46	455
Cu(s)	745	119	118	1088
Ag(s)	731	126	126	1019
Au(s)	890	223	223	1260
		Anions		
H (s)	1312	73	73	137
F (p)	2025	328	330	−258
Cl(p)	1451	349	351	−236
Br(p)	1326	325	340	−222
I (p)	1218	295	325	−200

[a] Ground-state values are from ref 2a, valence-state values have been calculated from ref 19, and the formation energies of the gaseous ions are from ref 2b.

crystal, the relativistic atomic charges on Au are +0.52, and +0.51 respectively,[20c] while our VSEN partial charge is $\delta_{VS} = +0.526$.

As discussed in refs 14a and 21, most other EN equalization models, e.g. the charge-dependent Hinze–Jaffé,[22a] the density functional-based Parr,[22b] and Gasteiger–Marsili[22c] EN functions, give charges which are too small by about a factor of 2. Importantly, the VSEN function is the only one for which the asymptotic reference VS energy converges to the energy of the free ions in case of $\delta \rightarrow 1$. In all of the other EN equalization schemes[22] the energy of separated, partially charged atoms falls much below that of the ground-state atoms and thus cannot converge at all to that of the corresponding free ions.

We here propose that the potential energies of solid MY(s) and molecular MY(g) are linearly related and possess a common reference VS energy. We test this proposition by correlating the published data for D_{VS} with the proposed valence-state-based lattice energy, $U_{VS} = U_{POT} + IDE$, data. For the whole set of 40 materials, listed in Table 3 and plotted in Figure 2, we find an excellent linear correlation with the correlation coefficient, $R = 0.994$. The standard deviations ($\pm SE$) of the slope and the intercept are shown in brackets. The standard error for the fitted data is 18.2 kJ mol^{-1}.

$$U_{VS}(calc) = 1.230(\pm 0.021)D_{VS} + 86.4(\pm 11.1) \text{ kJ mol}^{-1} \quad (8)$$

Comparing the results presented in Table 1 and Table 3, we find that the groups showing systematic positive and negative deviations with the simplistic VBT procedures, i.e. the alkali metal hydrides and the coinage metal monohalides, respectively, are well assessed by the new model. There are no systematic errors for any subset of materials. Thus, both the covalent effects for the coinage metal halides and the increased or modified core repulsion in the case of the hydrides seem common to both the

(21) (a) von Szentpály, L. *Int. J. Quantum Chem.* **2000**, *76*, 222−234. (b) Parr, R. G.; von Szentpály, L.; Liu, S. *J. Am. Chem. Soc.* **1999**, *121*, 1922−1924. (c) von Szentpály, L.; Rodriques, R. A.; Donald, K. J.; Lindner, H. Manuscript in preparation.

(22) (a) Hinze, J.; Jaffé, H.-H. *J. Am. Chem. Soc.* **1962**, *84*, 540−546. (b) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801−3807. (c) Gasteiger, J.; Marsili, M. *Tetrahedron* **1980**, *36*, 3219−3228.
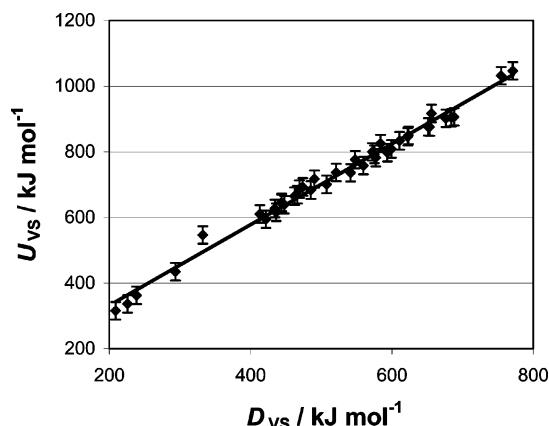
Table 3. Molecular and Solid-State Energy Data (in kJ mol^{-1}) for 25 Alkali Metal Hydrides and Halides, 10 Coinage Metal Halides, 5 Alkali Metals, and 3 Coinage Metals (the last are omitted from further consideration for reasons discussed in the text)[a]

	δ_{vs}	D_{vs}	IDE = $-^1/_2(1-\delta_{vs})$ $(I_{VS,M} - A_{VS,Y})$	U_{POT}^{BHF}	U_{vs} = U_{POT}^{BHF} + IDE	U_{vs}(calc)	% difference = $100[U_{vs}(calc) - U_{vs}]/U_{vs}$
LiH	0.473	572	−118	918	800	790	−1
NaH	0.498	508	−106	807	701	710	1
KH	0.571	448	−74	713	639	637	0
RbH	0.587	436	−68	684	616	622	1
CsH	0.615	422	−58	653	595	605	2
LiF	0.822	755	−17	1049	1032	1014	−2
LiCl	0.784	622	−18	864	846	851	1
LiBr	0.749	593	−23	820	797	816	2
LiI	0.712	541	−28	764	736	752	2
NaF	0.844	656	−13	930	917	893	−3
NaCl	0.814	548	−13	790	777	760	−2
NaBr	0.781	521	−17	754	737	727	−1
NaI	0.746	485	−22	705	683	683	0
KF	0.913	584	−4	829	825	804	−3
KCl	0.909	490	−3	720	717	689	−4
KBr	0.883	469	−5	691	686	663	−3
KI	0.853	444	−7	650	643	632	−2
RbF	0.928	575	−3	795	792	793	0
RbCl	0.93	474	−2	695	693	669	−4
RbBr	0.905	462	−3	668	665	654	−2
RbI	0.876	434	−5	632	627	620	−1
CsF	0.954	560	−1	759	758	774	2
CsCl	0.968	466	−0	670	670	659	−2
CsBr	0.946	444	−1	647	646	632	−2
CsI	0.919	413	−2	613	611	594	−3
CuF	0.642	771	−74	1121	1047	1034	−1
CuCl	0.545	688	−90	996	906	932	3
CuBr	0.497	651	−102	978	876	887	1
CuI	0.447	623	−116	966	850	853	0
AgF	0.651	684	−70	974	904	927	3
AgCl	0.556	611	−84	918	834	837	0
AgBr	0.508	599	−96	905	809	823	2
AgI	0.458	577	−110	892	782	796	2
AuCl	0.391	676	−164	1066	902	918	2
AuBr	0.334	653	−183	1059	876	890	2
Li₂; Li(s)	0	332	−230	777	547	495	−10
Na₂; Na(s)	0	294	−221	656	435	447	3
K₂; K(s)	0	239	−185	548	363	379	5
Rb₂; Rb(s)	0	226	−178	515	337	364	8
Cs₂; Cs(s)	0	209	−165	481	316	343	9
Cu₂; Cu(s)	0	507	−313	1298	985	778	−21
Ag₂; Ag(s)	0	506	−303	1172	869	657	−24
Au₂; Au(s)	0	558	−334	1374	1040	773	−35

[a] The ion demotion energy, IDE, is defined in eq 6c, the calculated valence-state-based lattice potential energy, U_{VS}(calc) is defined in eq 8 and the caption to Figure 2.

diatomic molecules and solids, so that a single linear relation between D_{VS} and U_{VS} is valid for all the systems considered, except for the coinage metals. For the sake of comparison, the equilibrium dissociation energy, D_e, correlates extremely poorly with both U_{VS} and U_{POT}: for our set of compounds, the correlation coefficients are $R \approx 0.02$ only.

Three different, partially opposing, effects contribute to the excellent linear correlation between U_{VS} and D_{VS}. In their expected order of importance, these are the following: (i) the Madelung factor increases the ionic part of the molecular interaction; (ii) on the other hand, the increased solid-state internuclear distance, R_0, reduces both the ionic and covalent interactions from their molecular values; and (iii) a shift toward larger partial charges on the atoms in the solid state as compared to those in the molecule affects the balance between the ionic and the covalent energy terms. The overall energetic influence of contribution (iii) is likely to be small due to a compensating

Figure 2. Valence-state-based lattice potential energy, U_{VS} ($= U_{POT}^{BHF}$ + IDE), plotted for 35 polar diatomic solids and 5 alkali metals (Table 3) against their valence-state dissociation energies, D_{VS}. The solid (best fit) least-squares line has the formula $U_{VS}(calc) = 1.230(\pm0.021)D_{VS}$ + $86.4(\pm11.1)$, the correlation coefficient is $R = 0.994$. The standard error for the fitted data, 18.2 kJ mol^{-1}, is shown by the error bars.

reduction of the covalent bond contribution in more ionic bonds, and the sum in energy shift is particularly difficult to assess. It is gratifying that these effects are well integrated into a single expression relating the depths of molecular and solid-state potential energies, D_{VS} and U_{VS}, respectively.

3.2. Homonuclear Systems. The plot of U_{VS} versus D_{VS} demonstrates that both the ionic solids, MY, and the alkali metals [treated as $M_2(s)$] fall onto the same regression line, whereas Hisham and Benson's reference[12b] to completely ionic dissociation products yielded two distinct linear regression lines in their plot of U_{POT} versus $1/R_0$. The unexpected success of their quasi-ionic metallic bonding remained unexplained by them. We here rationalize it by the Wigner–Seitz (nearly-free-electron) model of metals.[23,24] According to this model, the leading attractive term of the lattice energy is proportional to $1/R_{WS}$, the inverse of the Wigner–Seitz radius, while the latter is linearly related to nearest internuclear distance.[24]

We do not wish to infer that the bonding in ionic solids and in alkali metals is closely related. Rather, Scheme 2 and eq 8 may apply to very different materials, but only as long as their VS atoms-in-molecules and VS atoms-in-bulk-solids have sufficiently small differences in their electron configurations.

The coinage metals do not fit into the Wigner–Seitz model, a fact long acknowledged as due to the strong involvement of their d orbitals in metallic bonding.[24] For the transition metals, the cohesion is strongly affected by the d electrons. On the other hand, the valence shell s orbitals dominate the bond in the diatoms Cu_2, Ag_2, and Au_2.[25] Thus, we do not expect any simple relation between U_{VS} and D_{VS} for the coinage metals.

Here, for the first time, solid-state charges and energetics are successfully modeled by quantitative application of the isoelectronegativity principle. The free gaseous cations and anions (which appear in the BHF cycle) differ in their electronegativities,[14a] viz., $\chi\{M^+\} = I_{VS,M}$ and $\chi\{Y^-\}= A_{VS,Y}$, respectively. Because of the general inequality, $I_{VS,M} > A_{VS,Y}$, electronic

Table 4. Lattice Energies of the Alkali Metals Calculated by the VBT and Hisham−Benson (eq 7) Methods

	M/g mol^{-1}	ρ/g cm^{-3}	U_{POT}^{VBT}/kJ mol^{-1}	U_{POT}^a
Li(s)	6.94	0.534	773	774
Na(s)	23	0.9712	651	653
K(s)	39.1	0.86	544	544
Rb(s)	85.48	1.53	515	513
Cs(s)	132.91	1.873	484	478

^{a} $U_{POT} = 2\Delta_{subl}U + (I_0 - A_0) = 2(\Delta_{subl}H - RT) + (I_0 - A_0)$.

charge is transferred from Y^- to M^+ in achieving EN equalization. This stabilizes the energy by IDE $= -^1/_2(1-\delta_{VS})(I_{VS,M} - A_{VS,Y})$ to a new reference level which is common to both the EN-equalized gas-phase diatomic molecules, MY(g), and the solids, MY(s), in a unified scheme (Scheme 2), even in the limit, $Y = M$.

Encouraged by these results, we have checked whether a similar treatment, following the VBT procedure,[4] is meaningful for the alkali metals. As shown in Table 4, the lattice energies, U_{POT}^{VBT}, match those obtained by the Hisham−Benson protocol in eq 7 to a remarkable degree.

3.3. Predictions for Uncertain Data. We now turn to examine a few compounds for which some of the molecular or solid-state energy data are unknown or uncertain, viz. the coinage metal monohydrides, gold monofluoride, and gold monoiodide (see Table 5).

The solid coinage metal monohydrides are considered unstable with respect to dissociation into metals and molecular hydrogen.[26,27] The published U_{POT} data[2] show large discrepancies and are insufficiently consistent for inclusion in our linear regression. The molecular data are, however, available[15] and permit calculation of both types of lattice energies, viz. U_{VS} via eq 8 and U_{POT} by inclusion of IDE (see Table 5). The table also gives a comparison with the previously published lattice energies.[2a] Reasonable agreement is found for solid CuH, but our extrapolated U_{POT} values for AgH and AuH are significantly larger than the values listed in ref 2a. In particular, we feel that it is unreasonable for the lattice energy of AgH (in ref 2a) to be much smaller than that of CuH. We also calculate $U_{POT}\{AuH\}$ to be larger than that of CuH, in contrast to the listings in ref 2a.

Gold monofluoride is not known as a solid, but the diatomic molecule AuF has been predicted theoretically[28] and characterized experimentally.[29] Taking the best experimental estimate,[29a] $D_e \approx 310 \pm 40$ kJ mol^{-1} and our $\delta\{AuF\} = 0.526$,[15] and $\sum E_{hyb}$ $= 1.6$ kJ mol^{-1},[30] the values $D_{VS} \approx 735 \pm 40$ kJ mol^{-1} and IDE $= 133$ kJ mol^{-1} are calculated; thus, $U_{VS} \approx 990 \pm 50$ kJ mol^{-1} and $U_{POT}(calc) \approx 1120 \pm 50$ kJ mol^{-1} are extrapolated from eqs 6 and 8. Our U_{POT} may be compared to that of very recent density functional calculations by Söhnel et al.,[28c] from which a value of 1065 kJ mol^{-1} is extrapolated. Solid AuF is

(23) Wigner, E.; Seitz, F. *Phys. Rev.* **1933**, *43*, 804−810.
(24) Pettifor, D. *Bonding and Structure of Molecules and Solids;* Clarendon Press: Oxford, UK, 1995; p 125 ff.
(25) (a) Jeung, G.-H.; Barthelat, J. C. *J. Chem. Phys.* **1983**, *78*, 2097−2099. (b) Stoll, H.; Fuentealba, P.; Dolg, M.; Flad, J.; von Szentpály, L.; Preuss, H. *J. Chem. Phys.* **1983**, *79*, 5532−5542.

(26) (a) Wiberg, E.; Neumaier, H. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 35−38. (b) Andrews, L. *Chem. Soc. Rev.* **2004**, *33*, 123−132.
(27) (a) Fitzsimons, N. P.; Jones, W.; Herley, P. J. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 713−718. (b) Gelatt, C. D.; Ehrenreich, H. Weiss, J. A. *Phys. Rev. B* **1978**, *17*, 1940−1957.
(28) (a) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, *91*, 1762−1774. (b) Schwerdtfeger, P.; McFeaters, J. S.; Stephens, R. L.; Liddel, M. J.; Dolg, M.; Hess, B. A. *Chem. Phys. Lett.* **1994**, *218*, 362−366. (c) Söhnel, T.; Hermann, H.; Schwerdtfeger, P. *J. Phys. Chem. B* **2005**, *109*, 526−531.
(29) Schröder, D.; Hrušák, J.; Tornieporth-Oetting, I. C.; Klapötke, T. M.; Schwarz, H. *Angew. Chem.* **1994**, *106*, 223−225. (b) Evans, C. J.; Gerry, M. C. L. *J. Am. Chem. Soc.* **2000**, *122*, 1560−1561.
(30) See eq 6b for calculation of $\sum E_{hyb}$ from Bratsch's tables.[19]

Table 5. Data and Predictions for the Coinage Metal Monohydrides and Gold Monohalides[a]

MY	δ_{VS}	D_e	D_{VS}	IDE	U_{POT}^{BHF} ref 2a	U_{VS}(calc) eq 8	U_{POT}(calc)[b]	D_e(calc)
CuH	0.279	275	705	−242	(828), 1254	954	1196	
AgH	0.286	231	654	−235	(941)	891	1126	
AuH	0.143	302	769	−350	(1033), 1108	1032	1382	
AuF	0.526 (0.52)[20c]	310 ± 40	735 ± 40 see text	−133	n.a. (~1065)[28c]	990 ± 50	1120 ± 50	
AuCl	0.391	302	676	−164	1066	918	1082	
AuBr	0.334	286	653	−183	1059	890	1073	
AuI	0.276 (0.26)[32]	n.a.	633 see text	−205	1070	865 see text	n.a.	243 ± 18 see text

[a] See footnote *a* of Table 3 for definitions of quantities tabulated. The values for AuCl and AuBr are copied from Table 3 to facilitate comparisons. (n.a. = datum not available). [b] U_{POT}(calc) = U_{VS}(calc) − IDE.

here predicted to be marginally stable, with energy of formation of approximately $\Delta_f U \approx -100 \pm 50$ kJ mol^{-1}. This is in rough agreement with Schwerdtfeger's [28b] estimate of $\Delta_f U \approx -50 \pm 80$ kJ mol^{-1}, but in strong opposition to Waddington's prediction in 1959 of a Gibbs energy of formation $\Delta_f G \approx +230$ kJ mol^{-1}.[31]

If D_e and D_{VS} are unknown but values for U_{POT} and δ are available, we may estimate $U_{VS} = U_{POT} + IDE$, and the value of D_{VS} is obtained from the regression, eq 8, by reversing the procedure. In a next step, the spectroscopic dissociation energy $D_e = D_{VS} - \frac{1}{2}(1 + \delta_{VS})(I_{VS,M} - A_{VS,Y}) - \sum E_{hyb}$ is back calculated. Gold monoiodide, AuI, serves as our example (Table 5). U_{POT} is given[2a] to reasonable accuracy as 1070 kJ mol^{-1}, but D_e and thus D_{VS} are insufficiently known. Estimates for $D_e\{AuI\}$ range from 203[32] to 277 ± 10 kJ mol^{-1}, the latter using an approximate relation between estimations for the harmonic wavenumber and the anharmonicity constant.[33] Note that our $\delta\{AuI\} = 0.276$ agrees very well with the ionic character, $i_c = 0.26$, calculated from halogen quadrupole coupling constants.[33] We use data from Table 2 to find IDE = −205 kJ mol^{-1}, and thus, $U_{VS} = 865$ kJ mol^{-1}; then we obtain $D_{VS}\{AuI\} \approx 633 \pm 18$ kJ mol^{-1} by reversed regression. With $\sum E_{hyb} = 30$ kJ mol^{-1} (entirely due to averaging the spin−orbit splitting of iodine[19,30]) the value $D_e\{AuI\} \approx 243 \pm 18$ kJ mol^{-1} is calculated, which is in the middle of the range estimated in refs 32 and 33. As opposed to gold metal (as discussed above), the results for gold monohalides indicate that the relativistic effects are similar in magnitude and indeed transferable for these molecular and solid states.

4. Summary

We have introduced and tested a new method for evaluation of lattice energies for diatomic MY crystals, allowing for both ionic and covalent contributions. A generalization of the Born−Haber−Fajans cycle beyond highly ionic solids is proposed, based on the fundamental principle of electronegativity equalization. In our model the solid phase, MY(s), and molecular gas phase, MY(g), possess a common reference valence-state energy, i.e., that of $M^{\delta+} + Y^{\delta-}$. This energy differs from that of the sum for free ions by the ion demotion energy, IDE. Rather precise yet simple relations are found between the molecular valence-state dissociation energy, D_{VS}, the valence-state-based lattice energy, $U_{VS} = U_{POT} + IDE$, and the ion-based lattice energy, U_{POT}. The method is here applied to groups 1 and 11 monohalides and hydrides, as well as to the alkali metals, pending a wider range of VSAM parameters becoming available. A limitation of the model occurs for the coinage metals, Cu, Ag, and Au, where d orbitals are strongly involved in the metallic bonding, while the homonuclear molecular bond is dominated by s orbitals.

(31) Waddington, T. C. *Trans. Faraday Soc.* **1959**, *55*, 1531−1535.
(32) Söhnel, T.; Brown, R.; Kloo, L.; Schwerdtfeger, P. *Chem.−Eur. J.* **2001**, *7*, 3167−3173.
(33) Reynard, L. M.; Evans, C. J.; Gerry, M. C. L. *J. Mol. Spectrosc.* **2001**, *205*, 344−346.