



Novel correlation of Schottky constants with lattice energies for II–VI and I–VII compounds

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ARTICLE INFO

Article history:

Received 19 May 2010

Received in revised form

21 July 2010

Accepted 25 July 2010

In Memoriam of

Professor Hans Georg von Schnering

Available online 1 August 2010

Keywords:

II–VI

I–VII compounds

Vacancy densities

Lattice enthalpies

Correlation

ABSTRACT

Correlations of computed Schottky constants ($K_S = [V''_{zn}][V'_S]$) with structural and thermodynamic properties showed linear dependences of $\log K_S$ on the lattice energies for the Zn-, Cd-, Hg-, Mg-, and Sr-chalcogenides and for the Na- and K-halides. These findings suggest a basic relation between the Schottky constants and the lattice energies for these families of compounds from different parts of the Periodic Table, namely, $\Delta H_{f,L}^0 = -(2.303nRT \log K_S) + 2.303nRm_b + 2.303nRTi_b$.

$\Delta H_{f,L}^0$ is the experimental (Born–Haber) lattice energy (enthalpy), n is a constant approximately equal to the formal valence (charge) of the material, m_b and i_b are the slope and intercept, respectively, of the intercept b (of the $\log K_S$ versus $\Delta H_{f,L}^0$ linear relation) versus the reciprocal temperature. The results of this work also provide an empirical correlation between the Gibbs free energy of vacancy formation and the lattice energy.

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1. Introduction

Structural defects profoundly affect the electronic and other solid state properties of materials. The experimental development and theoretical understanding concerning the particular importance of vacancies for the luminescent behavior of II–VI compounds have been discussed in more detail earlier [1]. Recent ODMR and EPR studies on ZnS and ZnSe [2] are consistent with high temperature Hall measurements on pure and doped ZnSe [3], which show that doubly charged vacancies dominate the defect structure of this material. The importance of point defects for other semiconductor properties is indicated by the wide range of research activities in this field. Recent reports on vacancies are mainly concerned with their effects on properties, and not with the main topic of this investigation.

The close agreement between the computed vacancy density of ZnS [1] and experimental observations [4,5] within less than an order of magnitude raises the question of relations between vacancies and other solid state thermodynamic properties for this and related compounds.

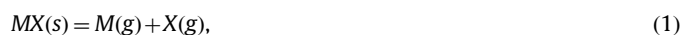
The specific objectives of this effort are to examine correlations of the Zn-chalcogenide group between computed vacancy concentrations (Schottky constants) and lattice dimensions, heats of vaporization, vapor pressures, and lattice energies. The unexpected linear dependence of $\log K_S$ on the lattice energies (enthalpies) for the Zn-chalcogenides led to an extension of these

computations to other II–VI (Cd-, Hg-, Mg-, and Sr-chalcogenides) and I–VII (Na- and K-halides) compounds. The combined linear dependences of the Schottky constants on the lattice enthalpies for seven groups of compounds from different parts of the Periodic Table provided the basis for the analysis of these findings.

Estimations of vacancy concentrations and their relation to basic properties are useful for the design of crystal growth experiments. The empirical results of this work provide new thermodynamic relationships and are expected to contribute to a “better understanding of defect problems... and useful guidelines for manipulation..., which still need improving” [6].

2. Computational procedures

The solid–gas phase equilibria of II–VI and of many other compounds are multi-component, multi-reaction systems [7]. The thermodynamic data relevant for the computation of Schottky constants, K_S (product of metal and non-metal equilibrium vacancy concentrations), as a function of temperature are limited to the vaporization reaction of the compound to monatomic gaseous species according to



where M is a group I or II metal, X is a group VI or VII element.

2.1. Computation of relevant thermodynamic properties

The thermodynamic data employed for the computation of the enthalpy of vaporization of reaction (1) are critically selected from

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the literature. The heats of formation, ΔH°_{298} , absolute entropies, S°_{298} , and the heat capacity functions, C_p° , of cubic ZnS(s), ZnSe(s), ZnTe(s), and of the gaseous species (reaction (1)) are from [8]. The corresponding data of the solid Cd-, Hg-, Mg- and Sr-chalcogenides, except of the oxides, are from [8]. The heat capacities of SrSe(s) ($12.0 + 1.26 \times 10^{-3}T - 1.55 \times 10^5 T^{-2}$), SrTe(s) ($11.0 + 1.26 \times 10^{-3}T - 1.55 \times 10^5 T^{-2}$), MgSe(s) ($11.20 + 1.97 \times 10^{-3}T$), and of MgTe(s) ($11.90 + 1.97 \times 10^{-3}T$) have been estimated based on the known data for the Sr- and Mg-sulfides and on those of related metal-chalcogenides. The values of ΔH°_{298} and S°_{298} for the solid oxides of Zn, Cd, Hg, Mg, and Sr are from [9] and their C_p° -values are from [10]. The corresponding values for the monatomic gaseous species O, Mg, Sr, Cd, and Hg are from [11]. The heats of formation and absolute entropies of the solid Na- and K-halides and of the monatomic gaseous metal and halogen species are from [9]. The heat capacities of all species are from [10]. Additional details of the ZnS and SrS multi-component, multi-reaction solid-vapor equilibria have been reported elsewhere [7].

2.2. Computation of atomic point (Schottky) defect concentrations

Although the basis and procedural details have been discussed earlier [1], for the convenience of the reader, the essential equations for the computation of K_S values in this work are given below. For doubly negatively and positively charged vacancies, the Schottky constant for the compound MX (e.g., ZnS) is given by the expression

$$K_S = [V''_{Zn}][V^2_S] \quad (2)$$

Applying the mass action law to a pure crystal with intrinsic Schottky defects, the Schottky constant can be estimated with the equation

$$K_S = \exp(-\Delta H^\circ_{S,T}(RT)^{-1}) \exp(\Delta S^\circ_{S,T}(R^{-1})) \quad (3)$$

The Schottky enthalpy, $\Delta H^\circ_{S,T}$, is the enthalpy required to move a metal and a non-metal ionic species from the bulk of the crystal to the surface (half-crystal position). As mentioned earlier [1], the entropy changes associated with the formation of vacancies (change of vibrational contributions) are considered minor for the compounds of present interest [6], and range from a few to about 10 R [1].

3. Results and discussion

Detailed multi-component, multi-reaction equilibrium computations in connection with this effort, but not reported here, confirm that the gaseous species of reaction (1) and the diatomic chalcogen are the dominant species in the vapor phase above the solids.

3.1. Concentration of intrinsic atomic point (Schottky) defects

The computation of vacancy densities in ZnSe and ZnTe via Eq. (3) is based on the free energy of vacancy formation. In accordance with the above definition of the Schottky enthalpy, the value of $\Delta H^\circ_{S,T}$ used for ZnS [1] and in this work is $\frac{3}{4}$ of the enthalpy of vaporization of MX(s) according to reaction (1). The validity of using the same fraction for the Zn- and other metal-compounds of the present investigation will be discussed later. For ZnSe(s), the enthalpy of reaction (1) is $\Delta H^\circ_{298} = 125.50$ kcal/mole. For the corresponding ZnTe(s) and ZnO(s) reactions, these values are 110.35 and 173.54 kcal/mole, respectively. The error limits of these quantities are less than ± 2 kcal/mole. With the above enthalpy fraction of $\frac{3}{4}$ [1], the Schottky enthalpies,

$\Delta H^\circ_{298,S}$ for ZnO(s), ZnSe(s), and ZnTe(s) are 130.16, 94.12, and 82.76 kcal/mole, respectively. The temperature dependences of these values (effects of the heat capacity functions) correspond to those of reaction (1).

Vacancy formation energies, as computed for ZnS (blende) [12] and discussed earlier [1], are not available for ZnO(s), ZnSe(s) and ZnTe(s). Thus, the above enthalpy and entropy values (5R (average), 10R (upper limit)) are employed for the computation of the Gibbs free energies of vacancy formation or Schottky energies, $\Delta G^\circ_{vac} = \Delta G^\circ_{S,T} = \Delta H^\circ_{S,T} - T\Delta S^\circ_{S,T}$ from which the Schottky constants, $K_S = \exp(-\Delta G^\circ_{S,T}/RT)$ (or $\log K_S = -(2.303RT)^{-1} \Delta G^\circ_{S,T}$) are obtained. The latter forms of Eq. (3) show that the dependences of $\log K_S$ on the Gibbs free energies of vacancy formation and on the Schottky enthalpies ($0.75 \Delta H^\circ_{T,vap}$) for different compounds at a fixed temperature are linear, the slopes of the straight lines are equal to the respective coefficients of $\Delta G^\circ_{T,vac}$ and $\Delta H^\circ_{T,vap}$ in the relevant expressions. Conventionally, Eq. (3) is used to plot $\log K$ values versus $1/T$ (e.g., K_p data from vapor pressure measurements) to derive heats and entropies of reaction for a specific compound. In this work, different groups of compounds are employed to investigate their vacancy concentrations in relation to the above and other thermodynamic properties.

The intrinsic vacancy concentrations ($K_S^{1/2}$) computed here for ZnO, ZnS [1], ZnSe, and ZnTe for stoichiometry ($[V''_M] = [V^2_X]$) and for ΔS values of 10 and 20 eu are shown in Fig. 1. (The defect density per cm^3 is based on the actual number of molecules per cm^3 .) From this and Avogadro's number, the defect density in moles of vacancy pairs per mole of Zn-chalcogenide can be obtained. The temperature dependence of $\Delta H^\circ_{S,298}$ is mentioned above, for the Schottky entropy ($\Delta S^\circ_{S,T}$) the above fixed values are employed. The very similar trends of the vacancy-temperature dependences of the zinc chalcogenides (Fig. 1) are quite apparent. The difference between the vibrational entropy changes used (10 and 20 eu) affects the vacancy concentrations (per cm^3) of these compounds by about one order of magnitude (Fig. 1). The vacancy concentrations of these materials differ by about two to three orders of magnitude at lower to medium temperatures and by about one order at higher temperatures. The increasing overlap of the vacancy densities between the different chalcogenides near the reported melting points of about 1500 K and above for ZnTe and ZnSe, respectively, indicates the influence of the (same) entropy values used.

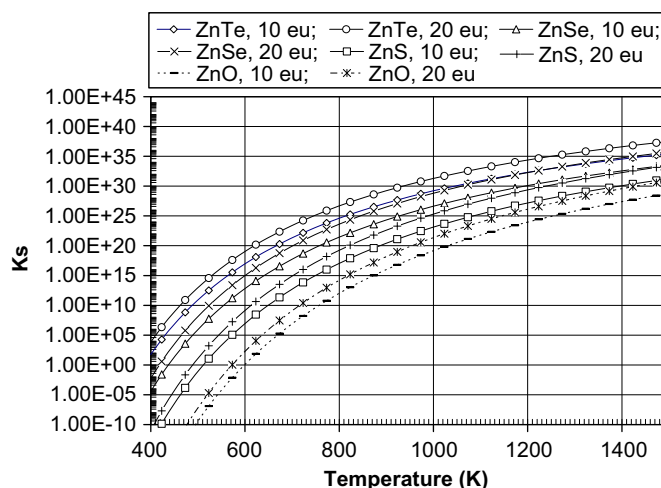


Fig. 1. Concentration of doubly ionized metal (non-metal) vacancies per cm^3 ZnS, ZnSe, ZnTe, and ZnO for different entropies of formation as a function of temperature.

As a part of high temperature Hall measurements of pure and doped ZnSe [3], the equilibrium concentration of doubly ionized metal and non-metal vacancies of the former at 800 °C and a zinc partial pressure of about 10^{-4} atm was reported to be about $2\text{--}3 \times 10^{15}$ (cm⁻³) [3]. The computed vacancy density of ZnSe (Fig. 1) for similar conditions is in close agreement with the reported data. The estimated vacancy densities for ZnTe (Fig. 1) are in reasonable agreement with experimental hole concentrations for different Zn pressures at the mean temperature (1000–1100 K) of investigation [13].

Point defect concentrations (cm⁻³) in doped ZnSe:Al, derived from Hall measurements [3] are from low temperatures to about 1200 K from several to about one order of magnitude greater [3] than computed for pure ZnSe in this work. Although consistent with thermodynamic expectations that Al doping increases Zn vacancy concentrations, the larger differences at lower temperatures suggest further refinements of the temperature dependences of the Schottky constants.

3.2. Correlation of vacancy concentrations of Zn-chalcogenides with structural and thermodynamic parameters

The overall trend in Fig. 1 shows that at all temperatures the vacancy densities increase from ZnO via ZnS and ZnSe to ZnTe, i.e., with increasing interatomic distance $d_{(A-B)}$ and decreasing bond strength of the different compound crystals. However, the vacancy densities (# of pairs/cm³) of these and of the other investigated compounds at or near room temperature increase non-linearly from the oxide to the telluride. The same is true for the log K_S versus $d_{(A-B)}$ relation (the Schottky constant K_S is also the square of the number of moles of vacancy pairs per mole compound).

The formation of vacancies and the computation of Schottky constants are inherently connected to the vaporization of the material. The dependences of the vacancy concentrations (# of vacancy pairs/cm³) of ZnS, ZnSe, and ZnTe at given temperatures on their respective metal and non-metal partial pressures were found to be not linear. With increasing temperature, these relations approach linearity.

3.3. Bonding properties and lattice energy computations

Because the formation of vacancies includes the transfer of charged species from the bulk to the surface of the crystal, one might expect this process to be dependent on the forces that hold the crystal lattice together. One measure of this is the lattice energy, as defined by the well-known Born–Haber cycle.

This model implies the interaction between fully charged gaseous ions to form a solid crystal. As discussed briefly below, the bonding in these compounds is not fully ionic, and we find surprisingly linear relations between log K_S and lattice energy for a considerable range of metal chalcogenides and halides. These observations form the basis of this work.

A comparison of experimental interatomic distances with those obtained from the ionic and covalent radii of the constituents [14] demonstrates the increasingly covalent bonding of the chalcogenides from the oxide to the telluride.

Lattice energies computed here based on the formal ($z=2$) and effective ionic charges (z^*) and the Born–Mayer Eq. (4),

$$U_L = -(1/4\pi\epsilon_0)N_A(z^{*2}e^2/d_{(A-B)})(1-(1/n)A), \quad (4)$$

provide an approximate measure of coulombic contributions. With the Madelung constant A (1.638055 for Zn-blende structures), the repulsion term $(1-(1/n))$ (n about 9 for ‘ionic’ type compounds), for $z=2$ and interatomic distances $d_{(A-B)}$ [14], Eq. (4) yields rounded lattice energy values for ZnS of 826 (3458), for ZnSe of 789 (3303), and for ZnTe of 732 (3065) kcal/mole (kJ/mol). The significantly smaller effective charges of the zinc and chalcogen atoms ($z_1^* = z_2^*$) [15,16] yield expectedly much lower lattice energy values. Both sets of data support the increasing covalent bonding of the chalcogenides, and suggest the use of the experimental Born–Haber cycle (B–H) for all compounds investigated.

The B–H lattice enthalpy employed here is the enthalpy change from the solid compound to the ionized gaseous species, i.e., the sum of the enthalpy of vaporization according to reaction (1) and of the ionization and electron affinity energies of the gaseous species, which is endothermic. The lattice enthalpy $\Delta H_{298,L}^\circ$ corresponds closely to the lattice energy $U_{0,L}^\circ$.

The enthalpies of vaporization are computed from the above literature data. The ionization energy, I_e , of Zn to Zn²⁺ is 630.8 kcal/gatom [17], those of Cd, Hg, Mg, Sr, Na, and K (Table 1) are also from [17]. Electron affinity energies, E_a , of O to O²⁻ (178 kcal/g atom), of S²⁻ (10.9) and of Se²⁻ (98 kcal/g atom) are based on recent computations [18]. The value of Te²⁻ (90 kcal/g atom) has been estimated from literature data of 82 [19] and 97 kcal/g atom [20]. The corresponding E_a -data of F, Cl, Br, and I are from [21]. The room temperature lattice enthalpies computed here for ZnS (886.74; 3712.6), ZnSe (854.23; 3576.5), ZnTe (831.14; 3479.8), and for ZnO (982.35; 4112.9) (kcal/mole; kJ/mol) are used in the further analyses. The corresponding thermochemical data from the above literature and the same procedures are employed for the lattice energy computations of the other compounds.

Table 1
Summary of relevant empirical and derived data of the compounds investigated.

Compound	n_{emp}	m_b	$I_{e,\text{emp}}$	$I_{e,\text{lit}}$	$I_{e,\text{emp}} - I_{e,\text{lit}}$	averg. i_b
Zn-Chalcog. ($n_{\text{form}}=2$)	$2.007 \pm 0.5\%$	$7.081\text{E}+04$	650.3 2722.7	630.8 2641.0	+19.5, +3.1%	4.149 11.36
Cd-Chalcog. ($n_{\text{form}}=2$)	$2.217 \pm 1.0\%$	$5.867\text{E}+04$	595.2 2492.0	597.3 2500.8	-2.1, -0.35%	5.483 16.58
Hg-Chalcog. ($n_{\text{form}}=2$)	$2.505 \pm 1\%$	$6.016\text{E}+04$	689.6 2887.2	673.2 2818.6	+16.4, +2.4%	4.102 14.02
Mg-Chalcog. ($n_{\text{form}}=2$)	$1.825 \pm 2\%$	$6.646\text{E}+04$	555.0 2323.7	523.0 2189.7	+32.0, +6.1%	3.179 7.91
Sr-Chalcog. ($n_{\text{form}}=2$)	$1.861 \pm 2\%$	$4.902\text{E}+04$	417.4 1747.6	385.7 1614.8	+31.7, +8.2%	1.463 3.71
Na-Halides ($n_{\text{form}}=1$)	$0.820 \pm 2\%$	$2.531\text{E}+04$	95.0 397.7	118.5 496.1	-23.5, 19.8%	1.655 1.85
K-Halides ($n_{\text{form}}=1$)	$0.762 \pm 2\%$	$2.460\text{E}+04$	85.8 359.2	100.1 419.1	-14.3, 14.3%	0.687 0.71

The first entries in columns 4 and 5 are in kcal, the second ones are in kJ. The second entries in column 7 are the numerical values of the third term of Eq. (7) for n_{emp} and room temperature (kcal). The numbers of figures have only computational significance.

3.4. Correlation of the Schottky constants of the Zn-, Cd-, Hg-, Mg- and Sr-chalcogenides and of the Na- and K-halides with their lattice enthalpies

The Schottky constants of the Zn- and Cd-chalcogenides as a function of temperature versus their lattice enthalpies are shown in Fig. 2. For a given compound, the slight curvature of the $\log K_S$ versus lattice enthalpy data with increasing temperature reflects the decreasing enthalpy of vaporization. The corresponding small decrease in lattice enthalpy is consistent with increasing lattice expansion with temperature. At any given temperature, the $\log K_S$ versus lattice enthalpy data for the different Zn- and Cd-chalcogenides yield straight lines, except for the oxides. The Hg-chalcogenides continue the unexpected trend of linear dependences for this group of II–VI compounds. For clarity reasons, they are not included in Fig. 2, but listed separately in Appendix A.

The $\log K_S$ versus ΔH°_L results for the Mg- and Sr-chalcogenides (including the deviation of the oxides) to compounds of the main group elements of the Periodic Table. These results confirm and support the observations of linearity for the different families of transition metal chalcogenides.

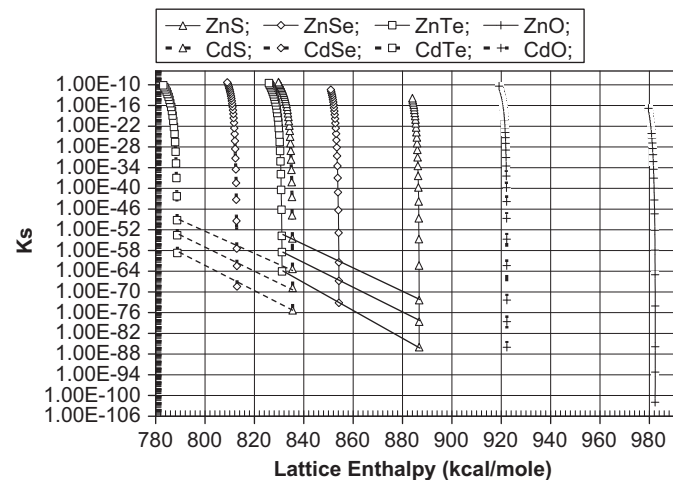


Fig. 2. Graphical representation of the Schottky constants ($\log K_S$) (based on $\Delta S = 10$ eu) of the Zn- and Cd-chalcogenides as a function of the lattice enthalpies and temperature.

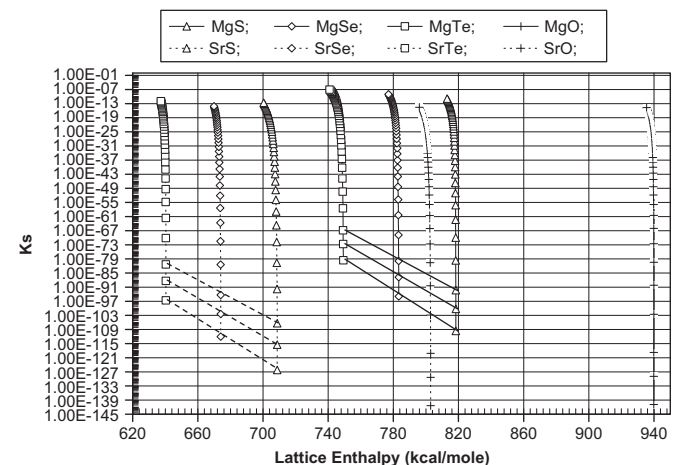


Fig. 3. Graphical representation of the Schottky constants ($\log K_S$) (based on $\Delta S = 10$ eu) of the Mg- and Sr-chalcogenides as a function of the lattice enthalpies and temperature.

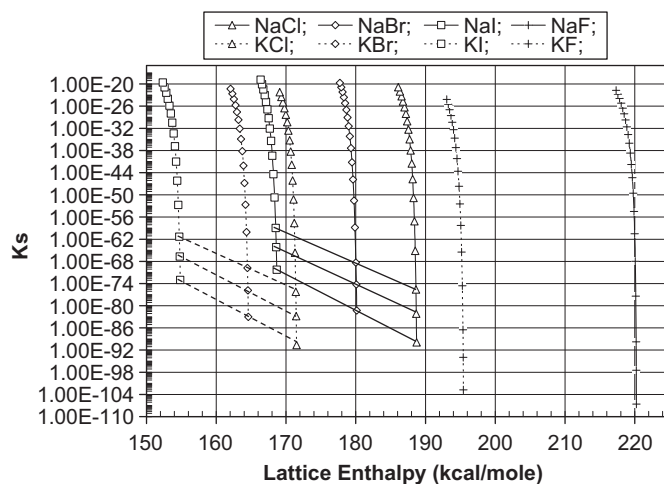


Fig. 4. Graphical representation of the Schottky constants ($\log K_S$) (based on $\Delta S = 10$ eu) of the Na- and K-halides as a function of the lattice enthalpies and temperature.

The linear $\log K_S$ versus ΔH°_L relations of the Na- and K-halides in Fig. 4 add a different class of compounds to these observations. In these cases, the fluorides do not follow the straight line relationships.

The combined results of Figs. 2–4 are the basis for the further analysis of the observed linear trends. The evaluation of the Zn-chalcogenides is discussed in more detail below as an example for the seven groups of compounds.

4. Analysis and discussion

The linear dependences of $\log K_S$ of the above compounds on the Gibbs free energies of vacancy formation, on the enthalpies of vaporization to monatomic species (reaction (1)), and on the experimental lattice enthalpies (Figs. 2–4) suggest similar thermodynamic relationships also for the latter correlations. The numerical values of the slopes of the $\log K_S$ versus $\Delta H^\circ_{T,L}$ data (of the straight lines in Figs. 2–4, Table 1) contain an additional quantity n (relative to that of Eq. (3)) and are $-(2.303nRT)^{-1}$; the intercept values of the straight lines (Figs. 2–4) are temperature dependent and not zero. These observations lead to the following empirical relation between $\log K_S$ and $\Delta H^\circ_{T,L}$, namely,

$$\log K_S = -(2.303nRT)^{-1} \Delta H^\circ_{T,L} + b. \quad (5)$$

For the Zn-chalcogenides, the average value of the quantity n in the denominator of Eq. (5) is $2.007 \pm 0.5\%$ over a range of 1200°C . The graphical representations of the intercepts b (Eq. (5)) of the seven groups of compounds versus the reciprocal temperature are linear (Fig. 5) yielding the expression

$$b = m_b/T + i_b. \quad (6)$$

As an example, for the Zn-compounds (excluding ZnO) the slope $m_b = 7.081E+04$, and the intercepts i_b for all groups of compounds are close to zero. The numbers of figures in the values of n and m_b have only computational significance. Combining Eqs. (5) and (6) and rearranging yields

$$\Delta H^\circ_{T,L} = -(2.303nRT \log K_S) + 2.303nRm_b + 2.303nRi_b, \quad (7a)$$

with $-2.303 RT \log K_S = \Delta G^\circ_{T,vac}$ (Eq. (3)) and with $2.303R = 4.5757$, Eq. (7a) becomes

$$\Delta H^\circ_{T,L} = n\Delta G^\circ_{T,vac} + 4.5757nm_b + 4.5757ni_b. \quad (7b)$$

The above empirical values of n and m_b (Table 1) yield a value of 650.3 kcal (2722.7 kJ) for the T -independent term of Eq. (7a) for

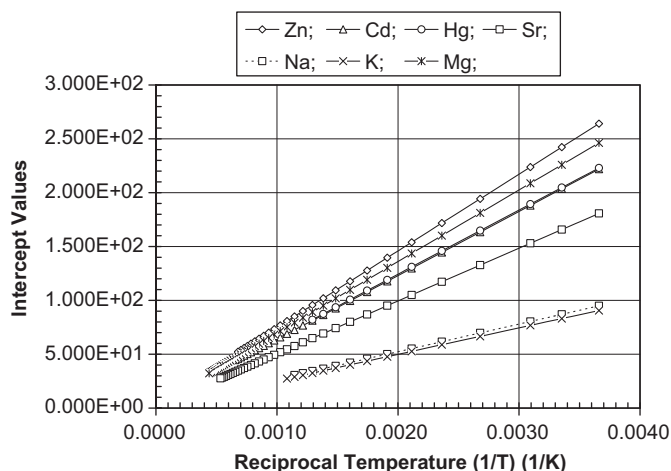


Fig. 5. Graphical representation of the intercept values b (Eq. (5)) of the Zn-, Cd-, Hg-, Mg- and Sr-chalcogenides and of the Na- and K-halides as a function of reciprocal temperature.

the Zn-chalcogenides. This number is within about 3% of the literature value of the zinc ionization energy (Table 1).

The values of n , m_b and i_b and of the derived data for the Cd- and Hg-chalcogenides (Table 1) show that the n -values are increasingly greater than 2, possibly owing to computational uncertainties and those of the thermochemical data employed. The values of the T -independent terms (Eq. (7a)) are again very close to the literature values of the ionization energies of Cd and Hg (Table 1).

The n -values of the Mg- and Sr-chalcogenides are about 20% lower than formal ionic charges of two (Table 1). The values of the T -independent terms (Eq. (7a)) of these groups are within less than 10% of the reported literature ionization energies of Mg and Sr (Table 1).

The empirical n -values of the Na- and K-halides (Table 1) are about 20% lower than their formal ionic charges, and the values for the T -independent term of Eq. (7a) are also lower. The n -numbers for the halides are sufficiently different from 2 and close enough to 1 to be consistent with the trends observed for the other groups, and provide additional support for the apparent physical meaning of these quantities.

In view of the complex interrelation between the variables of Eq. (7a) and the thermochemical data employed, and because of the varying degrees of covalency of these compounds, any further analysis of the effects of uncertainties on the results is not justified at this time.

It is noteworthy that the second term of Eq. (7a) corresponds within 10% to the ionization energies of the respective five metals of the chalcogenide groups. The use of $\frac{3}{4}$ of the heat of vaporization of reaction (1) for the enthalpy of vacancy formation (Eq. (3)) [16,1] appears to be a good choice for the Zn-, Cd-, Hg-, Mg-, and Sr-compounds. For the Na- and K-halides, the correspondence with the ionization energies of Na and K is within about 20%.

It might not be unreasonable to assume that the fraction of the enthalpy of vaporization (0.75) used here as the Schottky enthalpy would differ for the different groups and even for the individual compounds.

The combined findings suggest that the quantity n in Eqs. (5) and (7) may be related to the formal valence, oxidation state of the compounds investigated and that the second (T -independent) term may be related to the metal ionization energies of these groups of compounds.

Conventionally, I_e or E_a values can be obtained by equating the lattice energy $U_{0,L}^\circ$ (computed by a different model) to the

experimental Born–Haber lattice enthalpy $\Delta H_{298,L}^\circ$ ($\Delta H_{\text{vap}}^\circ + I_e + E_a$) for a specific compound. Applying this method to Eq. (7a), and using the literature ionization energy of zinc (Table 1, [17]) and the enthalpies of vaporization (reaction (1)) at 298 K for the individual Zn-compounds yields electron affinity energies within 10% of the above literature values [18]. Employing the literature electron affinities and the same enthalpies of vaporization yields ionization energies within 2% of the literature value for Zn. Similar results are obtained for the other families of compounds. These agreements show the internal consistency of the computational procedures and suggest an uncertainty of Eq. (7) in terms of larger (smaller) relative errors of the smaller (larger) quantities.

Because the lattice energies are partly based on coulombic attraction (repulsion) forces of charged species and on their distances, the ionization of atoms in the solid is at least formally related to their ionization (I_e) and electron affinity (E_a) energies. The dependences of $\log K_S$ of the metal–chalcogenides and halides on the electron affinity energies of the non-metal atoms are linear, as illustrated for the Zn-chalcogenides (Fig. 6) and Na-halides (Fig. 7), except for the oxides and fluorides. The latter contribute in part to their deviation from linearity with respect to the lattice enthalpy (Figs. 2–4). The linear dependences of $\log K_S$ on the electron affinities and, as mentioned above, on the heats of vaporization are necessary conditions for the linear dependence of $\log K_S$ on the Born–Haber lattice enthalpy employed in this work. The large ionization energy of mercury prohibits a linear correlation between $\log K_S$ and the ionization energies of the selenides (or other chalcogen) of different group II-metals (Fig. 8). Thus, for the above linear $\log K_S$ –lattice enthalpy correlations, the group is defined by the same metal component ($I_e = \text{constant}$) of the compounds.

There are many possible linear $\log K_S$ – ΔH_L° combinations. However, the apparent empirical ‘restrictions’ on n ($n \approx 2$ or 1) over wide temperature ranges, on the second term of Eq. (7a) ($\approx I_e$), and on K_S , significantly reduce the probability of accidental linear correlations. Under these conditions it is justified to propose that the empirical equations. (5) and (7a) represent a basic relationship between the Schottky constants and the lattice enthalpies for the above families of compounds. The lattice energy is related to the crystal structure and to the Gibbs free energy of vacancy formation (Eq. (7b)). The common types of structure of the groups of compounds investigated may partly explain the linear dependences of $\log K_S$ on the corresponding properties $\Delta G_{\text{vac}}^\circ$ and ΔH_L° .

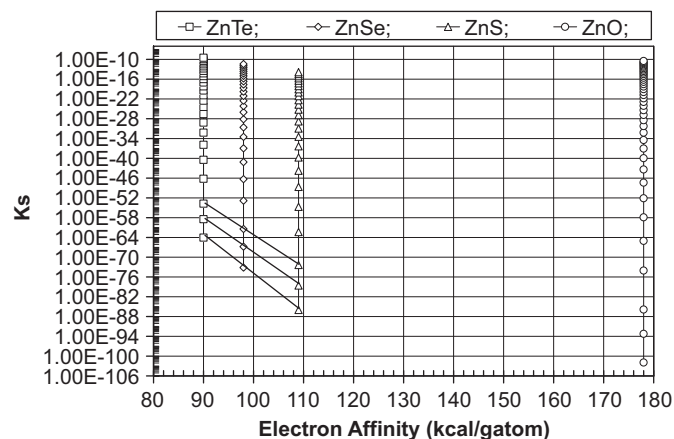


Fig. 6. Graphical representation of the Schottky constants ($\log K_S$) (based on $\Delta S = 10$ eu) of the Zn-chalcogenides as a function of the electron affinity energies of the chalcogen atoms and temperature.

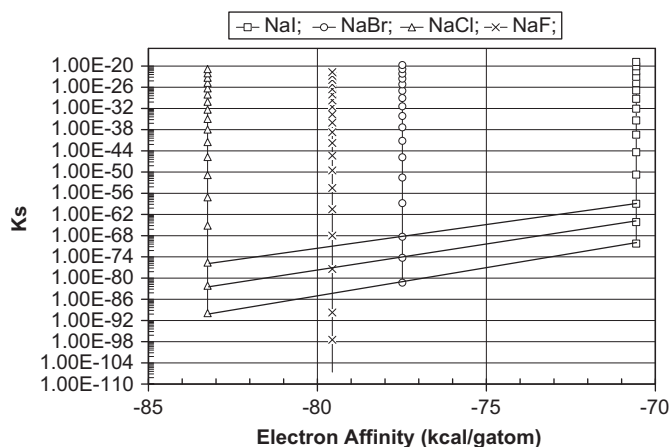


Fig. 7. Graphical representation of the Schottky constants ($\log K_S$) (based on $\Delta S = 10$ eu) of the Na-halides as a function of the electron affinity energies of the halogen atoms and temperature.

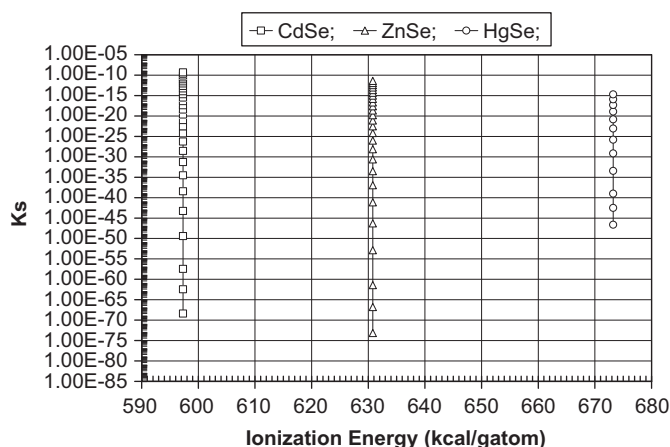


Fig. 8. Graphical representation of the Schottky constants ($\log K_S$) (based on $\Delta S = 10$ eu) of the Zn-, Cd-, and Hg-selenides as a function of the ionization energies of the gaseous metal atoms and temperature.

Because of the proposed physical meaning of the second term of Eq. (7a), namely, I_e , and the small magnitude of the third term at room temperature (the average value of i_b of all groups is about 3), it would be useful to express the latter quantity in terms of the lattice enthalpy. Based on all compounds investigated, the average quantity of the third term at room temperature, for n_{emp} or n_{form} , is $(0.0115 \pm 0.007) \Delta H_{\text{T,L}}^\circ$. That reduces Eq. (7a) to

$$\Delta H_{\text{T,L}}^\circ \approx -(2.303nRT \log K_S) + I_e + 0.0115 \Delta H_{\text{T,L}}^\circ, \quad (8a)$$

or

$$\log K_S \approx -(2.303nRT)^{-1} (0.99 \Delta H_{\text{T,L}}^\circ - I_e). \quad (8b)$$

The latter form is more useful for the computation of K_S values from lattice and ionization energies.

For the chalcogenides, the third term of Eq. (8a) corresponds to about the uncertainty of the lattice enthalpies, and to less than that for the alkali halides investigated. Thus, the third (T -dependent) term of Eq. (7) is considered to be a correction quantity for the Schottky constant and/or the lattice enthalpy. The close trends between the Cd- and Hg-chalcogenides and the Na- and K-halides (Fig. (5)) may also be due to computational and/or thermochemical uncertainties. The deviation of the oxides and fluorides from the observed linearity (Figs. 2–4) remains an important question at this time.

The combined results for the different groups and individual compounds (Table 1) support the validity of Eq. (7) and the apparent physical meaning of the quantities in this relationship. Although Eq. (7) is empirically correct, its theoretical basis is of primary interest for continued studies.

5. Summary and conclusions

Estimations of vacancy concentrations in ZnS [1] have been extended in this study to the other members of this family of compounds, namely, to ZnSe and ZnTe. The computed point defect densities are in close agreement with experimental data for ZnSe, and in reasonable agreement with measurements of hole concentrations in ZnTe.

More importantly, the systematic correlations of the Schottky constants ($\log K_S$) with the experimental lattice enthalpies and with the electron affinities for seven groups of compounds from different parts of the Periodic Table yielded unexpected linear dependences and a new empirical relationship, which have not been reported prior to this work. The analysis of these findings and their similarity to other thermodynamic correlations, such as the $\log K - \Delta G^\circ_{\text{T}}$ relation, strongly support the $\log K_S - \Delta H_{\text{T,L}}^\circ$ dependence as expressed by Eqs. (5) and (7a).

The agreements between the T -independent part of Eq. (7a) and the ionization energies of the metal components of the chalcogenides and halides support the suggested physical meaning of that term in the equation. The smaller T -dependent term (Eq. (7a)), which is nearly constant for all groups of compounds investigated, is considered a correction quantity of the Schottky constants and/or lattice enthalpies.

The theoretical basis of the above equations and of their interpretation is the main objective of further studies.

Acknowledgments

The author would like to thank his colleague R.A. Bailey for continued valuable discussions and constructive critique. He also acknowledges gratefully the use of departmental facilities.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.07.039.

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