

Thermodynamic Properties and Defect Structure of Nonstoichiometric Compounds

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Thermodynamic properties may vary to a considerable extent across the homogeneity range of a nonstoichiometric compound. It is shown that the variations in thermodynamic properties depend upon the nature and distribution of point defects in the lattice as well as upon the change in composition of the compound. A method of computing thermodynamic activities across the entire existence range of the nonstoichiometric compound is presented.

Introduction

It can be shown (1) thermodynamically that all crystalline inorganic compounds are normally nonstoichiometric (i.e., have variable compositions) above absolute zero. Brewer (2) has pointed out that thermodynamic activities, and therefore, the thermodynamic quantities calculated therefrom, may vary to a considerable extent across the existence range of a compound. For example, in MnO at 1650C, the oxygen activities range (3) from about 10^{-5} at the stoichiometric composition to 10^{-1} at $\text{MnO}_{1.04}$. Since the variation in activity may have pronounced effects on the prediction of chemical behavior, it is necessary to know the thermodynamic properties as a function of composition across the entire existence range of a compound.

Deviations from stoichiometry are due to imperfections in the lattice. Consider a compound MX_s , where M represents a metal (or the more electropositive element), X is a nonmetal (or the more electronegative element), and s is the ratio of X to M in the stoichiometric compound. For intermetallic compounds, X will represent the more volatile element for the purposes of later discussion. At any temperature above absolute zero, the lattice may contain six possible types of basic point defects; interstitial X atoms, X_I , metal vacancies, \square_M , X substitutionals (i.e., X atoms on M sites), X_M , X vacancies, \square_X , interstitial metal atoms, M_I , and M substitutionals, M_X . An excess quantity of any of the former three defects will lead to positive deviations from stoichiometry, $\text{MX}_{s+\delta}$, while an excess of any of the latter three will result in negative deviations from stoichiometry, $\text{MX}_{s-\delta}$.

In most solid compounds, the deviations from stoichiometry are so small that they are difficult to detect by usual experimental techniques. However, there is a large group of compounds, particularly those of the transition elements and intermetallic compounds, which exhibit wide compositional variations. These are usually referred to as nonstoichiometric compounds. The purposes of this paper are to show that the variation in thermodynamic properties of a nonstoichiometric compound is a function, not only of the defect concentration, but also of the defect structure (i.e., the type and distribution of defects in the crystal lattice) and to outline a method whereby the thermodynamic activity may be calculated as a function of composition across the whole existence range of a nonstoichiometric compound.

Configurational Entropies

The total free energy of a crystal MX_s containing only point defects may be written:

$$\begin{aligned}
 G = & N\mu_{\text{MX}_s} + N_{\square_M}g_{\square_M} + N_{\square_X}g_{\square_X} + N_{\text{IM}}g_{\text{IM}} \\
 & + N_{\text{IX}}g_{\text{IX}} + N_{\text{M(X)}}g_{\text{M(X)}} + N_{\text{X(M)}}g_{\text{X(M)}} \\
 & - kT \ln \left[\frac{N!}{N_{\square_M}! N_{\text{X(M)}}! (N - N_{\square_M} - N_{\text{X(M)}})!} \right. \\
 & \times \frac{(sN)!}{N_{\square_X}! N_{\text{M(X)}}! (sN - N_{\square_X} - N_{\text{M(X)}})!} \\
 & \left. \times \frac{(\alpha N)!}{N_{\text{IM}}! N_{\text{IX}}! (\alpha N - N_{\text{IM}} - N_{\text{IX}})!} \right] \quad (1)
 \end{aligned}$$

N is the number of metal atom sites, sN the number of X atom sites, and αN the number of interstices in

TABLE I
CONFIGURATIONAL ENTROPIES, S_c , OF INTRINSIC DEFECTS FOR $n_1 = 0.01$

Defect type	Intrinsic defect concentration, n_i	$S_c(\text{eu})$	
		NaCl-type structure	Fluorite structure
Schottky ($\square_M + \square_X$)	$N_{\square_M}/N = N_{\square_X}/sN$	0.223	0.334
Frenkel ($M_I + \square_M$)	$N_{IM}/N = N_{\square_M}/N$	0.236	0.223
Anti-Frenkel ($X_I + \square_X$)	$N_{IX}/sN = N_{\square_X}/sN$	0.236	0.417
Interstitial ($M_I + X_I$)	$N_{IM}/N = N_{IX}/sN$	0.250	0.306
Antistructure ($M_X + X_M$)	$(s+1)N_{M(X)}/sN - (s+1)N_{X(M)}/sN$	0.125	0.169
$M_X + \square_M$	$(s+1)N_{M(X)}/sN = N_{\square_M}/N$	0.174	0.195
$M_X + X_I$	$(s+1)N_{M(X)}/sN = N_{IX}/sN$	0.188	0.284
$X_M + \square_X$	$(s+1)N_{X(M)}/sN = N_{\square_X}/sN$	0.174	0.302
$X_M + M_I$	$N_{IM}/N = (s+1)N_{X(M)}/sN$	0.188	0.191

the lattice where s and α are constants characteristic of the crystal structure. N_{\square_M} , N_{\square_X} , N_{IM} , N_{IX} , $N_{X(M)}$, $N_{M(X)}$ are the numbers of metal vacancies, X atom vacancies, metal interstitials, X interstitials, X substitutionals, and M substitutionals, respectively, and g_{\square_M} , g_{\square_X} , g_{IM} , g_{IX} , $g_{X(M)}$, $g_{M(X)}$ are the corresponding free energies of formation of the defects (other than the contribution from configurational entropy). μ_{M_X} is the free energy of the ideal defect-free crystal. The \ln term in Eq. (1) represents the configurational entropy of the crystal due to the presence of defects. In practice there are rarely more than two types of basic point defects present in the lattice. At the stoichiometric composition, two opposite types (those causing positive and those causing negative deviations from stoichiometry) are present in equivalent concentrations. The concentration of defect pairs at the stoichiometric composition expressed in terms of the ratio of the number of defects to the total number of sites in the lattice is frequently referred to as the *intrinsic defect concentration*, n_i . Expressions for intrinsic defect concentration for each of the nine possible types of intrinsic defect pairs are shown in the second column of Table I. Using these expressions, the following relations for configurational entropy may be derived from the \ln term in Eq. (1) for each type of intrinsic defect.

Schottky Defects:

$$S_c/R = (s+1)(n_i - 1) \ln(1 - n_i) - n_i(s+1) \ln n_i$$

Frenkel Defects:

$$S_c/R = (n_i - 1) \ln(1 - n_i) + (n_i - \alpha) \ln(\alpha - n_i) - 2n_i \ln n_i + \alpha \ln \alpha$$

Anti-Frenkel Defects:

$$S_c/R = s(n_i - 1) \ln(1 - n_i) - sn_i \ln s + (sn_i - \alpha) \ln(\alpha - sn_i) - 2sn_i \ln n_i + \alpha \ln \alpha$$

Interstitial Defects:

$$S_c/R = (sn_i + n_i - \alpha) \ln(\alpha - sn_i - n_i) - n_i \ln n_i - sn_i \ln(sn_i) + \alpha \ln \alpha$$

Antistructure Defects:

$$S_c/R = \ln[(s+1)/(s+1 - sn_i)] + s \ln[(s+1)/(s+1 - n_i)] + [sn_i/(s+1)] \ln[(s+1 - sn_i) \times (s+1 - n_i)/sn_i^2]$$

($M_X + \square_M$) Defects:

$$S_c/R = (n_i - 1) \ln(1 - n_i) + s \ln(s+1) + [s(n_i - s - 1)/(s+1)] \times \ln(s+1 - n_i) - [n_i(2s+1)/(s+1)] \ln n_i$$

($M_X + X_I$) Defects:

$$S_c/R = s \ln(s+1) + [s(n_i - s - 1)/(s+1)] \\ \times \ln(s+1 - n_i) \\ + \alpha \ln \alpha + (sn_i - \alpha) \ln(\alpha - sn_i) \\ - sn_i \ln s \\ - [sn_i(s+2)/(s+1)] \ln n_i$$

($X_M + \square_X$) Defects:

$$S_c/R = \ln(s+1) + [(sn_i - s - 1)/(s+1)] \\ \times \ln(s+1 - n_i) \\ + s(n_i - 1) \ln(1 - n_i) - sn_i \ln n_i \\ - [sn_i/(s+1)] \ln(sn_i)$$

($X_M + M_I$) Defects:

$$S_c/R = \ln(s+1) + [(sn_i - s - 1)/(s+1)] \\ \times \ln(s+1 - sn_i) \\ + (n_i - \alpha) \ln(\alpha - n_i) - [sn_i/(s+1)] \ln s \\ + \alpha \ln \alpha - [n_i(2s+1)/(s+1)] \ln n_i$$

Thus, each type of intrinsic defect leads to a different relation for configurational entropy. The third and fourth columns in Table I show comparisons of values obtained from these relations for 1% intrinsic defects ($n_i = 0.01$) in an NaCl-type structure ($s = 1$, $\alpha = 2$) and a fluorite-type structure ($s = 2$, $\alpha = 1$). It is seen that the configurational entropy may differ by a factor of almost $2\frac{1}{2}$ (e.g., from Anti-Frenkel to Anti-structure defects in the case of the fluorite-type structure). The variance among values is due mainly to the fact that each particular type of defect is distributed over a different number of sites. It should be mentioned that of the nine possible defect types listed in Table I, only five, Schottky, Frenkel, Anti-Frenkel, Anti-structure, and ($X_M + \square_M$) defects have ever been observed (4).

As the compound deviates from the stoichiometric composition, the concentration of one type of point defect of the intrinsic defect pair increases, while the concentration of the other type decreases (the product of the concentrations of the two types of basic point defects remains essentially constant (5)), so that at large deviations from stoichiometry, the assumption can be made that only one type of basic point defect is present. Using this assumption, an expression for the change in configurational entropy, ΔS_c , as a function of deviation from stoichiometry, δ , may be derived for each type of defect from the \ln term in Eq. 1. In accordance with the formula $MX_{s\pm\delta}$, the general relationship between δ and defect concentration is:

$$\delta = \pm \frac{N_{IX} - N_{\square X} + s(N_{\square M} - N_{IM}) + (s+1)(N_{X(M)} - N_{M(X)})}{N + N_{IM} + N_{M(X)} - N_{\square M} - N_{X(M)}} \quad (2)$$

For positive deviations from stoichiometry, the following relations were obtained:

X Interstitials:

$$\Delta S_c/R = \alpha \ln [\alpha/(\alpha - \delta)] + \delta \ln [(\alpha - \delta)/\delta]$$

M Vacancies:

$$\Delta S_c/R = \ln [(s + \delta)/s] + [\delta/(s + \delta)] \ln (s/\delta)$$

X Substitutionals:

$$\Delta S_c/R = s \ln [s(s + \delta + 1)/(s^2 + s\delta + s - \delta)] \\ + [\delta/(s + \delta + 1)] \\ \times \ln [(s^2 + s\delta + s - \delta)/\delta].$$

The variation of ΔS_c with δ is shown in Fig. 1 for various values of s and α . It can be seen that the dependence of configurational entropy on the degree of nonstoichiometry is different for each type of point defect. For negative deviations from stoichiometry, the following expressions for the change in configurational entropy with δ were obtained:

X Vacancies:

$$\Delta S_c/R = s \ln [s/(s - \delta)] + \delta \ln [(s - \delta)/\delta]$$

M Interstitials:

$$S_c/R = \alpha \ln [\alpha(s - \delta)/(\alpha s - \alpha\delta - \delta)] \\ + [\delta/(s - \delta)] \ln [(\alpha s - \alpha\delta - \delta)/\delta]$$

X Substitutionals:

$$S_c/R = s \ln [s(s + 1 - \delta)/(s^2 + s - s\delta - \delta)] \\ + [\delta/(s + 1 - \delta)] \\ \times \ln [(s^2 + s - s\delta - \delta)/\delta].$$

Similar curves to those shown in Fig. 1 may be obtained for negative deviations from stoichiometry. Therefore, the type of defects present in a nonstoichiometric compound may be deduced from the variation of configurational entropy with composition. Experimentally, one usually measures the thermodynamic activity as a function of composition.

Thermodynamic Activities at Large Deviations from Stoichiometry

The following expressions for thermodynamic activity of the X component, a_X , of a nonstoichiometric compound, $MX_{s\pm\delta}$, as a function of defect concentration have been derived (5) from Eq. (1). Each type of point defect leads to a different functional relationship between a_X and δ because of the differences in the number of sites over which the defects may be distributed, and also because of

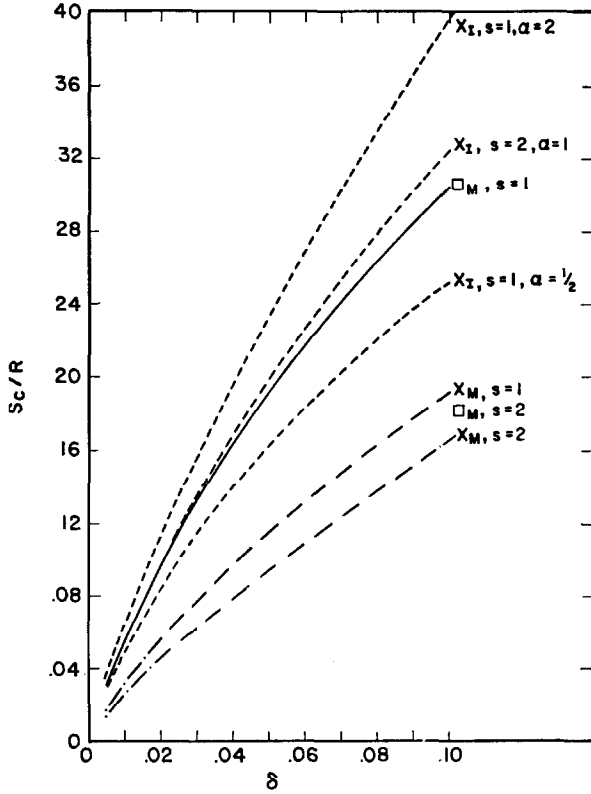


FIG. 1. Configurational entropies as a function of stoichiometry in the compound, $MX_{s+\delta}$.

dissimilar changes in the total number of sites on defect formation. Similar relations may be derived in terms of the M component.

For M vacancies:

$$a_X = C_{\square M} \left[\frac{N_{\square M}^{1/s} (\alpha N - N_{IM} - N_{IX})^{\alpha/s} (sN - N_{\square X} - N_{M(X)})}{N^{1/s} (\alpha N)^{\alpha/s} (sN)} \right] \quad (3)$$

where

$$C_{\square M} = \exp [(\mu_{MX_s} + g_{\square M})/skT]. \quad (4)$$

At large deviations from stoichiometry $N_{\square M} \gg N_{IM}, N_{IX}, N_{\square X}, N_{M(X)}$; $\delta = sN_{\square M}/(N - N_{\square M})$, and Eq. (3) may be rewritten:

$$a_X = C_{\square M} [\delta/(s + \delta)]^{1/s}. \quad (5)$$

For X interstitials:

$$a_X = C_{IX} [N_{IX}/(\alpha N - N_{IX} - N_{IM})] \quad (6)$$

where

$$C_{IX} = \exp(g_{IX}/kT). \quad (7)$$

For large deviations from stoichiometry $N_{IX} \gg N_{IM}$, $\delta = N_{IX}/N$, and Eq. (6) becomes:

$$a_X = C_{IX} [\delta/(\alpha - \delta)]. \quad (8)$$

For X substitutionals:

$$a_X = C_{X(M)} \times \left[\frac{N_{X(M)} (sN - N_{\square X} - N_{M(X)})^s (\alpha N - N_{IM} - N_{IX})^\alpha}{N (sN)^s (\alpha N)^\alpha} \right]^{1/(s+1)} \quad (9)$$

where

$$C_{X(M)} = \exp [(\mu_{MX_s} + g_{X(M)})/(s+1)kT]. \quad (10)$$

For large deviations from stoichiometry $N_{X(M)} \gg N_{\square X}, N_{M(X)}, N_{IM}, N_{IX}$; $\delta = (s+1)N_{X(M)}/(N - N_{X(M)})$, and Eq. (9) becomes:

$$a_X = C_{X(M)} [\delta/(s + \delta + 1)]^{1/(s+1)}. \quad (11)$$

For X vacancies:

$$a_X = C_{\square X} [(sN - N_{\square X} - N_{M(X)})/N_{\square X}] \quad (12)$$

where

$$C_{\square X} = \exp(-g_{\square X}/kT). \quad (13)$$

For large deviations from stoichiometry $N_{\square X} \gg N_{M(X)}$, $\delta = N_{\square X}/N$ and Eq. (13) becomes:

$$a_X = C_{\square X} [(s - \delta)/\delta]. \quad (14)$$

For M interstitials:

$$a_X = C_{IM} \times \left[\frac{(\alpha N - N_{IM} - N_{IX})^{\alpha+1} (sN - N_{\square X} - N_{M(X)})}{sN_{IM} N^2 (\alpha N)^\alpha} \right]^{1/s} \quad (15)$$

where

$$C_{IM} = \exp [(\mu_{MX_s} - g_{IM})/skT]. \quad (16)$$

For large deviations from stoichiometry $N_{IM} \gg N_{IX}, N_{\square X}, N_{M(X)}, N_{\square M}, N_{X(M)}$; $\delta = sN_{IM}/(N + N_{IM})$ and Eq. (16) becomes:

$$a_X = C_{IM} [(\alpha s - \alpha \delta - \delta)^{\alpha+1} / \delta (\alpha s - \alpha \delta)^\alpha]^{1/s} \quad (17)$$

For M substitutionals:

$$a_X = C_{M(X)} (sN - N_{\square X} - N_{M(X)}) \times \left[\frac{(N - N_{\square M} - N_{X(M)}) (\alpha N - N_{IM} - N_{IX})^\alpha}{N_{M(X)} (sN)^s (\alpha N)^\alpha N} \right]^{1/(s+1)} \quad (18)$$

where

$$C_{M(X)} = \exp [(\mu_{MX_s} - g_{M(X)})/(s+1)kT]. \quad (19)$$

For large deviations from stoichiometry $N_{M(X)} \gg N_{\square M}, N_{X(M)}, N_{IM}, N_{IX}$; $\delta = (s+1)N_{M(X)}/(N + N_{X(M)})$ and Eq. (19) becomes:

$$a_X = C_{M(X)} (s+1)(s - \delta) / [(s^2 + s - s\delta)^s \delta]^{1/(s+1)}. \quad (20)$$

Eqs. (5), (8), and (11) apply for positive deviations from stoichiometry and Eqs. (14), (17), and (20) apply for negative deviations from stoichiometry.

It is apparent that if the types of defects responsible for the deviations from stoichiometry and the values of the appropriate constants C_{defect} (containing the energies of defect formation g_{defect}) are known, the thermodynamic activity as a function of deviation from stoichiometry, δ , may be computed at large deviations from stoichiometry using Eqs. (5), (8), (11), (14), (17), and (20). Conversely, the nature of the predominant defect and the values of the constants may be determined by comparing experimental activity data at large deviations from stoichiometry with the same set of equations. This has been done (5) for several systems. The case of positive deviations from stoichiometry in lanthanum dihydride at 706C is illustrated in Fig. 2. (If the standard state of hydrogen is taken as H_2 gas at 1 Torr, the activity of hydrogen in the hydride may be expressed as the square root of the equilibrium hydrogen pressure in Torr). The computed curves were obtained from Eqs. (5), (8), and (11) by calculating the values of the constants, $C_{\square_{\text{La}}}$, C_{H} , and $C_{\text{H(La)}}$, which gave the best fit with the data in each case. Lanthanum dihydride has the fluorite structure so that $\alpha = 1$ and $s = 2$. The shapes or slopes of the curves in each case are determined by

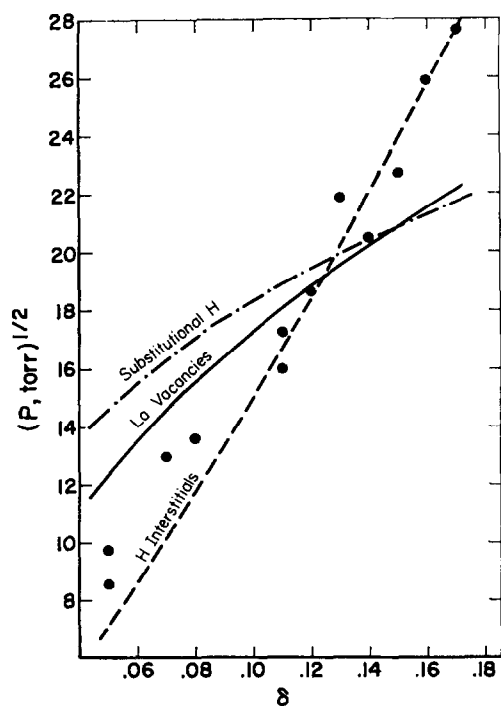


FIG. 2. Activity of hydrogen in $\text{LaH}_{2+\delta}$ as a function of deviation from stoichiometry at 706C. Data of Korst and Warf.

the particular function of δ which is characteristic of that type of defect. The constants merely determine the relative height of each curve on the ordinate. It is seen here that the activity data of Korst and Warf (6) give the best fit for the case of interstitial hydrogen. This is in accordance with neutron diffraction (7) and NMR studies (8) which have established that the defects are indeed hydrogen interstitials.

The deviation of the computed curve from the experimental points as the concentration approaches stoichiometry ($\delta = 0$) is due to the increased concentration of the opposite defect of the intrinsic defect pair. As mentioned above, Eqs. (5), (8), (11), (14), (17), and (20) were derived with the assumption that only one type of basic point defect is present. Consequently, they are not valid in the vicinity of the stoichiometric composition.

In a similar manner the experimental data at large negative deviations from stoichiometry can be used to determine the predominant defect in this region and also the value of the corresponding constant. The data for lanthanum dihydride at 706C are shown in Fig. 3. The computed curves were obtained from Eqs. (14), (17), and (20). It appears that hydrogen vacancies are the predominant defects at large negative deviations from stoichiometry. Here again, deviation of the computed curve from the experimental data is observed as δ approaches zero. The

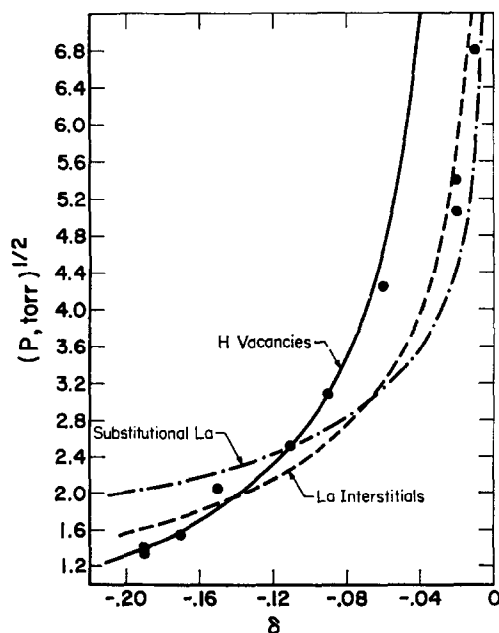


FIG. 3. Activity of hydrogen in $\text{LaH}_{2-\delta}$ as a function of deviation from stoichiometry at 706C. Data of Korst and Warf.

intrinsic defect for LaH_2 is therefore the Anti-Frenkel defect, hydrogen interstitials and hydrogen vacancies.

Computation of Activities

In order to illustrate how the activity across the entire existence range (including compositions in the vicinity of and at the stoichiometric composition) may be calculated, let us consider the case of Anti-Frenkel defects in lanthanum dihydride in detail.

Anti-Frenkel Defects

For Anti-Frenkel defects ($X_I + \square_X$), Eq. (2) may be written:

$$\delta = (N_{IX} - N_{\square_X})/N \quad (21)$$

and Eqs. (6) and (12) become:

$$a_X = C_{IX}[N_{IX}/(\alpha N - N_{IX})] \quad (22)$$

and

$$a_X = C_{\square_X}[(sN - N_{\square_X})/N_{\square_X}] \quad (23)$$

respectively. Elimination of N_{IX} and N_{\square_X} from Eqs. (21)–(23) yields:

$$(\alpha - \delta)a_X^2 + C_{\square_X}(\alpha - s - \delta)a_X - \delta C_{IX}a_X = C_{IX}C_{\square_X}(s + \delta). \quad (24)$$

For $\text{LaH}_{2 \pm \delta}$, this equation becomes:

$$(1 - \delta)a_H^2 - (\delta C_{IH} + \delta C_{\square_H} + C_{\square_H})a_H = C_{IH}C_{\square_H}(2 + \delta). \quad (25)$$

It was shown in the previous section that C_{IH} and C_{\square_H} can be determined from hydrogen activity data

at large positive and negative deviations from stoichiometry, respectively. For a hydrogen standard state of hydrogen gas at 1 Torr pressure, the values calculated were $C_{IH} = 135$ and $C_{\square_H} = 0.146$ at 706C. Utilizing these values, the activity across a wide composition range of lanthanum dihydride (including the stoichiometric composition) may be computed from Eq. (25). The result is illustrated in Fig. 4 where it can be seen that the points at $\delta = 0.08, 0.07, \text{ and } 0.05$ which previously were above the calculated curve in Fig. 2, and the points at $\delta = -0.01$ and -0.02 , which were considerably below the calculated curve in Fig. 3, are now much closer to the curve computed from Eq. (25).

As shown in Eqs. (7) and (13), the constants C_{IH} and C_{\square_H} contain the free energies of defect formation g_{IH} and g_{\square_H} with respect to some standard state. In the case discussed above, the standard state is hydrogen gas at 1 Torr pressure. Therefore, g_{IH} is the free energy of formation of a hydrogen interstitial by addition of an H atom to the crystal from hydrogen gas at 1 Torr. g_{\square_H} is the free energy of formation of a hydrogen vacancy by removal of an H atom from the crystal to hydrogen gas at 1 Torr. Since these free energies are in terms of some arbitrary standard state, the values of C_{IH} and C_{\square_H} cannot be computed independently. However, the ratio C_{\square_H}/C_{IH} is independent of standard state. We can write:

$$C_{IH}/C_{\square_H} = \exp[(g_{\square_H} + g_{IH})/kT] = \exp(g_{AF}/kT) \quad (26)$$

where g_{AF} is the sum of the free energies of removing

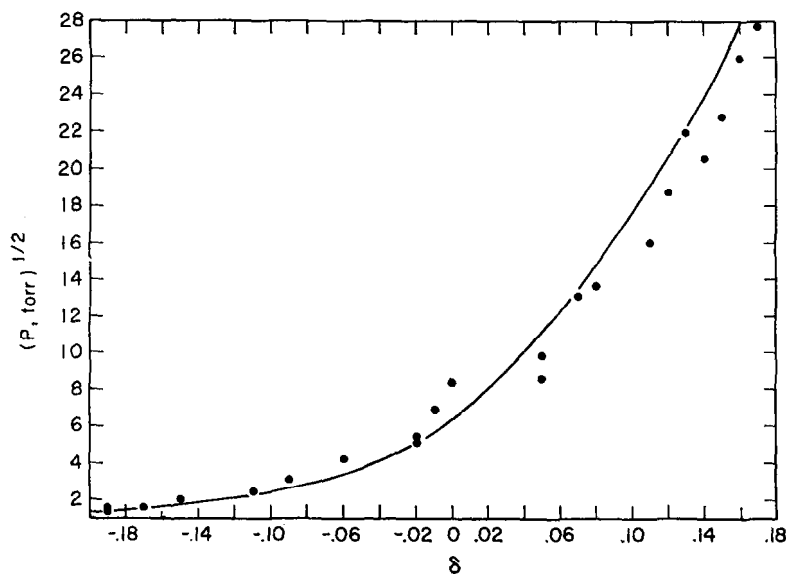


FIG. 4. Comparison of activity data of Korst and Warf for $\text{LaH}_{2 \pm \delta}$ at 706C with the corresponding curve calculated from Eq. (25).

an H atom to its standard state to form a vacancy plus the free energy of removing the H atom from the same standard state and placing it into an interstice in the crystal. Thus, the energy of the standard state is canceled out and g_{AF} is merely the free energy of intrinsic Anti-Frenkel defects; i.e., the energy necessary to remove an H atom from its normal site and place it into an interstice.

The energy of intrinsic defect formation may be computed from lattice energies (9) so that ratio $C_{\square H}/C_{IH}$ may be obtained independent of activity measurements. Therefore, in some cases, it is only necessary to obtain data at one side of the stoichiometric composition (either large positive or large negative deviations from stoichiometry) in order to calculate activities across the entire existence range of a compound. In addition, if the ratio of constants is known at one temperature, it may be calculated at other temperatures from Eq. (26).

By equating Eqs. (22) and (23) at the stoichiometric composition where $N_{\square X} = N_{IX}$, a relation between the ratio of constants and the intrinsic defect concentration, n_i (as defined in Table I) may be obtained:

$$C_{IX}/C_{\square} = (s - sn_i)(\alpha - sn_i)/(sn_i)^2.$$

Consequently, if the intrinsic defect concentration is obtained in an independent manner (e.g., density measurements), the ratio of constants can be computed. Conversely, the intrinsic defect concentration may be calculated from the constants obtained from activity measurements at large deviations from stoichiometry.

Schottky Defects

For the case of Schottky defects, Eqs. (2), (3), and (12) may be written:

$$\delta = \frac{sN_{\square M} - N_{\square X}}{N - N_{\square M}}$$

$$a_X = C_{\square M} \left[\frac{N_{\square M}^{1/s}(sN - N_{\square X})}{sN^{(1+s)/s}} \right] \quad (27)$$

$$a_X = C_{\square X} [(sN - N_{\square X})/N_{\square X}]. \quad (28)$$

By eliminating $N_{\square M}$ and $N_{\square X}$ from these three equations, the following expression relating activity to δ for Schottky defects is obtained:

$$(a_X + C_{\square X})^{s+1}(s + \delta) = C_{\square M}^s [C_{\square X}(s + \delta) + \delta a_X] \quad (29)$$

For compounds with one-to-one stoichiometry ($s = 1$), Eq. (29) becomes:

$$(1 + \delta) a_X^2 + (2C_{\square X} + 2\delta C_{\square X} - \delta C_{\square M}) a_X + C_{\square X}(1 + \delta)(C_{\square X} - C_{\square M}) = 0.$$

From Eqs. (4) and (13) we see that the ratio of constants in this case is:

$$C_{\square M}/C_{\square X} = \exp [(\mu_{MX_s} + g_{\square M} + sg_{\square X})/skT] \quad (30)$$

$g_{\square M}$ and $g_{\square X}$ are the free energies of formation of an M vacancy and an X vacancy by removing an M atom and an X atom to their respective standard states, and μ_{MX_s} is the free energy of formation of a formula unit of MX_s from M atoms and X atoms in their standard states. Therefore $(\mu_{MX_s} + g_{\square M} + sg_{\square X})$ is the free energy of formation of Schottky defect, i.e., the energy necessary to remove an M atom and s X atoms from their normal sites to create vacancies and to form new M and X sites. This quantity can be calculated from lattice energies (9).

From Eqs. (27) and (28) and the definitions of intrinsic defect concentration in Table I, the following relationship is obtained for Schottky defects:

$$C_{\square M}/C_{\square X} = n_i^{-(s+1)/s}.$$

In a manner similar to the ones used for Anti-Frenkel and Schottky defects, the relations between thermodynamic activity and deviation from stoichiometry, δ , may be derived for each of the remaining seven types of possible intrinsic defect pairs. These are outlined below.

Frenkel Defects

For the case of Frenkel defects, Eqs. (2), (3), and (15) may be rewritten as follows:

$$\delta = s(N_{\square M} - N_{IM})/(N + N_{IM} - N_{\square M}) \quad (31)$$

$$a_X = C_{\square M} [N_{\square M}(\alpha N - N_{IM})^\alpha / \alpha N^{\alpha+1}]^{1/s} \quad (32)$$

$$a_X = C_{IM} [(\alpha N - N_{IM})^{\alpha+1} (N - N_{\square M}) / \alpha^\alpha N_{IM} N^{\alpha+1}]^{1/s}. \quad (33)$$

It is not possible to get a general analytic relation between a_X and δ by simple algebraic manipulation. However, in specific cases when α and s are known, a_X as a function of δ may be obtained by elimination of $N_{\square M}$ and N_{IM} from Eqs. (31)–(33).

The ratio of constants in this case is:

$$C_{\square M}/C_{IM} = \exp [(g_{\square M} + g_{IM})/skT]$$

where $g_{\square M} + g_{IM}$ is the energy necessary to form a Frenkel defect. Also, from Eqs. (32) and (33) and Table I at $\delta = 0$,

$$C_{\square M}/C_{IM} = \alpha^{1-\alpha} (\alpha - n_i) (1 - n_i) / n_i^2.$$

Interstitial Defects

For the case where the intrinsic defects are interstitial defects, Eqs. (2), (6), and (15) may be written:

$$\delta = (N_{IX} - sN_{IM}) / (N + N_{IM}) \quad (34)$$

$$a_X = C_{IX}[N_{IX}/(\alpha N - N_{IX} - N_{IM})] \quad (35)$$

$$a_X = C_{IM}[(\alpha N - N_{IM} - N_{IX})^{\alpha+1}/N_{IM}(\alpha N)^\alpha]^{1/s}. \quad (36)$$

Eliminating N_{IX} and N_{IM} from Eqs. (34)–(36) yields the following relationship between a_X and δ

$$a_X^s \alpha^\alpha [C_{IX}(s + \delta) + a_X(s + \delta + 1)]^\alpha [a_X \alpha - a_X \delta - C_{IX} \delta] \\ = C_{IM}^s C_{IX}^{\alpha+1} (\alpha \delta + \alpha \delta + \delta)^{\alpha+1}. \quad (37)$$

It can be seen that this is at least a cubic equation in a_X , and it becomes much higher order if $s, \alpha > 1$. Therefore, it is advantageous to use a computer to work out the exact variation of a_X with δ for specific values of C_{IX} and C_{IM} .

From Eqs. (7) and (16):

$$C_{IX}/C_{IM} = \exp[(\mu_{MX_s} + sg_{IX} - g_{IM})/skT],$$

and from Eqs. (35) and (36) and Table I:

$$C_{IX}/C_{IM} = [(\alpha - n_i - sn_i)^{\alpha+s+1}/s^s \alpha^\alpha n_i^{s+1}]^{1/s}.$$

Antistructure Defects

For antistructure defects, Eqs. (2), (9) and (18) become:

$$\delta = (s + 1)(N_{X(M)} - N_{M(X)})/(N + N_{M(X)} - N_{X(M)}) \quad (38)$$

$$a_X = (C_{X(M)}/N)[N_{X(M)}(sN - N_{M(X)})^s/s^s]^{1/s+1} \quad (39)$$

$$a_X = C_{M(X)}(sN - N_{M(X)})(N - N_{X(M)})^{1/(s+1)}/ \\ N(s^s N_{M(X)})^{1/(s+1)}. \quad (40)$$

Here again, it is not possible to obtain a general analytic expression relating a_X and δ , but by eliminating $N_{M(X)}$ and $N_{X(M)}$ from Eqs. (38)–(40) for specific values of s and α , and using EDP techniques, a_X as a function of δ may be computed for specific values of $C_{X(M)}$ and $C_{M(X)}$.

From Eqs. (10) and (19) we have:

$$C_{X(M)}/C_{M(X)} = \exp[(g_{X(M)} + g_{M(X)})/(s + 1)kT]$$

and from Eqs. (39), (40) and Table I:

$$C_{X(M)}/C_{M(X)} = [(s + 1 - n_i)(s + 1 - sn_i)/sn_i^2]^{1/(s+1)}.$$

M Vacancy plus M Substitutional Defects

For ($\square_M + M_X$) defects, Eqs. (2), (3), and (18) become:

$$\delta = [sN_{\square M} - (s + 1)N_{M(X)}]/(N - N_{\square M}) \quad (41)$$

$$a_X = C_{\square M} N_{\square M}^{1/s} (sN - N_{M(X)})/sN^{(s+1)/s} \quad (42)$$

$$a_X = C_{M(X)}(sN - N_{M(X)})[(N - N_{\square M})/N_{M(X)} \\ \times (sN)^s N]^{1/(s+1)} \quad (43)$$

As in the cases of interstitial defects and antistructure defects, a general analytic expression cannot be obtained by eliminating $N_{M(X)}$ and $N_{\square M}$ from Eqs. (41) to (43). However, a_X as a function of δ

may be obtained for specific values of $s, C_{\square M}$, and $C_{M(X)}$.

From Eqs. (4) and (19) we may write:

$$C_{\square M}/C_{M(X)} = \exp[(\mu_{MX_s} + sg_{\square M} + g_{\square M} + sg_{M(X)})/s(s + 1)kT]$$

and from Eqs. (42), (43) and Table I:

$$C_{\square M}/C_{M(X)} = [(1 - n_i)(s + 1)/n_i^{2(s+1)/s}]^{1/s+1}.$$

X Interstitial plus M Substitutional Defects

For ($X_I + M_X$) defects, Eqs. (2), (6), and (18) may be written:

$$\delta = [N_{IX} - (s + 1)N_{M(X)}]/(N + N_{M(X)}) \quad (44)$$

$$a_X = C_{IX}[N_{IX}/(\alpha N - N_{IX})] \quad (45)$$

$$a_X = C_{M(X)}(sN - N_{M(X)})[(\alpha N - N_{IX})^\alpha/N_{M(X)} \\ (sN)^s (\alpha N)^\alpha]^{1/s+1} \quad (46)$$

Eliminating N_{IX} and $N_{M(X)}$ from Eqs. (44)–(46) yields the following relationship:

$$a_X^{s+1} [s(a_X + C_{IX})(s + 1 + \delta)]^s (a_X \alpha - \delta a_X - \delta C_{IX}) \\ (a_X + C_{IX})^\alpha \\ = C_{M(X)}^{s+1} C_{IX}^\alpha [(a_X + C_I)(s^2 + s + s\delta + \delta) - a_X \alpha]^{s+1}. \quad (47)$$

It is seen that this equation involves a_X to at least the fifth power (for $s = 1$ and $\alpha = 1$), thus making the use of a computer desirable for obtaining the explicit dependence of a_X on δ for specific cases.

From Eqs. (7) and (19) we obtain:

$$C_{IX}/C_{M(X)} = \exp[(sg_{IX} + g_{IX} + g_{M(X)} - \mu_{MX_s})/(s + 1)kT]$$

and from Eqs. (45), (46) and Table I we obtain:

$$C_{IX}/C_{M(X)} = [(\alpha - sn_i)^{\alpha+s+1}(s + 1 - n_i)^{s+1}/\alpha^\alpha s^{s+1}(s + 1)^s n_i^{s+2}]^{1/s+1}.$$

X Substitutional plus X Vacancy

For the ($X_M + \square_X$) intrinsic defect, Eqs. (2), (9), and (12) may be written:

$$\delta = [(s + 1)(N_{X(M)} - N_{\square X})]/(N - N_{X(M)}) \quad (48)$$

$$a_X = C_{X(M)}[N_{X(M)}(sN - N_{\square X})^s/(sN)^s N]^{1/s+1} \quad (49)$$

$$a_X = C_{\square X}(sN - N_{\square X})/N_{\square X}. \quad (50)$$

Eliminating $N_{X(M)}$ and $N_{\square X}$ from Eqs. (48)–(50) yields the following relationship between a_X and δ :

$$a_X(a_X + C_{\square X})^{s+1}(s + 1 + \delta) \\ = C_{X(M)}^{s+1}(sC_{\square X} + \delta a_X + \delta C_{\square X}). \quad (51)$$

From Eqs. (10) and (13) we obtain:

$$C_{X(M)}/C_{\square X} = \exp \{ [\mu_{MX_s} + g_{X(M)} + (s+1)g_{\square X}] / (s+1) / kT \}$$

and from Eqs. (49), (50) and Table I:

$$C_{X(M)}/C_{\square X} = [(1 - n_i)(s+1)/sn_i^{s+2}]^{1/s+1}.$$

X Substitutional plus Metal Interstitial Defects

For the $(X_M + M_i)$ defect, Eqs. (2), (9), and (15) become:

$$\delta = \frac{(s+1)N_{X(M)} - sN_{IM}}{N + N_{IM} - N_{X(M)}} \quad (52)$$

$$a_X = C_{X(M)} \left[\frac{N_{X(M)}(\alpha N - N_{IM})^\alpha}{(\alpha N)^\alpha N} \right]^{1/(s+1)} \quad (53)$$

$$a_X = C_{IM} \left[\frac{(\alpha N - N_{IM})^{\alpha+1} (N - N_{X(M)})}{N_{IM} N (\alpha N)^\alpha} \right]^{1/s} \quad (54)$$

As in some of the previous cases, a general expression for a_X as a function of δ cannot be obtained in this case. However, for specific values of s , δ , $C_{X(M)}$ and C_{IM} , a_X can be computed at various values for δ .

From Eqs. (10) and (16) we obtain:

$$C_{X(M)}/C_{IM} = \exp \{ [sg_{X(M)} + (s+1)g_{IM} - \mu_{MX_s}] / (s+1) / kT \}$$

and from Eqs. (53), (54) and Table I:

$$C_{X(M)}/C_{IM} = [(\alpha - n_i)^{\alpha+s+1} (s+1 - sn_i)^{s+1} / \alpha^\alpha s^s (s+1) n_i^{2s+1}]^{1/s(s+1)}$$

Conclusion

It has been shown that the configurational entropy and, therefore, the chemical potential and thermodynamic activity of a nonstoichiometric compound depend upon the nature of the defects present as well as their concentration. From Eqs. (5), (8), (11), (14), (17), and (20), the nature of the defects responsible for the nonstoichiometry may be deduced from activity measurements at large deviations from stoichiometry. Utilizing this information, the thermodynamic activity as a function of composition may be computed across the existence range (including the stoichiometric composition) of a

nonstoichiometric compound from Eqs. (24), (29), and (31)–(54). The free energies of defect formation and the intrinsic defect concentrations also may be calculated from activity measurements.

It should be pointed out that the treatment presented here neglects interactions between defects. Interactions may become important at very large deviations from stoichiometry or low temperatures or both. Relations between a_X and δ at large deviations from stoichiometry equivalent to Eqs. (5), (8), (11), (14), (17) and (20) have been worked out for the case of defect interactions (10), and these may be used to derive a_X as a function of δ across the whole existence range in the manner described in the previous section, although the algebra would be considerably more cumbersome.

In nonstoichiometric semiconducting compounds, the distribution of electronic defects must be taken into account at temperatures above which the defect ionizes. This can be done (11) relatively simply by an additional term in the expression for configurational entropy.

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