Appendix A

Thermodynamics and Normalisation

A.1 Reaction Equilibria

The following derivation is based on that of Kröger and Vink [201]. The laws of thermodynamics state that, at equilibrium, the sum of the thermodynamic potentials of the reactants is equal to the sum of the thermodynamic potential of the products, i.e.

$$\sum_i n_i \mu_i = 0 \tag{A.1}$$

where n_i is the number of atoms of i in the reaction and μ_i is its corresponding thermodynamic potential:

$$\mu_i = h_i - Ts_i \tag{A.2}$$

where h_i and s_i are the partial enthalpy and partial entropy of i. μ_i is also a function of x_i, the concentration of i, and it follows from statistics (providing that the system is closed) that:

$$\mu_i = (\mu_i)_\circ + kTlnx_i \tag{A.3}$$

where $(\mu_i)_\circ$ is the thermodynamic potential of i under standard conditions (273 K). Combining A.3 and A.1;

$$\sum n_i \left((\mu_i)_\circ + kTlnx_i\right) = 0 \tag{A.4}$$

$$\Rightarrow \sum n_i(\mu_i)_\circ + \sum n_i kTlnx_i = 0 \tag{A.5}$$

$$\Rightarrow \sum n_i lnx_i = \frac{-\sum n_i(\mu_i)_\circ}{kT} \tag{A.6}$$

$$\Rightarrow \Pi x_i^{n_i} = \exp\left(\frac{-\sum n_i(\mu_i)_\circ}{kT}\right) \tag{A.7}$$

where $\Pi x_i^{n_i}$ is the product of $x_i^{n_i}$ with different values of i, the values of n_i corresponding to the products is positive, with that corresponding to the reactants is negative. The law of mass action states that this is equal to the equilibrium constant, K;

$$\Pi x_i^{n_i} = K \tag{A.8}$$

Combining A.7, A.8 and A.2;

$$K = \exp\left(\frac{\sum n_i(s_i)_\circ}{kT}\right) \cdot \exp\left(\frac{-\sum n_i(h_i)_\circ}{kT}\right) = C\exp\left(\frac{-\sum n_i(h_i)_\circ}{kT}\right) \tag{A.9}$$

where C is the reaction constant for the process. For a reaction in thermodynamic equilibrium, $\sum n_i(h_i)_\circ$ is the reaction energy. For example, for the Schottky reaction, this is the enthalpy for the total Schottky process.

A.2 Thermodynamic Approximations

The reaction energies presented in this thesis are internal energies. As such they do not account for the entropy or PV (pressure $\times$ volume) components in the Gibbs free energy. The reason this approximation does not cause a significant error is that the reaction energies calculated here are used to discuss relative rather than absolute values.

The approximation detailed below is taken from Kröger [3]. If an equilibrium exists between two reactants A and B and two products C and D:

$$aA + bB \rightleftharpoons cC + dD \tag{A.10}$$

The equilibrium condition can then be applied:

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K = \exp\left(\frac{-\Delta G}{kT}\right) \tag{A.11}$$

where K is the equilibrium constant for the reaction, ΔG is the Gibbs free energy, k is the Boltzmann constant, T is the temperature kelvin and square brackets indicate a concentration. This relationship can then be expanded using $\Delta G = \Delta H - T\Delta S$ with H being the enthalpy and S being the entropy:

$$K = \exp\left(\frac{-\Delta H}{kT}\right) \cdot \exp\left(\frac{\Delta S}{k}\right) \tag{A.12}$$

If the change in entropy (ΔS) is small, it follows that $\exp\left(\frac{\Delta S}{k}\right) \approx 1$. Hence, the approximation is possible:

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} \approx \exp\left(\frac{-\Delta H}{kT}\right) \tag{A.13}$$

It is therefore possible to assume that $\Delta G \approx \Delta H$ for this type of equilibrium with no external stimulus. This approximation has been used successfully in the past, for example Zacate *et al.* [27].

A.3 Normalisation Factor Worked Examples

A.3.1 Schottky Defect Process

In order to compare different defect reactions, with different numbers of defects, an equivalence must be determined. This equivalence is that the reaction energies are

normalised per defect following the approach detailed below for the worked example of a Schottky process in a perovskite ABO_3.

$$A_A^X + B_B^X + 3O_O^X \rightleftharpoons V_A''' + V_B''' + 3V_O^{\bullet\bullet} + ABO_3 \tag{A.14}$$

Electroneutrality condition:

$$3[V_O^{\bullet\bullet}] = [V_A'''] + [V_B'''] \tag{A.15}$$

Corresponding Equation of State:

$$[V_O^{\bullet\bullet}]^3[V_A'''][V_B'''] = \exp\left(\frac{-\Delta H}{kT}\right) \tag{A.16}$$

For a pure Schottky reaction it also follows that $[V_A'''] = [V_B''']$ so that the electoneutrality condition gives;

$$3[V_O^{\bullet\bullet}] = 2[V_A'''] \tag{A.17}$$

and

$$3[V_O^{\bullet\bullet}] = 2[V_B'''] \tag{A.18}$$

Substituting the neutrality conditions into the equation of state the concentrations of the individual defects can be expressed as,

$$\frac{9}{4}[V_O^{\bullet\bullet}]^5 = \exp\left(\frac{-\Delta H}{kT}\right) \tag{A.19}$$

$$[V_O^{\bullet\bullet}] = \sqrt[5]{\frac{4}{9}} \exp\left(\frac{-\Delta H}{\mathbf{5}kT}\right) \tag{A.20}$$

It can be seen from the above equation that the normalisation factor (in bold) for the Schottky process is 5. The same approach can also be applied to the other defects in the reaction, however, different pre-exponential multipliers will develop as is illustrated by the case for V_A'''.

If we want to solve for the V_A''' defect concentration we can again use the charge neutrality conditions to give;

$$\left(\frac{2}{3}\right)^3 [V_A''']^5 = \exp\left(\frac{-\Delta H}{kT}\right) \tag{A.21}$$

$$[V_A'''] = \left(\frac{2}{3}\right)^{\frac{3}{5}} \exp\left(\frac{-\Delta H}{\mathbf{5}kT}\right) \tag{A.22}$$

A.3.2 Anion Frenkel disorder and extrinsic defects in ZnF_2

The anion Frenkel reaction in ZnF_2 is;

$$F_F^X \rightleftharpoons F_i' + V_F^{\bullet} \tag{A.23}$$

and the corresponding mass action equation [201] is;

$$\frac{[F_i'][V_F^{\bullet}]}{[F_F^X]} = \exp\left(\frac{-\Delta H_F}{kT}\right) \tag{A.24}$$

where ΔH_F is the total calculated energy for Equation A.23.If this is the dominant reaction then electroneutrality would dictate that;

$$[F_i'] = [V_F^\bullet] \tag{A.25}$$

and Equation A.24 can be rewritten to yield;

$$[F_i'] = \exp\left(\frac{-\Delta H_F}{2kT}\right) \tag{A.26}$$

The energy that is of significance in order to determine the F^- ion interstitial concentration (or fluorine vacancy concentration) is therefore $\Delta H_F/2$. The value 2 is the normalization factor for this reaction. An equivalent analysis for extrinsic reactions can also be carried out. For example, assuming Equation 6.8, for Li^+ solution, so that Li^+ interstitial compensation is dominant (Chapter 6), electroneutrality would dictate that;

$$[Li_i^\bullet] = [Li'_{Zn}] \tag{A.27}$$

and the mass action equation becomes;

$$[Li'_{Zn}] = \exp\left(\frac{-\Delta H_{sol}}{2kT}\right) \tag{A.28}$$

The energies for the isolated defect reactions reported in this thesis have been normalized. When defect clusters are formed, the component defect positions are spatially correlated. This limits the configurational contribution and alters the mass

action equations so that the normalization factor becomes unity (in the case where all defects are bound into a cluster).