

Electronic Supplementary Information

Tuning metal oxides defect chemistry by thermochemical quenching

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Derivation of the ratio between the concentrations of the charge states of a quenched defect

To compute the ratios of the charge states of a certain ionic defect at the quenched state, we consider, without loss of generality, the example of oxygen vacancies domination regime where they are charge balanced by electrons. It is important to note that the combination of charged oxygen vacancies that gives the minimum free energy will be achieved while maintaining the quenching constraint that the total number of oxygen vacancies remains constant.

The difference in Gibbs free energy between the quenched defective crystal and the perfect ideal crystal (ΔG) at the final temperature ($T = 300$ K in this study) is given by

$$\Delta G = [V_O^\times]E_f(V_O^\times) + [V_O^\cdot]E_f(V_O^\cdot) + [V_O^{\cdot\cdot}]E_f(V_O^{\cdot\cdot}) + n_c E_f(n_c) - T\Delta S_1 - T\Delta S_2 - T\Delta S_3 - T\Delta S_{elec} \quad (1)$$

Where, $E_f(V_O^\times)$, $E_f(V_O^\cdot)$, and $E_f(V_O^{\cdot\cdot})$ represent the *equilibrium* formation energies of neutral, (1+) and (2+) oxygen vacancies respectively. While, ΔS_1 , ΔS_2 , and ΔS_3 are the increase in entropy due to configurational disorder introduced to the crystal by the 3 oxygen vacancies charge states. Similarly $E_f(n_c)$ and ΔS_{elec} are the formation energy of electrons and the change in the configurational electronic entropy. n_c is the concentration of electrons.

By applying the Boltzmann equation for the entropy of a disordered system:

$$S = k \ln W \quad (2)$$

Where k is the Boltzmann constant and W is the number of ways of distributing n defects over N lattice sites:

$$W = \frac{N!}{(N-n)!n!} \quad (3)$$

Accordingly,

$$S = k \ln \frac{N!}{(N-n)!n!} \approx k\{N \ln(N) - (N-n) \ln(N-n) - n \ln(n)\} \quad (4)$$

Where in the latter equation we used the standard Stirling approximation. By substituting the entropy expression in equation (1)

$$\begin{aligned}
\Delta G = & [V_o]E_f(V_o) + [V_o^{\bullet}]E_f(V_o^{\bullet}) + n_c E_f(n_c) \\
& - kT \{N \ln N - (N - [V_o]) \ln(N - [V_o]) - [V_o] \ln([V_o])\} \\
& - kT \{N \ln N - (N - [V_o^{\bullet}]) \ln(N - [V_o^{\bullet}]) - [V_o^{\bullet}] \ln([V_o^{\bullet}])\} \\
& - kT \{N_c \ln N_c - (N_c - n_c) \ln(N_c - n_c) - n_c \ln(n_c)\} \quad (5)
\end{aligned}$$

In the latter equation N_c is the effective density of states at the conduction band. Note that in this derivation we appeal to this simplified picture of representing the electronic density of stat. More rigorously this should be an integration of the density of states as in the manuscript. Here we aim at simplifying the notation.

For the quenched state:

$$[V_o^{\times}] + [V_o] + [V_o^{\bullet}] = \text{constant} = n_v \quad (6),$$

Where n_v is the total number of vacancies frozen from high temperature. Thus,

$$[V_o^{\times}] = n_v - [V_o] - [V_o^{\bullet}] \quad (7)$$

And from the charge neutrality

$$n_c = [V_o] + 2[V_o^{\bullet}] \quad (8)$$

Therefore by substituting back in equation 5,

$$\begin{aligned}
\Delta G = & [V_o]E_f(V_o) + [V_o^{\bullet}]E_f(V_o^{\bullet}) + (n_v - [V_o] - [V_o^{\bullet}])E_f(V_o^{\times}) + ([V_o] + 2[V_o^{\bullet}])E_f(n_c) \\
& - kT \{N \ln N - (N - [V_o]) \ln(N - [V_o]) - [V_o] \ln([V_o])\} \\
& - kT \{N \ln N - (N - [V_o^{\bullet}]) \ln(N - [V_o^{\bullet}]) - [V_o^{\bullet}] \ln([V_o^{\bullet}])\} \\
& - kT \{N \ln N - (N - n_v + [V_o] + [V_o^{\bullet}]) \ln(N - n_v + [V_o] + [V_o^{\bullet}])\} \\
& - (n_v - [V_o] - [V_o^{\bullet}]) \ln(n_v - [V_o] - [V_o^{\bullet}]) \\
& - kT \{N_c \ln N_c - (N_c - [V_o] - 2[V_o^{\bullet}]) \ln(N_c - [V_o] - 2[V_o^{\bullet}])\} \\
& - ([V_o] + 2[V_o^{\bullet}]) \ln([V_o] + 2[V_o^{\bullet}]) \quad (9)
\end{aligned}$$

Subject to the constraints (equations 6 and 8) which are fixed total number of oxygen vacancies and charge neutrality, we minimize the Gibbs free energy by requiring null partial derivatives as in equations 10 and 17 below.

$$\frac{\partial(\Delta G)}{\partial([V_o])} = 0 \quad (10)$$

$$\begin{aligned}
0 = & E_f(V_o) - E_f(V_o^{\times}) + E_f(n_c) - kT \{1 + \ln(N - [V_o]) - 1 - \ln([V_o])\} \\
& - kT \{-1 - \ln(N - n_v + [V_o] + [V_o^{\bullet}]) + 1 + \ln(n_v - [V_o] - [V_o^{\bullet}])\} \\
& - kT \{1 + \ln(N_c - [V_o] - 2[V_o^{\bullet}]) - 1 - \ln([V_o] + 2[V_o^{\bullet}])\} \quad (11)
\end{aligned}$$

Therefore, by rearrangement,

$$E_f(V_o) - E_f(V_o^{\times}) + E_f(n_c) = kT \ln \frac{(N - [V_o])(n_v - [V_o] - [V_o^{\bullet}]) (N_c - [V_o] - 2[V_o^{\bullet}])}{[V_o](N - n_v + [V_o] + [V_o^{\bullet}]) ([V_o] + 2[V_o^{\bullet}])} \quad (12)$$

But in the dilute limit,

$$(N - [V_o]) \approx (N - n_v + [V_o] + [V_o]) \approx N \quad (13)$$

And from equations 6 and 8 we have $([V_o] + 2[V_o]) = n_c$, $(n_v - [V_o] - [V_o]) = [V_o]$

Thus,

$$E_f(V_o) - E_f(V_o^\times) + E_f(n_c) = kT \ln \frac{[V_o^\times](N_c - n_c)}{[V_o]n_c} \quad (14)$$

$$\frac{[V_o^\times]}{[V_o]} = \frac{n_c}{(N_c - n_c)} \exp \left[\frac{E_f(n_c)}{kT} \right] \frac{\exp \left[\frac{-E_f(V_o^\times)}{kT} \right]}{\exp \left[\frac{-E_f(V_o)}{kT} \right]} \quad (15)$$

And since $n_c = N_c \exp \left[\frac{-E_f(n_c)}{kT} \right]$

Then,

$$\frac{[V_o^\times]}{[V_o]} = \frac{\exp \left[\frac{-E_f(V_o^\times)}{kT} \right]}{\exp \left[\frac{-E_f(V_o)}{kT} \right]} \quad (16)$$

Similarly,

$$\frac{\partial(\Delta G)}{\partial([V_o])} = 0 \quad (17)$$

$$\begin{aligned} 0 = & E_f(V_o) - E_f(V_o^\times) + E_f(n_c) - kT \{1 + \ln(N - [V_o]) - 1 - \ln([V_o])\} \\ & - kT \{-1 - \ln(N - n_v + [V_o] + [V_o]) + 1 + \ln(n_v - [V_o] - [V_o])\} \\ & - kT \{2 + \ln(N_c - [V_o] - 2[V_o]) - 2 - 2\ln([V_o] + 2[V_o])\} \end{aligned} \quad (18)$$

By simplifying analogously to the earlier differentiation with respect to $[V_o]$:

$$E_f(V_o) - E_f(V_o^\times) + 2 E_f(n_c) = kT \ln \frac{[V_o^\times](N_c - n_c)^2}{[V_o]n_c^2} \quad (19)$$

Then,

$$\frac{[V_o^\times]}{[V_o^{\cdot\cdot}]} = \frac{\exp\left[\frac{-E_f(V_o^\times)}{kT}\right]}{\exp\left[\frac{-E_f(V_o^{\cdot\cdot})}{kT}\right]} \quad (20)$$

From equations 16 and 20, it is clear that the ratio between the 3 charged states of oxygen vacancy at quenched state is:

$$[V_o^\times] : [V_o^\cdot] : [V_o^{\cdot\cdot}] = \exp\left[\frac{-E_f(V_o^\times)}{kT}\right] : \exp\left[\frac{-E_f(V_o^\cdot)}{kT}\right] : \exp\left[\frac{-E_f(V_o^{\cdot\cdot})}{kT}\right] \quad (21)$$

Which is the same equilibrium ratio we get by using the Boltzmann expression:

$$[V_o^q] = N_o \exp\left[\frac{-E_f(V_o^q)}{kT}\right] \quad (22)$$

This derivation can be applied to any other charge compensation regime and will lead to the same conclusion. Independent of the number of charge states included, this derivation will always give the same expression for the concentration ratios.