**Statistical Thermodynamics of Defects in Ceria and Perovskite Based Oxides**

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**Introduction**

Ceria dioxide and perovskite oxides form a very interesting class of redox materials. Both can exhibit partial reduction as a function of temperature and pressure without major structural changes.

\[ \text{MO}_x \rightleftharpoons \text{MO}_x \delta + \frac{\delta}{2} \text{O}_2 \]  
(1)

These remarkable redox properties have lead to many applications as redox catalysts. The high ionic conductivity of these materials has also lead to them being investigated as oxygen ion electrolytes for use in solid oxide fuel cells and electrolysis. We are interested in these materials for solar powered thermochemical H2O and CO2 splitting cycles, as well as for thermochemical oxygen pumping. This family of materials allow us to tune the thermodynamics properties of our redox cycle to cover a range of applications.

**Equation of State**

Using the equations 2 and 3 an analytical equation of state can be determined, giving \( \delta (p_{0T}, T) \).

**Configuration Entropy**

The key feature of the model is the configuration entropy associated with the defects. The statistical model indicates the defects form clusters:

\[ O_2^+ + M_{3M}^+ = V_0 + 2M_{3M}^+ + \frac{\delta}{2} O_2, \quad V_0 + 2M_{3M}^+ = M_{3M}^+ V_0 M_{3M}^+ \]  
(4)

\[ \Delta S_{\text{con}} = \frac{1}{2} \ln (\delta_m - \delta) - \ln (\delta) + \ln (\omega_{M_{3M}^+ V_0 M_{3M}^+}) \]  
(5)

- The lower entropy change for Ce0.85Zr0.15O2 can be attributed to Zr\(^{4+}\) ions blocking Ce\(^{3+}\/4+\) lattice cites and reducing the degrees of freedom for the clusters, \( \omega_{M_{3M}^+ V_0 M_{3M}^+} \).
- In the case of the perovskite Ca0.8Sr0.2MnO3, each oxygen vacancy only has two nearest neighbor Mn\(^{3+}\/4+\) sites and therefore, there is only one configuration for each cluster, which is contributing to the much lower change in entropy for this reaction.

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