A First-Principles-Based Sub-Lattice Formalism for Predicting Off-Stoichiometry in Materials for Solar Thermochemical Applications: The Example of Ceria

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Theoretical models that reliably can predict off-stoichiometry in materials via accurate descriptions of underlying thermodynamics are crucial for energy applications. For example, transition-metal and rare-earth oxides that can tolerate a large number of oxygen vacancies, such as CeO₂ and doped CeO₂, can split water and carbon dioxide via a two-step, oxide-based solar thermochemical (STC) cycle. The search for new STC materials with a performance superior to that of state-of-the-art CeO₂ can benefit from predictions accurately describing the thermodynamics of oxygen vacancies. The sub-lattice formalism, a common tool used to fit experimental data and build temperature-composition phase diagrams, can be useful in this context. Here, sub-lattice models are derived solely from zero-temperature quantum mechanics calculations to estimate fairly accurate temperature- and oxygen-partial-pressure-dependent off-stoichiometries in CeO₂ and Zr-doped CeO2. Physical motivations for deriving some of the "excess" sub-lattice model parameters directly from quantum mechanical calculations, instead of fitting to minimize deviations from experimental and/or theoretical data, are identified. Important limitations and approximations of the approach used are specified and extensions to multi-cation oxides are also suggested to help identify novel candidates for water and carbon dioxide splitting and related applications.

1. Introduction

Many energy-relevant materials exhibit off-stoichiometric compositions.^[1–8] For example, most electrodes in intercalation

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batteries^[9–13] and semiconductors in nonsilicon photovoltaics^[14–17] exhibit vacancies and/or other point defects in at least one set of sites (or a sub-lattice) within their structure. Other materials are off-stoichiometric in their equilibrium bulk form, such as FeO (wüstite), which exhibits \approx 5–10% Fe-vacancies at room temperature.^[18,19]

Off-stoichiometric oxides can produce renewable fuels and fuel precursors (H₂, CO, etc.) via a two-step solar thermochemical (STC) process that splits water (STCH) or CO₂ (STCC), as illustrated in Figure 1.^[20-25] The first step in a STC cycle is thermal reduction (TR), in which a near-stoichiometric oxide (MO, in Figure 1) is heated to high temperatures (e.g., T > 1573 K) in an environment of low partial pressure of oxygen (p_{O_2}) leading to spontaneous oxygen loss and the formation of an oxygen-deficient oxide $(MO_{x-\delta}, \delta > 0)$. Prior to the second step, $MO_{x-\delta}$ is cooled to a lower temperature (e.g., $\approx 873-1373$ K), where the oxide is no longer driven thermodynamically to form oxygen vacancies and the stoichiometric MO_x is stable (or sufficiently metastable).

Then, the reduced oxide spontaneously splits steam (or CO_2) to generate H_2 (or CO) and is re-oxidized to MO_r . This step is called the water-splitting (WS) step, which generates hydrogen when steam is introduced (and similarly generates CO when CO₂ is present). The gas phase during the WS step is introduced preferably under counter-flow conditions. This is because the gas phase in a stagnant reactor is changed only when the reoxidation is complete, while, in counter-flow, pure steam is introduced against the oxidized MO_r (or small δ , at low enough temperatures) and is allowed to be reduced progressively as it flows against a progressively reduced oxide. Thus, countercurrent conditions are useful in enhancing the thermodynamics of re-oxidation^[26,27] by exposing steam at its highest oxidizing potential to $MO_{x-\delta}$ that typically becomes harder to oxidize as $\delta \rightarrow 0$. The source of heat in the TR step often is concentrated sunlight,^[23] accompanied by heat recuperation while cooling the reduced oxide to the lower temperature. While the current state-of-the-art (SOA) for STCH performance is pure CeO₂,^[28-32] screening for novel oxides that show superior efficiency is an active area of research^[33–42] where theory plays an important role.



Figure 1. Schematic of solar thermochemical water splitting, involving a thermal reduction step at a high temperature and low partial pressure of oxygen ($MO_x \rightarrow MO_{x-\delta}$) and a water splitting step at a lower temperature ($MO_{x-\delta} \rightarrow MO_x$).

One daunting challenge in theoretically screening STCH candidates is to predict accurately the oxygen off-stoichiometries as a function of T and p_{O_2} (Section 2). Specifically, models must capture adequately all entropic contributions^[42,43] due to off-stoichiometry, such as vacancies exhibiting configurational entropy within the oxygen and cation sub-lattices in an oxygendeficient $MO_{r=\delta}$. Changes in composition also alter vibrational, electronic, and magnetic entropy contributions. Accounting for entropy contributions typically requires extensive calculations, with subsequent post-processing and/or parameterization. For example, configurational entropy in solids usually is evaluated via a "cluster expansion"^[44-46] parameterized via density-functionaltheory(DFT)-based calculations,^[47-52] requiring a large set of input configurations (≈100 for several systems,^[53,54] although the exact number of configurations required is highly systemdependent^[55-57]) enumerated over large supercells, as well as careful parameterization to ensure predictability. Moreover, generalizing a binary cluster expansion to a ternary or a pseudoternary system can incur a dramatically higher computational cost.^[58,59] Estimating vibrational entropy, done by calculating the phonon spectrum,^[60] also carries significant expense since the number of unique displacements calculated using DFT increases dramatically with larger supercells. Consequently, several STCH theoretical screening studies typically have employed the oxygen vacancy formation energy as a proxy for the enthalpy of reduction ($\Delta H_{\rm red}$), while not accounting for entropic contributions (ΔS_{red}) to determine the off-stoichiometry dependence on *T* and p_{O_2} .^[38,41] There have been some theoretical studies that have examined specific entropic contributions and their impact for a STCH process.^[42,43,51] In any case, given the importance of entropy in high-temperature phenomena such as STCH,^[43] the development of first-principles-based thermodynamic models enabling a swift estimation of Gibbs energies for oxides as a function of temperature and off-stoichiometry should advance the fidelity of such screenings. This article presents such a formalism.

In this work, which is illustrated as a workflow in **Figure 2**, we parameterize a thermodynamic sub-lattice model (Section 3) using a total of 14 distinct DFT-based calculations (computational details in the Experimental Section) to predict oxygen offstoichiometry in pure CeO₂ under TR and WS conditions and subsequently validate against an experimentally derived model (Section 4.1). Sub-lattice models or the compound energy formalism (CEF).^[61] in the spirit of CALPHAD-style^[62–66] assessments, are used widely to refine temperature-composition phase diagrams, where model parameters are fit to minimize deviations from experimental measurements (see left panel of Figure 2). Here, we utilize the sub-lattice model of Zinkevich et al.,^[67] developed from Ce-O experimental data (Section 3.1). We study pure CeO₂ in order to benchmark our predictions for a system with robust experimental data^[68] and that is currently the SOA for STCH. We also extend the binary Ce-O model, using another \approx 40 distinct configurations, to describe the ternary Ce-Zr-O system (Sections 3.2 and 4.2) for which no sub-lattice model yet exists. Our first-principles-derived model offers a reliable estimation of oxygen off-stoichiometry under TR and WS conditions for both undoped and Zr-doped CeO₂.

Further, combining DFT with a sub-lattice model enables the identification of underlying physics of model parameters (e.g., "excess" interactions), which otherwise are fit to reproduce experiments. Although DFT previously has supplemented experimental data in constructing sub-lattice models,^[65,66,69–71] here we avoid experimental data entirely and parameterize a sub-lattice model solely using DFT to produce an entirely independent theoretical model. Prior examples of sub-lattice models obtained solely from DFT-based data do exist.^[72–78] However, such models have been used primarily for intermetallics and not ionic materials (such as Ce-O and Zr-Ce-O) that usually involve several noncharge-neutral "end-members" (Section 3.1) whose energies are not trivial to obtain theoretically. Note that there is an ongoing effort by the developers of FactSage software^[79] in building sublattice models by combining the 0 K DFT data from the Materials Project database^[80] with high-throughput computing^[81] and/or machine learning to obtain vibrational entropy as a function of temperature (middle panel in Figure 2). Here, we directly obtain all of our model parameters from 0 K DFT-based calculations (i.e., we approximate Gibbs energies as the total energies at 0 K, or $G \approx E$, see right panel of Figure 2) instead of fitting to an existing data set. We also identify limitations and approximations in our approach, along with possible future improvements. Ultimately, quantum-based sub-lattice models may enable a rapid identification of novel off-stoichiometric candidates for STC and related applications.

2. Thermodynamics of Solar Thermochemical Hydrogen Generation

Because STCH involves the exchange of O-atoms between a solid $(MO_x/MO_{x-\delta})$ and a gas (O_2/H_2O-H_2) , estimating the oxygen chemical potential (μ_O) separately in each phase efficiently decouples the thermodynamics of the solid from the gas. While μ_O of the solid (μ_O^s) and gas (μ_O^g) will be identical when they are in equilibrium (μ_O^{eq}) , the reduction (re-oxidation) of the solid will be spontaneous when μ_O^s is higher (lower) than μ_O^g . Formally, under TR/WS conditions, μ_O^g (TR/WS) is given by Equations (1) and (2):

$$\mu_{\rm O}^{\rm g}$$
 (TR) = $\mu_{\rm O}^{\circ} + \frac{1}{2}RT\ln\frac{p_{\rm O_2}}{p^{\circ}}$ (1)



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Figure 2. Workflows employed in constructing classical CALPHAD models using experimental data (left highlighted box), and theory-driven approaches using only 0 K DFT calculations (this work) and a combination of 0 K calculations and DFT-derived vibrational entropy data (approach adopted by FactSage^[79] developers). Green, red, and blue boxes indicate steps involving measurements or calculations, thermodynamic properties obtained, and sub-lattice model construction, respectively.

$$\mu_{\rm O}^{\rm g}$$
 (WS) = $G_{\rm H_2O}$ (g) - $G_{\rm H_2}$ (g) + $RT \ln \frac{p_{\rm H_2O}}{p_{\rm H_2}}$ (2)

where $\mu_{\rm O}^{\circ} = \frac{1}{2} G_{O_2}(\mathbf{g}) = \frac{1}{2} H_{O_2}(\mathbf{g}) - \frac{1}{2} TS_{O_2}(\mathbf{g})$ is the oxygen chemical potential of pure O₂ gas at a reference pressure, with *G*, *H*, *S* corresponding to Gibbs energy, enthalpy, and entropy, respectively. p° is the reference pressure, here set to 1 atm. Experimental $\mu_{\rm O}^{\circ}$, $G_{\rm H_2O}(\mathbf{g})$, and $G_{\rm H_2}(\mathbf{g})$ are obtained from the National Institute of Standards and Technology database.^[82] For the solid, $\mu_{\rm O}^{\rm s}$ is the derivative of the Gibbs energy of the oxide $(G_{\rm MO_x})$ with respect to the oxygen concentration (*x*, Equation (3)), where our DFT-based model estimates $G_{\rm MO_x}$ for STC-relevant *x* (Section 3).

$$\mu_{\rm O}^{\rm s} = \frac{dG_{\rm MO_x}}{dx} \tag{3}$$

Note that increasing the efficiency of a STC cycle requires either exceptionally good heat recovery or small temperature differences between the TR and WS steps,^[27] while practical considerations suggest "reasonable" upper and lower bound temperatures for TR and WS to be \approx 1673 and \approx 873 K, respectively. Such considerations also yield a lower bound on p_{O_2} during TR to be \approx 10 Pa (\approx 10⁻⁴ atm) and a H₂:H₂O product ratio of at least 1:9 in WS (i.e., 10% H₂ yield). Thus, the TR and WS conditions of primary interest are T = 1673 K and $p_{O_2} = 10$ Pa, and T = 873 K and $\frac{p_{H_2O}}{p_{H_2}} = 9$, respectively. Also, capacity of a given oxide material can be quantified in terms of *m*mol (or standard units of volume, 22.4 cm³ *m*mol⁻¹) of gas evolved (either O₂ or H₂) per unit of oxide. For example, the TR resulting in an oxygen concentration, x = 1.999 from stoichiometric-CeO₂ (or an oxygen vacancy concentration, $\delta = 0.001$ per CeO₂ formula unit), corresponds to an oxygen evolution capacity of $\approx 1.5 \text{ mmol}$ (mol atom)⁽⁻¹⁾ of oxide (or $\approx 34 \text{ cm}^3$ (mol atom)⁽⁻¹⁾ oxide).

Oxides with smaller $\Delta H_{\rm red}$, that is, smaller costs to undergo reduction and form oxygen vacancies, tend to exhibit higher oxygen deficiency during TR but potentially lower H₂ evolution (relative to the TR oxygen deficiency, due to the lower driving force for oxidation) during WS.^[21,83] On the other hand, lower $\Delta S_{\rm red}$ indicates lower driving force to form oxygen vacancies, thereby leading to lower oxygen deficiencies but higher H₂ production (relative to TR oxygen deficiencies but higher H₂ production (relative to TR oxygen deficiency) during WS. Thus, STC efficiency is determined by the ability of MO_x to exhibit an optimal $\Delta H_{\rm red}$ and $\Delta S_{\rm red}$, and to tolerate a wide swing in oxygen off-stoichiometry over TR and WS temperatures. Given $G_{\rm MO_x}$ as a function of *x* (Equation (3)), $\Delta H_{\rm red}$ and $\Delta S_{\rm red}$ at a given *T* are evaluated (and normalized per O-atom) using Equations (4a) and (4b), respectively, where the angular brackets indicate averaged quantities from *x* to *x* – δ .

$$\Delta H_{\rm red} = \left\langle -\frac{dH_{\rm MO_x}}{dx} \right\rangle + \frac{1}{2}H_{\rm O_2}\left(g\right)$$
(4a)

$$\Delta S_{\rm red} = \left\langle -\frac{dS_{\rm MO_x}}{dx} \right\rangle + \frac{1}{2}S_{\rm O_2}\left(g\right)$$
(4b)

Using the average in Equation (4) yields the $\Delta H_{\rm red}$ and $\Delta S_{\rm red}$ that is averaged from the stoichiometric (say MO₂) to an offstoichiometric composition, MO_{2- δ}, while the derivatives in Equation (4) yield the instantaneous enthalpy and entropy of reduction at a given off-stoichiometric composition, MO_x. Note that $\Delta H_{\rm red}$ as defined in Equation (4a) is a better indicator of the net ADVANCED SCIENCE NEWS www.advancedsciencenews.com

heat input required to remove one oxygen and to induce an offstoichiometry of δ than the instantaneous quantity.

3. Solution Thermodynamics Using the Sub-Lattice Formalism

In this section, we briefly introduce the concepts behind the CEF and subsequently define the sub-lattice models for pure and Zr-doped CeO₂. When two components (e.g., pure elements), A and B, form a solution phase (A_yB), the Gibbs energy of the solution phase ($G_{A_{n,B}}$) can be written as

$$G_{A_vB} = \gamma G_A^\circ + G_B^\circ + \Delta G_{mix}$$
⁽⁵⁾

where G_{A}° , G_{B}° are the Gibbs energies of the pure components, also known as end-members, A and B. ΔG_{mix} contains the enthalpic and entropic contributions that lead to the formation of the solution phase from the pure components. Therefore, if the temperature (*T*) dependence of G_A° , G_B° , and ΔG_{mix} and the composition (y) dependence of ΔG_{mix} are known, then the Gibbs energy of the solution phase can be estimated accurately across the T - y space, which in turn can be used to calculate the overall A-B phase diagram. However, when multiple components (such as in ternary, quaternary, quinary, etc., systems) form a solution phase, $\Delta G_{
m mix}$ may not be trivial to determine experimentally or calculate theoretically. In this context, the CEF^[61,62] provides a robust thermodynamic framework to estimate the Gibbs energy of a solution phase in multi-component systems, using available experimental and/or theoretical data on chemical potentials, enthalpies, heat capacities, etc. The readers are directed to the literature for further reading about the CEF.[63,84-87]

Generalizing Equation (5) for any multi-component system, the Gibbs energy of a given solution phase (G^{soln}) can be written as

$$G^{\rm soln} = G^{\rm end-members} - TS^{\rm soln} + G^{\rm excess} + G^{\rm phys}$$
(6)

where $G^{\text{end-members}}$ is the sum of the Gibbs energies of the endmembers, S^{soln} is the configurational entropy of the solution phase, G^{excess} is the excess Gibbs energy not captured by the end-members and the configurational entropy contributions, and G^{phys} is the Gibbs energy arising from any physical or phase transformations in the solution phase (e.g., a ferromagnetic \rightarrow paramagnetic transition). $G^{\text{end-members}}$ for a solution phase with a single sub-lattice is the weighted sum of all of the pure components, that is,

$$G^{\text{end-members}} = \sum_{i} x_{i} G_{i}^{\circ}$$
(7)

 x_i is the site fraction, equivalent to the mole fraction in this case, of component i within the solution phase. When the solution phase exhibits two distinct sub-lattices (k, l) with two distinct components (A, B)_k in sub-lattice k and (C, D)_l in sub-lattice *l*, then *G*^{end-members} is written as

$$G^{\text{end-members}} = \gamma_{\text{A}}^{k} \gamma_{\text{C}}^{l} G_{\text{A:C}}^{\circ} + \gamma_{\text{B}}^{k} \gamma_{\text{C}}^{l} G_{\text{B:C}}^{\circ} + \gamma_{\text{A}}^{k} \gamma_{\text{D}}^{l} G_{\text{A:D}}^{\circ} + \gamma_{\text{B}}^{k} \gamma_{\text{D}}^{l} G_{\text{B:D}}^{\circ}$$
(8)

 y_X^z in Equation (8) is the site fraction of species X on sub-lattice z, with $G_{X:Y}^\circ$ representing the Gibbs energy of a configuration with sub-lattices k and l completely occupied by components X and Y, respectively. For higher-order, multi-component, multi-sub-lattice systems, $G^{\text{end-members}}$ can be generalized in a similar manner.

 S^{soln} in Equation (6) is assumed to be the ideal configurational entropy within each sub-lattice of the solution phase. Mathematically, this is equivalent to:

$$S^{\rm soln} = -R\Sigma_z n_z \Sigma_X y_X^z \ln y_X^z \tag{9}$$

where *R* is the universal gas constant and n_z is the total number of sites (normalized per formula unit) of sub-lattice *z* in the solution phase. Although it is an assumption that configurational entropy exhibits ideal behavior in a multi-component, multi-sublattice system, precedence for such sub-lattice models accurately describing phase behavior in several systems does exist.^[87]

While the G^{phys} component in Equation (6) is included only if there are strong first- or second-order phase transformations or other unique physical changes in the solution phase, G^{excess} typically is expressed in terms of binary interaction parameters (*L*) using the functional form of Equation (10) for the (A, B)_k(C, D)_l system.

$$G^{\text{excess}} = \gamma_{A}^{k} \gamma_{B}^{k} \gamma_{C}^{l} L_{A,B:C} + \gamma_{A}^{k} \gamma_{B}^{k} \gamma_{D}^{l} L_{A,B:D} + \gamma_{A}^{k} \gamma_{C}^{l} \gamma_{D}^{l} L_{A:C,D} + \gamma_{B}^{k} \gamma_{C}^{l} \gamma_{D}^{l} L_{B:C,D}$$
(10)

Here, each *L* term can have both a temperature dependence (typically of the a + bT functional form) and a concentration dependence that usually is expressed as a Redlich–Kister (RK) power series.^[88]

$$L_{\rm A,B:C} = \Sigma_i \left(\gamma_{\rm A}^k - \gamma_{\rm B}^k \right)^i L_{\rm A,B:C}^i$$
(11)

Note that the *i* terms in Equation (11) represent the exponent and an index for the *y* and the *L* terms, respectively. Although several higher-order RK terms (large *i* in L^i) can be used, the standard practice is to restrict *i* to a maximum of 3, and often no more than 1.^[61] Note, that in addition to binary terms, higher-order interaction terms (i.e., *L* for ternary, quaternary, etc., interactions) can be employed within the CEF.

3.1. Sub-Lattice Model in CeO,

Figure 3 illustrates the sub-lattice model used for fluorite-CeO_x, which is based on stoichiometric-CeO₂ that exhibits the fluorite structure containing one Ce site (Ce sub-lattice) and two oxygen sites (O sub-lattice). Two possible species can occupy each of its two sub-lattices, namely, Ce⁴⁺ (green circles/polyhedra in Figure 3) and Ce³⁺ (orange circles/polyhedra) in the Ce sub-lattice and oxygen (red circles) and vacancies (Va, blue circles) in the O sub-lattice, necessitating a four-component, two-sub-lattice model. As a result, the relevant end-members for CeO_x within the sub-lattice framework involve all Ce and O sites occupied by: i) Ce⁴⁺ and O (stoichiometry of Ce⁴⁺O₂, top right); iii) Ce⁴⁺





Figure 3. Sub-lattice model for Gibbs energy of fluorite-CeO_x (*G*^F) using end-members consisting of Ce⁴⁺ (green circles) and Ce³⁺ (orange circles) in the Ce sub-lattice and oxygen ions (red circles) and vacancies (Va, blue circles) in the oxygen sub-lattice. *L*₀ and *L*₁ are excess interactions and *S*^{soln} is ideal configurational entropy. *a*, *b*, and *c* refer to the principal co-ordinates of the fluorite unit cell.

and Va (Ce⁴⁺Va₂, bottom left); and iv) Ce³⁺ and Va (Ce³⁺Va₂, bottom right). Thus, $G^{\text{end-members}}$ and S^{soln} for CeO_x can be expressed analogously to Equations (8) and (9) as

$$G^{\text{end-members}} = \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \gamma_{\text{O}}^{\text{O}} G_{\text{Ce}^{4+:O}}^{\circ} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{O}}^{\text{O}} G_{\text{Ce}^{3+:O}}^{\circ} + \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \gamma_{\text{Va}}^{\text{O}} G_{\text{Ce}^{4+:Va}}^{\circ} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{Va}}^{\text{O}} G_{\text{Ce}^{3+:Va}}^{\circ}$$
(12)

$$S^{\text{soln}} = -R \left(\gamma_{\text{Ce}^{4+}}^{\text{Ce}} \ln \gamma_{\text{Ce}^{4+}}^{\text{Ce}} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \ln \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \right) -2R \left(\gamma_{\text{O}}^{\text{O}} \ln \gamma_{\text{O}}^{\text{O}} + \gamma_{\text{Va}}^{\text{O}} \ln \gamma_{\text{Va}}^{\text{O}} \right)$$
(13)

The multiplicative factor of 2 before the O sub-lattice in Equation (13) signifies that there are two O sites per Ce site within the fluorite structure.

Oxygen off-stoichiometry, δ in $\text{CeO}_{2-\delta}$, can vary between 0 (fully oxidized) and 0.5 (fully reduced) per CeO_2 formula unit, with the STC-relevant range for x in CeO_x thus being $1.5 \leq x \leq 2$. Importantly, most end-members of CeO_x in the sub-lattice model have net charge, which makes it difficult to estimate theoretically or experimentally the corresponding end-member Gibbs energy (G°). For example, in the case of Ce^{3+}O_2 , where all Ce sites are occupied by Ce^{3+} ions, the cation sub-lattice is deficient by a charge of +1 per Ce^{3+}O_2 formula unit. Indeed, only the Ce^{4+}O_2

end-member, which simply represents stoichiometric CeO_2 , is charge-neutral. Thus,

$$G_{Ce^{4+}:O}^{\circ} = G_{CeO_2}^{F}$$
(14)

The superscript F in $G_{CeO_2}^F$ represents the fluorite structure. To estimate the Gibbs energies of non-charge-neutral endmembers, the CEF formalism normally uses reference states and/or reciprocal relations.^[61,62] For example, G° for the Ce⁴⁺Va₂ end-member can be referenced to the Gibbs energies of stoichiometric CeO₂ and oxygen gas (i.e., using two charge-neutral reference states), as in Equation (15).

$$G_{Ce^{4+}:Va}^{\circ} = G_{CeO_2}^{F} - G_{O_2}(g)$$
(15)

To determine G° for Ce^{3+} : O and Ce^{3+} : Va end-members, Zinkevich et al.,^[67] defined a reference state and reciprocal relation, also used here. Specifically, a combination of $\frac{3}{4}Ce^{3+}$: O and $\frac{1}{4}Ce^{3+}$: Va end-members gives rise to a fluorite structure with a charge-neutral stoichiometry of Ce_2O_3 , that is, 25% of all O sites within the fluorite structure are vacant. Notably, Ce_2O_3 is a stable oxide within the Ce-O binary system and exhibits a hexagonal structure at 298 K,^[89,90] although the fluorite polymorph can form in a metastable manner at STCH-relevant temperatures.^[91]

$$\frac{1}{2} G_{Ce_2O_3}^{F} = G_{CeO_{1,5}}^{F} = \frac{3}{4} G_{Ce^{3+}:O}^{\circ} + \frac{1}{4} G_{Ce^{3+}:Va}^{\circ} + 2RT \left(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4}\right)$$
(16)

where the entropic contribution to $G_{CeO_{1.5}}^{F}$ arises from the co-existence of O and Va within the O sub-lattice. With three relations defining three of the four end-members, the following reciprocal relation is employed to determine the final end-member. Physically, the reciprocal relation assumes—frankly, without justification—that the energy to evolve O₂(g) from the Ce⁴⁺O₂ end-member ($G_{Ce^{4+}:O}^{\circ} - G_{Ce^{4+}:Va}^{\circ}$) is equivalent to evolving O₂(g) from Ce³⁺O₂ ($G_{Ce^{3+}:O}^{\circ} - G_{Ce^{3+}:Va}^{\circ}$).

$$G^{\circ}_{Ce^{4+}:O} - G^{\circ}_{Ce^{4+}:Va} = G^{\circ}_{Ce^{3+}:O} - G^{\circ}_{Ce^{3+}:Va}$$
(17)

Apart from $G^{\text{end-members}}$ and S^{soln} (Equations (12) and (13)), Zinkevich et al.,^[67] also utilized binary interaction parameters in defining the excess Gibbs energy (Equation (18)), which was crucial to obtaining an accurate description of all experimental data in their sub-lattice model.

$$G^{\text{excess}} = \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{Ce}^{4+}}^{\text{O}} \gamma_{\text{O}}^{\text{C}} L_{\text{Ce}^{3+},\text{Ce}^{4+};\text{O}} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{Ce}^{4+}}^{\text{O}} \gamma_{\text{Va}}^{\text{Ce}} L_{\text{Ce}^{3+},\text{Ce}^{4+};\text{Va}} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{O}}^{\text{O}} \gamma_{\text{Va}}^{\text{O}} L_{\text{Ce}^{3+};\text{O},\text{Va}} + \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \gamma_{\text{O}}^{\text{O}} \gamma_{\text{Va}}^{\text{O}} L_{\text{Ce}^{4+};\text{O},\text{Va}}$$
(18)

To minimize the number of excess parameters, Zinkevich et al.,^[67] used two unique parameters by setting, again without justification

$$L_{Ce^{3+}:O,Va} = L_{Ce^{4+}:O,Va} = 0; L_{Ce^{3+},Ce^{4+}:O} = L_{Ce^{3+},Ce^{4+}:Va}$$
$$= L_{Ce^{3+},Ce^{4+}}$$
(19)

Moreover, the authors^[67] used the following constant and firstorder RK terms to define the interaction parameter (see Section 3.1.1 for further discussion).

$$L_{Ce^{3+},Ce^{4+}} = L^{0}_{Ce^{3+},Ce^{4+}} + \left(\gamma^{Ce}_{Ce^{3+}} - \gamma^{Ce}_{Ce^{4+}}\right) L^{1}_{Ce^{3+},Ce^{4+}}$$
(20)

Through this work, we will use the notations of L_0 and L_1 for $L_{Ce^{3+},Ce^{4+}}^0$ and $L_{Ce^{3+},Ce^{4+}}^1$, respectively. Thus, the excess Gibbs energy has the final functional form as written in Equation (21).

$$G^{\text{excess}} = \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \left(L_0 + \left(\gamma_{\text{Ce}^{3+}}^{\text{Ce}} - \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \right) L_1 \right)$$
(21)

Note that the y_0^{O} and y_{Va}^{O} site-fractions of Equation (18) drop out in Equation (21), because setting $L_{Ce^{3+},Ce^{4+};O} = L_{Ce^{3+},Ce^{4+};Va}$ (Equation (19)) gives rise to a $y_0^{O} + y_{Va}^{O}$ term, which equals 1 always. Finally, combining $G^{\text{end-members}}$, S^{soln} , and G^{excess} , the Gibbs

Finally, combining $G^{\text{end}-\text{members}}$, S^{soln} , and G^{excess} , the Gibbs energy of the fluorite-CeO_x phase ($G^{\text{F}}_{\text{CeO}_x}$) can be expressed, as in Equation (22):

$$\begin{aligned} G_{CeO_{x}}^{F} &= \gamma_{Ce^{4+}}^{Ce} \gamma_{O}^{O} G_{CeO_{2}}^{F} \\ &+ \gamma_{Ce^{3+}}^{Ce} \gamma_{O}^{O} \left(G_{CeO_{1,5}}^{F} + \frac{1}{4} G_{O_{2}} \left(g \right) - 2RT \left(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) \right) \\ &+ \gamma_{Ce^{4+}}^{Ce} \gamma_{Va}^{O} \left(G_{CeO_{1,5}}^{F} - G_{O_{2}} \left(g \right) \right) \\ &+ \gamma_{Ce^{3+}}^{Ce} \gamma_{Va}^{O} \left(G_{CeO_{1,5}}^{F} - \frac{3}{4} G_{O_{2}} \left(g \right) - 2RT \left(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) \right) \\ &+ RT \left(\gamma_{Ce^{4+}}^{Ce} \ln \gamma_{Ce^{4+}}^{Ce} + \gamma_{Ce^{3+}}^{Ce} \ln \gamma_{Ce^{3+}}^{Ce} \right) \\ &+ 2RT \left(\gamma_{O}^{O} \ln \gamma_{O}^{O} + \gamma_{Va}^{O} \ln \gamma_{Va}^{O} \right) \\ &+ \gamma_{Ce^{3+}}^{Ce} \gamma_{Ce^{4+}}^{Ce} \left(L_{0} + \left(\gamma_{Ce^{3+}}^{Ce} - \gamma_{Ce^{4+}}^{Ce} \right) L_{1} \right) \end{aligned}$$
(22)

Equation (22) can be simplified further by expanding the site-fractions with respect to x, as $y_{Ce^{4+}}^{Ce} = 2x - 3$, $y_{Ce^{3+}}^{Ce} = 4 - 2x$, $y_0^O = \frac{x}{2}$ and $y_{Va}^O = 1 - \frac{x}{2}$, which ultimately results in Equation (23). The site-fractions are defined such that $y_{Ce^{4+}}^{Ce} = 1$, $y_{Ce^{3+}}^{Ce} = 0$, $y_0^O = 1$, and $y_{Va}^O = 0$ at x = 2 (fully oxidized CeO₂) and $y_{Ce^{4+}}^{Ce} = 0$, $y_{Ce^{3+}}^{Ce} = 1$, $y_0^O = 0.75$, and $y_{Va}^O = 0.25$ at x = 1.5 (fully reduced CeO_{1.5}).

$$\begin{aligned} G_{CeO_{x}}^{F} &= G_{CeO_{2}}^{F} - (4 - 2x) \left(G_{CeO_{2}}^{F} - G_{CeO_{1.5}}^{F} + 2RT \left(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4} \right) \right) \\ &+ RT \left(\gamma_{Ce^{4+}}^{Ce} \ln \gamma_{Ce^{4+}}^{Ce} + \gamma_{Ce^{3+}}^{Ce} \ln \gamma_{Ce^{3+}}^{Ce} \right) \\ &+ 2RT \left(\gamma_{O}^{O} \ln \gamma_{O}^{O} + \gamma_{Va}^{O} \ln \gamma_{Va}^{O} \right) \\ &+ \gamma_{Ce^{3+}}^{Ce} \gamma_{Ce^{4+}}^{Ce} \left(L_{0} + \left(\gamma_{Ce^{3+}}^{Ce} - \gamma_{Ce^{4+}}^{Ce} \right) L_{1} \right) \end{aligned}$$
(23)

After calculating all of the input parameters in Equation (23) $(G_{CeO_2}^F, G_{CeO_1,5}^F, G_{O_2}(g), L_0, L_1)$, we evaluate with DFT the energies



Figure 4. Graphic representation of the definitions of L_0 and L_1 within the sub-lattice model. While the horizontal axis represents oxygen composition within CeO_x, the vertical axis represents the formation energy of a given configuration with respect to the reference states, namely CeO₂^F and CeO_{1.5}^F, where the multiplicative factors 2x - 3 and 4 - 2x correspond to $\gamma_{Ce^{3+}}^{Ce}$ (or $1 - 2\delta$ for δ in CeO_{2- δ}) and $\gamma_{Ce^{3+}}^{Ce}$ (or 2δ), respectively. The blue circle represents the formation energy of an isolated oxygen vacancy $(E_{CeO_x}^{Va_O})$ within CeO₂, while the red diamond represents the formation energy of two oxygen vacancies $(E_{CeO_x}^{2Va_O})$.

 $(G \approx E)$ of all other binary Ce-oxides (e.g., hexagonal-Ce₂O₃^[92]) and also evaluate the lowest Gibbs energy of the solid phase as a function of oxygen composition. Subsequently, the derivative of the lowest Gibbs energy with respect to the oxygen concentration yields the oxygen chemical potential within the solid (μ_{O}^{s} , see Equation (3)), which then is equated with the oxygen chemical potential in the gas phase (μ_{O}^{g}) to determine the equilibrium oxygen concentration ($x_{eq} = 2 - \delta_{eq}$) for a given *T* and p_{O_2} .

3.1.1. Excess Terms

Physically, L_0 and L_1 signify the excess interactions between Ce³⁺ and Ce4+ within the Ce sub-lattice due to the presence of O vacancies in the O sub-lattice. Specifically, L_0 and L_1 exhibit a quadratic and cubic dependence on x for $G^{\rm F}$ in Equation (23) since each $y_{\rm c}^{\rm F}$ depends linearly on x. As logarithmic (entropic) terms in Equation (23) contribute to ΔS_{red} (of Equation (4)), L_0 and L_1 signify slope and curvature, respectively, of $\Delta H_{\rm red}$ as a function of *x*. L_0 , which represents excess interactions between Ce³⁺ and Ce⁴⁺ not captured by the end-members, can be referenced to the theoretically calculated enthalpy (\approx internal energy, *E*) of an isolated oxygen vacancy in stoichiometric CeO₂ ($H_{CeO_x}^{Va_O} \approx E_{CeO_x}^{Va_O}$, where $\delta \to 0; x \to 2$), as illustrated by the solid blue circle in Figure 4. This is because the simultaneous existence (and interactions) of Ce³⁺ and Ce⁴⁺ in the Ce sub-lattice is possible physically only when a vacancy exists in the O sub-lattice. On the other hand, L_1 represents interactions between Ce³⁺ and Ce⁴⁺ not captured by both end-members and L_0 , such as additional interactions between multiple oxygen vacancies. We therefore define L_1 via theoretically calculating the (lowest) energy of two oxygen vacancies

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in stoichiometric CeO₂ ($E_{CeO_{x'}}^{2Va_0}$, $x' \rightarrow 2$), as indicated by the red diamond in Figure 4.

Additionally, the calculated $E_{CeO_x}^{Va_O}$ (and $E_{CeO_x}^{2Va_O}$) have to be scaled appropriately with the energies of the reference structures, since L_0 (and L_1) represents contributions not captured by the endmember G° (and L_0) terms. Mathematically, L_0 is defined in terms of x or δ as

$$L_{0} = \frac{E_{CeO_{x}}^{Va_{O}} - (2x - 3)E_{CeO_{2}}^{F} - (4 - 2x)E_{CeO_{1.5}}^{F}}{2(2 - x)};$$

$$L_{0} = \frac{E_{CeO_{x}}^{Va_{O}} - (1 - 2\delta)E_{CeO_{2}}^{F} - 2\delta E_{CeO_{1.5}}^{F}}{2\delta}$$
(24)

where the multiplicative factors scaling $E_{CeO_2}^F$ and $E_{CeO_{1.5}}^F$ arise from the lever rule of thermodynamics, and the denominator ensures that L_0 is defined per O-vacancy, that is, L_0 represents the slope of $E_{CeO_x}^F$ (Figure 4). The Gibbs energies of the reference CeO_2^F and $CeO_{1.5}^F$ states in Equation (24) are approximated by their corresponding internal energies ($G \approx E$). The multiplicative factor of 2 in the denominator is to ensure that the L_0 , as defined here, is compatible with our sub-lattice model defined per the CeO_2 formula unit instead of as in Zinkevich et al.,^[67] where L_0 is defined per Ce_2O_4 formula unit. Similarly, we define L_1 as

$$L_{1} = \frac{E_{\text{CeO}_{x'}}^{2\text{Va}_{\text{O}}} - (2x' - 3) E_{\text{CeO}_{2}}^{\text{F}} - (4 - 2x') E_{\text{CeO}_{1.5}}^{\text{F}}}{2 - x'} - 2L_{0};$$

$$L_{1} = \frac{E_{CeO_{2-2\delta}}^{2Va_{O}} - (1 - 4\delta) E_{CeO_{2}}^{F} - 4\delta E_{CeO_{1.5}}^{F}}{2\delta} - 2L_{0}$$
(25)

Note that L_1 , as expressed above, is compatible with our definition of $G_{CeO_x}^F$ (Equation (23)), which is normalized per CeO₂ formula unit. The factor of 2 multiplying L_0 in Equation (25) signifies that there are twice the number of oxygen vacancies in calculating $E_{CeO_x}^{2Va_0}$ as compared to $E_{CeO_x}^{Va_0}$, that is, 2 - x' = 2(2 - x). Hence, L_1 captures the excess interactions not already captured by L_0 (and the end-members), since L_1 will be zero if the introduction of an additional oxygen vacancy is simply equivalent to the energy of two isolated oxygen vacancies.

3.2. Sub-Lattice Model in Zr-Doped CeO_x

Although sub-lattice models based on experimental data have yet to be developed for Zr-doped CeO_x, the CEF is general enough that the model developed for pure CeO_x can be extended for the Zr-doped system, as has been done for similar oxides.^[93] With Zr-doping, the Ce sub-lattice will contain three species, namely Ce⁴⁺, Zr⁴⁺, and Ce³⁺, while the O sub-lattice contains O and Va. Note that Zr is not redox-active in doped-CeO_x but has been known to reduce $\Delta H_{\rm red}$ and thereby increase the equilibrium oxygen off-stoichiometry.^[30,32,94,95] To account for Zr⁴⁺ in the Ce sub-lattice, the energies of two additional end-members, namely G^o_{Zr⁴⁺:O} and G^o_{Zr⁴⁺:O}, need to be evaluated, similar to the end-members of

undoped-CeO_x. Specifically, we reference $G^{\circ}_{Zr^{4+}:O}$ to stoichiometric ZrO₂ in the fluorite structure, that is,

$$G^{\circ}_{\mathrm{Zr}^{4+}:\mathrm{O}} = G^{\mathrm{F}}_{\mathrm{ZrO}_{2}} \tag{26}$$

While the ground-state structure of stoichiometric ZrO_2 is monoclinic, ZrO_2 can exhibit a fluorite structure isostructural with fluorite-CeO₂ at higher temperatures.^[96] Thus, $G_{\text{ZrO}_2}^{\text{F}}$ can be evaluated using DFT-based calculations ($G_{\text{ZrO}_2}^{\text{F}} \approx E_{\text{ZrO}_2}^{\text{F}}$). Similar to $G_{\text{Ce}^{4+:Va}}^{\circ}$, we define the Gibbs energy of the non-charge-neutral end-member $G_{\text{Zr}^{4+:Va}}^{\circ}$ using O₂ (g) as the reference:

$$G_{Zr^{4+}:Va}^{\circ} = G_{ZrO_{2}}^{F} - G_{O_{2}} (g)$$
(27)

The configurational entropy contribution in Zr-doped CeO_x is modified from Equation (13) to be:

$$S^{\text{soln}} = -R \left(\gamma_{\text{Ce}^{4+}}^{\text{Ce}} \ln \gamma_{\text{Ce}^{4+}}^{\text{Ce}} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \ln \gamma_{\text{Ce}^{3+}}^{\text{Ce}} + \gamma_{\text{Zr}^{4+}}^{\text{Ce}} \ln \gamma_{\text{Zr}^{4+}}^{\text{Ce}} \right) - 2R \left(\gamma_{\text{O}}^{\text{O}} \ln \gamma_{\text{O}}^{\text{O}} + \gamma_{\text{Va}}^{\text{O}} \ln \gamma_{\text{Va}}^{\text{O}} \right)$$
(28)

Additionally, we introduce four excess parameters, all normalized per the (Ce,Zr)O₂ formula unit, to describe interactions among: i) binary Ce⁴⁺-Zr⁴⁺ ($L^0_{Ce^{4+},Zr^{4+}}$) referenced to half the Gibbs energy ($\approx E$) of the CeZrO₄ fluorite-based superstructure; ii) binary Ce³⁺-Zr⁴⁺ ($L^0_{Ce^{3+},Zr^{4+}}$) referenced to one-quarter of the Gibbs energy ($\approx E$) of cubic-Ce₂Zr₂O₇; iii) ternary Ce³⁺-Ce⁴⁺-Zr⁴⁺ ($L^0_{Ce^{4+},Ce^{3+},Zr^{4+}}$), referenced to a combination of one Zr and one oxygen vacancy within a CeO₂ supercell; and iv) ternary Ce³⁺-Ce⁴⁺-Zr⁴⁺ ($L^1_{Ce^{3+},Ce^{4+},Zr^{4+}}$), referenced to one Zr and two oxygen vacancies in a CeO₂ supercell. All excess parameters are normed appropriately to the energy scale of the end-members, analogous to Equations (24) and (25). The overall *G*^{excess} for Zr-Ce-O ternary, combining L_0 and L_1 terms for binary Ce-O, is written as in Equation (29):

$$G^{\text{excess}} = \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \left(L_0 + \left(\gamma_{\text{Ce}^{3+}}^{\text{Ce}} - \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \right) L_1 \right) + \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \gamma_{Zr^{4+}}^{\text{Ce}} L_{\text{Ce}^{4+},Zr^{4+}}^{0} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{Zr^{4+}}^{\text{Ce}} L_{\text{Ce}^{3+},Zr^{4+}}^{0} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \gamma_{Zr^{4+}}^{\text{Ce}} L_{\text{Ce}^{3+},Zr^{4+}}^{0} + \gamma_{\text{Ce}^{3+}}^{\text{Ce}} \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \gamma_{Zr^{4+}}^{\text{Ce}} \left(\gamma_{\text{Ce}^{3+}}^{\text{Ce}} - \gamma_{\text{Ce}^{4+}}^{\text{Ce}} \right) L_{\text{Ce}^{3+},\text{Ce}^{4+},Zr^{4+}}^{1}$$

$$(29)$$

Similar to undoped-CeO_x, we evaluate all of the input parameters in Equations (23), (26), and (29) and the energies of all binary and ternary oxides within the Ce-Zr-O system to obtain the lowest Gibbs energy as a function of the oxygen composition (and x_{eq} as a result) at different Ce:Zr ratios in Zr-doped CeO_x.

4. Results

4.1. Pure CeO_x

Figure 5a plots the comparison between experimental (green, data from Zinkevich et al.^[67]) and theoretical (red) μ_{O} as a



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Figure 5. Experimental (green lines) versus theoretical (red lines) predictions of oxygen chemical potential in CeO_x as a function of x in pure CeO₂ at a)

298 K, $p_{O_2} = 1$ atm, b) TR (1673 K, $p_{O_2} = 10$ Pa), and c) WS (873 K, $p_{H_2O}/p_{H_2} = 9$) conditions. d) Evolution of $\frac{dH_{CeO_x}^r}{dx}$, which is related to $-\Delta H_{red}$, in CeO_x as a function of x at 1673 K, without any excess interaction terms (blue lines), with only the L_0 term (red lines) and with both L_0 and L_1 terms (green curves). e) Equilibrium oxygen concentration (x_{eq} in CeO_x) as a function of temperature at $p_{O_2} = 10$ Pa (solid curve (experiment) and diamonds (theory)) and $p_{O_2} = 10^{-12}$ Pa (dashed curve (experiment) and hollow diamonds (theory)), where the net $G_{CeO_x}^F$ includes either only the L_0 term (red symbols) or both the L_0 and L_1 terms (green curves and symbols).

function of x in CeO_x at 298 K for STCH-relevant concentrations $(1.5 \le x \le 2)$. The zero of the vertical axis is set to the free energy of O₂ (g) at 0 K, that is, $G_{O_2}(g) \approx E_{O_2}(g) \equiv 0$. The change in $H_{O_2}(g)$ from 298 K to 0 K is neglected $(S_{O_2}(g) = 0 \text{ at } 0 \text{ K})$, resulting in $\mu_{\rm O}^{\rm g} = -0.31$ eV at 298 K and $p_{\rm O_2} = 1$ atm from the $-TS_{O_2}$ (g) contribution (Equation (1)). A stable composition in Figure 5a spans a range of $\mu_{\rm O}$ (e.g., stoichiometric CeO₂ spans $-3.8 \leq \mu_{\odot} \leq 0$ eV, green line), while a constant μ_{\odot} spanning a range of x indicates a two-phase equilibrium (e.g., CeO_2) and Ce₇O₁₂ co-exist at $\mu_0 = -3.8$ eV). Qualitative agreement exists between the theoretical and experimental variations in $\mu_{\rm O}$. For example, both experiments and theory find Ce₇O₁₂ (x = 1.71), which is an ordered, fluorite-based superstructure of reduced-CeO₂, to be stable at 298 K in addition to fluorite-CeO₂ and hexagonal-Ce₂O₃. While errors in predicted (versus experimental) μ_0 for x < 1.5 (not relevant to STCH) are due to mixing DFT+U^[92,97] (for Ce-oxides) and DFT (for Ce-metal) energies (Experimental Section), the differences in the range of $\mu_{\rm O}$ for CeO_2 and Ce_7O_{12} arise from the specific U value employed^[92] and from comparing 0 K energies to experimental enthalpies at 298 K.

Analogous to Figure 5a, we compare theoretical and experimental $\mu_{\rm O}$ under STCH-relevant TR (at 1673 K, Figure 5b) and WS (at 873 K, Figure 5c) conditions. The orange (purple) line in Figure 5b (Figure 5c) corresponds to $p_{\rm O_2} = 10$ Pa ($\frac{p_{\rm H_2O}}{p_{\rm H_2}} = 9$). Dashed green and dotted red lines (Figure 5b,c), as well as corresponding annotations, indicate equilibrium oxygen off-stoichiometries ($x_{\rm eq}$ in CeO_x) from the experimental and

theoretical models, respectively $(\mu_{\rm O}^{\rm s} = \mu_{\rm O}^{\rm g} \equiv \mu_{\rm O}^{\rm eq})$. For example, under TR, the experimental and theoretical models estimate $x_{\rm eq} \approx 1.986$ and ≈ 1.988 , respectively, equivalent to $\delta_{\rm eq} = 0.014$ and 0.012 (Figure 5b and its inset). Similarly, $x_{\rm eq} \approx 1.999$ in both theory and experimental models under WS (Figure 5c). Thus, the DFT-based sub-lattice model yields accurate oxygen off-stoichiometry estimates for STCH-relevant conditions, which bodes well for using similar models of other STCH candidates.

The robust agreement between the theoretical and experimental models at small off-stoichiometries (x > 1.975) degrades at smaller x. For example, theory estimates that fluorite-CeO should remain stable only up to $\delta \approx 0.075$ ($x \approx 1.925$), while experiments indicate a maximum $\delta \approx 0.31$ ($x \approx 1.69$, inset of Figure 5b). The wide discrepancy at lower x originates in the artificial stabilization of Ce₇O₁₂ at 1673 K due to the neglect of vibrational entropy within the theoretical model (Ce_7O_{12} is not stable beyond 1321 K experimentally^[67]). Fluorite-CeO_x is stable up to δ ≈ 0.13 ($x \approx 1.87$) in the theoretical model when Ce₇O₁₂ is not included as a competing phase (dotted blue line in Figure 5b). The fair agreement between theoretical and experimental models at low oxygen off-stoichiometry for TR and WS (Figure 5b,c) relevant conditions highlights that vibrational entropy differences within solid phases, at the corresponding temperatures, can be neglected^[98] for practical STCH, providing a sufficiently accurate and less expensive approach.

Figure 5d displays variations in $\frac{dH_{ceO_x}^F}{dx}$, related to ΔH_{red} via Equation (4), versus *x* at 1673 K, where solid (dashed) lines indicate quantities from the experimental (theoretical) model. The



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Figure 6. Theoretical oxygen chemical potentials, as a function of *x* in (Ce,Zr)O_x at Zr doping levels of 0% (solid red), 10% (dashed green), 20% (dashed ot blue), and 30% (dotted brown). a) TR (1673 K) and b) WS (973 K) conditions, where the orange and purple lines indicate $p_{O_2} = 10$ Pa and $\frac{p_{H_2O}}{p_{H_2}} = 9$, respectively.

formation of competing phases (e.g., hexagonal-Ce₂O₃) is not considered in Figure 5d to ensure a direct comparison of the theoretical and experimental models. Blue, red, and green lines in Figure 5d signify, respectively, that $H_{CeO_x}^F$ contains no excess interaction terms (L_0 or L_1), only L_0 , and both L_0 and L_1 . $\frac{dH_{CeO_x}^F}{dx}$ there-

fore is independent of *x* without the excess terms, and L_1 . $\frac{dx}{dx}$ interefore is independent of *x* without the excess terms, and L_1 add a slope and a curvature, respectively (Equation (23)). Significantly, $\frac{dH_{CeO_x}^F}{dx}$ is the isolated oxygen vacancy formation energy in stoichiometric CeO₂ as $x \rightarrow 2$, where the theoretical-modelpredicted value of ≈ 4.15 eV agrees well with the experimentalmodel-predicted ≈ 4.33 eV.^[67] Additionally, the concave curvature of both the experimental and theoretical $\frac{dH_{CeO_x}^F}{dx}$ (green) highlights that the oxygen vacancies become progressively easier to create as *x* decreases from 2 (up to $x \approx 1.85$), a unique feature of pure-CeO_x compared to doped-CeO_x and several oxide perovskites.^[83] When $x \ll 1.85$, $\frac{dH_{CeO_x}^F}{dx}$ becomes significantly more negative and oxygen vacancies become harder to create.

Figure 5e shows x_{eq} versus *T* at TR-relevant $p_{O_2} = 10$ Pa (solid lines and solid diamonds) and at $p_{O_2} = 10^{-12}$ Pa (dashed lines and hollow diamonds), where x_{eq} is calculated only from theoretical (solid and hollow diamonds) and experimental (solid and dashed curves) models without considering competing Ce-oxides. We also plot x_{eq} adding just L_0 (red diamonds), and adding both L_0 and L_1 (green diamonds) to the overall $G_{CeO_*}^F$ (Equation (23)), while the experimental model is plotted including both L_0 and L_1 . Interestingly, adding L_1 hardly changes the theoretically predicted x_{eq} , under both $p_{O_2} = 10$ and 10^{-12} Pa and across temperatures, with a maximum deviation (at 1473 K, 10^{-12} Pa) of <10 % in x per CeO_x . Theoretical predictions (including that of L_0 and L_1) agree well with experimental x_{eq} at $p_{O_2} = 10$ Pa, highlighted by a maximum deviation of ≈ 0.02 per CeO_x (theoretical CeO_{1.96} versus experimental CeO_{1.94} at 1873 K). Theory deviates significantly from experiment at $p_{O_2} = 10^{-12}$ Pa, especially at intermediate temperatures (1273–1473 K), for example, $x_{eq}^{\text{theory}} \approx 1.92$ (green diamond) and $x_{eq}^{experiment} \approx 1.84$ at 1273 K. This dramatic deviation is due to the high concavity of the experimental $\frac{dH_{CeO_x}^F}{dx}$ curve (solid green line in Figure 5d) for 1.7 < *x* < 1.9.

4.2. Zr-Doped CeO_x

Similar to Figure 5b,c, we plot the theoretical μ_0 as a function of x in Zr-doped CeO_x at Zr-contents of 0% (pure-CeO_x, red curves), 10% (dashed green), 20% (dash-dot blue), and 30% (dotted brown) in Figure 6. Panels a and b correspond to TR (1673 K) and WS (973 K; note this is higher than the 873 K used in main text for pure ceria, vide infra) conditions, respectively, with the orange and purple lines reflecting the relevant oxygen partial pressures. We do not compare the predictions of Figure 6 with experimental data, because i) sub-lattice models fitting to available experimental (gas evolution and other thermodynamic) data, which would provide an apples-to-apples comparison, are not available; and ii) experiments that measure directly the O₂ gas evolved, such as by Hao et al.,^[31] may overestimate the overall gas evolution due to practical constraints of measuring gas content precisely,^[30] and the observed sublimation of CeO₂ at temperatures above 1600 K.^[99] However, TGA measurements can provide accurate measurements when $p_{\rm O_2}$ is well-controlled, [100] and often will be the only measurements available for theory to compare with.

Notably, as Zr-content increases, the net reduction (and the extent of stable oxygen off-stoichiometry) of Zr-doped CeO_x increases under TR conditions, in qualitative agreement with experiments.^[30,31,99] For example, at 1673 K and $p_{O_2} = 10$ Pa, x_{eq} is 1.988, 1.985, and 1.982 at 0%, 10%, and 20% Zr-doping, respectively. Additionally, increasing Zr-content also destabilizes the oxide without any oxygen off-stoichiometry, that is, (Ce,Zr)O₂. Indeed, Ce_{0.7}Zr_{0.3}O₂ (dotted brown line in Figure 6a) is not stable at 1673 K against O₂ gas at $p_{O_2} = 1$ atm ($\mu_O = -2.02$ eV) and should phase-separate to Ce_{0.8}Zr_{0.2}O_x and ZrO₂ domains. The prediction of phase separation is in qualitative agreement with experimental observations of surface segregation of ZrO₂, in conjunction with selective sublimation of CeO₂, upon thermal

reduction at 1683 K in $Ce_{0.85}Zr_{0.15}O_2$.^[99] Thus, large-scale doping of Zr within CeO_x will be counter-productive to ensure reduction (and subsequent re-oxidation) under reasonable STCH conditions. However, Zr-addition does stabilize larger offstoichiometric compositions, under highly reducing conditions (e.g., $Ce_{0.7}Zr_{0.3}O_{1.8}$ is stable at $\mu_{O} \approx -4.08$ eV).

Interestingly, none of the Zr-doped configurations are stable thermodynamically at 873 K, and the doped oxide should phase separate into CeO_r and ZrO_2 domains. This may be a cause for the poor long-term cyclability of Zr-doped CeO₂ compared to pure-CeO₂, as Zr⁴⁺ ions are known to exhibit long-range diffusion and segregation within the fluorite structure under STCH conditions.^[30] Hence, to compare quantitatively pure and doped CeO_x, we chose the WS temperature to be 973 K in Figure 6b instead of 873 K used in Figure 5c. Among the various Zr-dopant concentrations considered (i.e., 10%, 20%, and 30%), only the 10% Zr-doped fluorite phase is stable at 973 K and yields $x_{\rm eq} \approx$ 1.996 as compared to ≈ 1.997 for pure-CeO_x. Thus, higher Zrdoped contents should phase separate into $Ce_{0.9}Zr_{0.1}O_x$ and ZrO_2 domains at 973 K. Nevertheless, higher Zr-doped compositions may also exist in a metastable manner at 973 K (or 873 K) without explicitly forming Ce-rich and ZrO2 domains due to kinetic barriers, which are difficult to quantify theoretically or experimentally. Note that relying on kinetic barriers for materials that will have to cycle over very many cycles probably would not be a wise strategy.

5. Discussion

In this work, we have constructed a sub-lattice model (Figures 3 and 4), parameterized entirely using 0 K DFT-based calculations (Figure 2) for undoped and Zr-doped CeO2, which form the SOA for water and/or CO_2 splitting using a STC cycle (Figure 1). Specifically, we based our theoretical model (Section 3 and Figure 3) on the sub-lattice framework for undoped CeO_r that was built and fit to experimental data by Zinkevich et al.^[67] Subsequently, we extended our model to make predictions on the ternary Ce-Zr-O system. Importantly, our theoretical model's predictions are in fair agreement with experimental observations for both undoped and Zr-doped CeO_x (Figures 5 and 6), with a high degree of quantitative accuracy at low oxygen off-stoichiometries under TR and WS conditions. Our work highlights that fully DFT-based sub-lattice models, upon careful validation, can enable the discovery and optimization of candidate off-stoichiometric oxides for STC applications.

The CEF approximation^[61,62] often benefits from error cancellation. Ideal solution configurational entropy for all sub-lattices is a major assumption, especially in systems with a short-range order^[101] and/or binding between different species (e.g., Ce³⁺, dopant, and oxygen vacancies^[102]); entropy overestimates can cancel within the excess terms. In the case of CeO_x, the electrostatic attraction between Ce³⁺ and oxygen vacancies will dominate at low temperatures. Hence, the Ce³⁺ formed should be "adjacent" to the oxygen vacancies,^[95] which we indeed observe in our 0 K calculations (see Figure S1, Supporting Information). However, at higher temperatures (especially the range of interest for STCH, 873–1673 K), gains in configurational entropy can offset such Ce³⁺-oxygen vacancy binding. Hence, the

sub-lattice model in this work (and in Zinkevich et al.^[67]) uses the assumption of ideal mixing between the Ce³⁺ and Ce⁴⁺ in the Ce sub-lattice and between oxygen ions and vacancies in the oxygen sub-lattice. Despite the assumption of ideal mixing potentially leading to an overestimation of the configurational entropy, subtle error cancellation enables the sub-lattice model to reliably model the CeO_x system, as highlighted by the good predictions of the experimental model by Zinkevich et al.^[67] versus measurements. Indeed, multiple examples exist of sub-lattice models yielding robust phase diagrams while using ideal solution entropy.[61,62,101] The error cancellation alluded to here should occur between the excess terms and the configurational entropy, which can be understood within the framework of a regular solution model. Note that the L_0 term is analogous to the mixing enthalpy (H_{mix}) in a regular solution. A negative (positive) value of $H_{\rm mix}$ in a regular solution favors clustering (phase separation) of the individual components, while the ideal solution entropy (i.e., mixing entropy or S_{mix}) favors a random solution. Hence, errors in overestimating S_{mix} can cancel the over (under) estimation of $H_{\rm mix}$, leading to a physically reasonable description of the underlying solution phase. Such error cancellation also seems to benefit the theoretical model, as highlighted by the robust agreement between the theoretical and experimental models in this work.

In general, a good estimate of the "enthalpy of mixing" and ideal solution entropy is sufficient to describe chemical systems that behave in a regular or sub-regular-solution-like manner. In the case of sub-lattice models, usage of L_0 and L_1 excess terms, such as in the case of CeO_x, is approximately equivalent to a sub-regular model. This probably explains why using 0 K vacancy formation energies to obtain L_0 and L_1 (i.e., a robust estimate of the enthalpy of mixing), in conjunction with ideal solution of mixing within the Ce and O sub-lattices yields fairly accurate estimates of off-stoichiometry at higher temperatures. Although we used the lowest-energy oxygen vacancy configurations in CeO_x to obtain both L_0 and L_1 , the effect of including both excess terms does not seem to have a compounding effect in increasing or decreasing the excess Gibbs energy (Figure 5d) across oxygen concentrations. For example, L_0 (L_1) increases (decreases) the absolute value of $\frac{dH}{dx}$ in Figure 5d, particularly at low oxygen off-stoichiometries $(x \ge 1.9)$, which corresponds to decreasing (increasing) the energy required to form oxygen vacancies in CeO_x . Thus, at low oxygen deficiencies, L_0 and L_1 contribute in contrasting manners to the overall excess Gibbs energy, which might mitigate any error in over- or under-estimating the excess interactions. To account for short-range interactions between Ce³⁺ and oxygen vacancies, particularly at low temperatures, modified sub-lattice models that account for short-range order and/or binding can be used. However, obtaining enthalpy and/or entropy estimates for phases including short-range order and/or binding using DFT-based calculations can incur significant computational expense.

Having energies of non-charge-neutral end-members referenced to neutral phases or constrained via reciprocal relationships also are approximations within the CEF. Errors from these approximations will affect model quality. Nevertheless, models built on experimental data nominally retain a high degree of predictability,^[87] provided the fit is good. Although a preliminary examination of our model's predictability was done here (Figure 5e), the general applicability of theoretical models for more complicated materials and different thermodynamic conditions requires further evaluation.

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The degradation of the agreement between theoretical and experimental models at large off-stoichiometries in undoped CeO_x (Figure 5b, x < 1.975) can be attributed to the lack of vibrational entropy contributions associated with the spurious stabilization of Ce₇O₁₂ under TR conditions. Although better quantitative agreement with experiments is possible if vibrational entropy is explicitly included,[51,52,98,103-105] the increase in computational expense can be prohibitive. Specifically, phonon calculations for the reference states (CeO_2 , CeO_{15}^F and O_2), the competing Ce-oxides (Ce₇O₁₂, hexagonal-Ce₂O₃), and all possible x in off-stoichiometric CeO_x (in principle) would be needed. A prior study constructing a DFT-based cluster expansion on CeO_x indeed did report better agreement with experiments when vibrational entropy contributions at CeO₂ and CeO₁₉₁ were included.^[51] The focus in the present work, though, was to compare the accuracy of sub-lattice models based on "simple and cheap" 0 K DFT-based calculations against qualitative and quantitative experimental trends. It is not surprising that more accurate predictions can be obtained via theoretical models with higher degrees of complexity and costs of computation,^[72] but such accurate methods are not practical for materials screening. Nevertheless, we have included an estimate of the errors that can arise in μ_0 predictions with and without including the T dependence of $G_{CeO_2}^F$, $G_{CeO_{15}}^F$, L_0 and L_1 in Section S1, Supporting Information.

The availability of an experimental model guided our CEF parameterization. However, in systems without such models, rules and procedures must be formalized to build theoretical models. Conventional "rules of thumb" exist,^[61,62] such as minimizing the number of excess parameters, employing only charge-neutral reference states, and utilizing charge-preserving reciprocal relations. To build reliable theoretical models for higher-component systems (e.g., STCH-relevant ternary/quaternary/quinary oxide perovskites^[38,41]), such rules of thumb will be crucial because the number of end-members (and hence reference states) required to construct a model will increase with increasing components. For example, ternary-LaMnO₃ (versus binary-CeO₂) requires 24 (versus four) end-members and five (versus three) reference configurations,^[106] when going beyond simpler descriptors such as the energy difference between the perovskite and brownmillerite phases.[34,107] Excess parameters in theoretical models must be estimated with a physical justification and the values appropriately normed so as to ensure robust predictability. Rigorous quantification of errors in both experimental and theoretical model predictions will add insight and guide future work.

6. Conclusion

STC processes offering sustainable pathways to fuels require oxides tolerant to significant oxygen off-stoichiometry over a wide *T* and p_{O_2} range. Consequently, any theoretical framework for screening STC candidates must describe off-stoichiometry well and demonstrate predictive capability. Here, we parameterized a thermodynamic sub-lattice model solely using quantum calculations and we demonstrated its ability to predict equilibrium oxygen off-stoichiometries under STCH-relevant conditions, validated against SOA undoped and Zr-doped CeO₂. Specifically, we calculated energies of reference states and excess parameters needed to build a CEF model and benchmarked our predictions against a model fit to experimental data. We identified a physical way to estimate directly the excess parameters, which conventionally are fit to experimental and/or theoretical data. Similar theoretical models, after careful validation, will be useful for discovering novel off-stoichiometric materials for STC and related applications.

7. Experimental Section

Computational Methods: All DFT calculations were done spinpolarized using the Vienna ab initio simulation package, utilizing the all-electron, frozen-core, projector augmented-wave theory.[108-110] The planewave basis, expanded up to a kinetic energy cutoff of 520 eV, was sampled on a dense Γ -point-centered k-point mesh (with a spacing of ≈ 0.03 Å⁻¹) for all oxide structures. The total energies were converged to within 0.01 meV and the atomic forces were converged to <|0.03| eV Å⁻¹, similar to computational parameters used in our earlier work.^[92] The starting structures of all binary and ternary Ce- and Zr-oxides were taken from the Inorganic Crystal Structure Database.[111] Electron exchangecorrelation (XC) was described using the strongly constrained and appropriately normed (SCAN) functional,^[112] with a Hubbard $U^{[97]}$ correction of 2 eV added to the Ce's 4f orbitals to correct for spurious self-interaction errors common within transition-metal and rare-earth oxides. The choice of U value was based on our previous study that benchmarked oxidation energies of metal oxides, including binary Ce-oxides.^[92] A U to Zr was not added since it nominally was present in its +4-oxidation state and hence does not contain open-shell d electrons. Additionally, a U correction was not added to calculate the total energies of any elemental species (Ce/Zr/O₂), as it was not appropriate for metals or molecules. Note that we prefer to use the SCAN+U framework instead of the previously employed^[113,114] local density approximation (LDA^[115])+U or a generalized gradient approximation ($GGA^{[116]}$)+U for two reasons: i) SCAN is a more accurate and more well-founded functional than LDA/GGA since it satisfies all 17 known constraints of a XC functional $^{\left[112\right] }$ and ii) the absolute U correction required with SCAN is normally lower compared to LDA/GGA, consistent with SCAN containing more of the correct XC physics.^[92]

All possible symmetry-distinct oxygen-vacancy configurations were enumerated within the conventional CeO2 unit cell to evaluate the energy of CeO^F₁₅ and we used the lowest energy obtained. For estimating $E_{O_2}(g)$, an isolated oxygen molecule was placed in an asymmetric 15 Å \times 16 Å \times 17 Å cell to obtain the triplet electronic ground state of O2. The oxygen vacancy formation energy in CeO2 and Zr-doped CeO2 (to define L_0 and $L_{Ce^{3+},Ce^{4+},Zr^{4+}}^0$, respectively) was calculated using a 2 \times 2 \times 2 supercell of the conventional fluorite structure. For estimating the vacancy-vacancy interaction energy (to define L_1 and $L_{Ce^{3+},Ce^{4+},Zr^{4+}}^1$), all of the symmetry-distinct configurations of two vacancies were enumerated within the $2 \times 2 \times 2$ supercell and we used the lowest energy among the considered configurations. Finally, the pymatgen^[117] toolkit was used to construct the Ce-O2 (and Ce-Zr-O2) phase diagram and determine the oxygen chemical potential in the solid phase $(\mu_{\rm O}^{\rm s})$ as a function of T. Unless specified otherwise, Gibbs energies of all stoichiometric ($G_{CeO_2}^F$, $G_{CeO_{1.5}}^F$, $G_{ZrO_2}^F$, $G_{CeZrO_4}^F$, $G_{Ce_2Zr_2O_7}^F$) structures (Equations (5) and (26))were approximated as internal energies (E) calculated at 0 K (e.g., $G_{CeO_2}^F \approx E_{CeO_2}^F$ (theory)). For O₂ (g), its enthalpy (H_{O_2} (g)) was approximated as the total energy of an isolated O_2 molecule at 0 K $(E_{O_2}(g)).$

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

density functional theory, off-stoichiometric materials, solar thermochemical water splitting, sub-lattice models, thermodynamic modeling

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