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Solar Salt above 600 °C: Impact of Experimental Design on Thermodynamic Stability Results

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Abstract: Thermal energy storage (TES) based on molten salts has been identified as a key player in the transition from fossil fuels to renewable energy sources. Solar Salt, a mixture of NaNO₃ (60 wt%) and KNO₃ (40 wt%), is currently the most advanced heat transfer and storage material used in concentrating solar power (CSP) plants. Here, it is utilized to produce electricity via a Rankine cycle, with steam temperatures reaching 550 °C. The goal of this study is to increase the operating temperature of solar salt to over 600 °C, allowing it to be adapted for use in high-temperature Rankine cycles with steam temperatures greater than 600 °C. Yet, this goal is impaired by the lack of available thermodynamic data given the salt's complex high-temperature decomposition and corrosion chemistry. The study explores the thermodynamics of the decomposition reactions in solar salt, with a focus on suppressing decomposition into corrosive oxide ions up to a temperature of 620 °C. The results provide a new understanding of the stabilization of solar salt at previously unexplored temperatures with effective utilization of gas management techniques.

Keywords: molten salt; nitrite formation; oxide formation; high-temperature chemistry; thermal energy storage; concentrated solar power (CSP)



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1. Introduction

Providing dispatchable renewable energy at a GWh scale has become increasingly significant in the last decade. Thermal energy storage (TES) based on molten nitrate salts is currently the standard solution in several concentrated solar power (CSP) plants to provide dispatchable electricity during day- and night-times. Solar salt, a mixture of 60 wt% NaNO₃ and 40 wt% KNO₃, is a commonly used TES material for temperatures up to 565 °C [1–3]. The overall efficiency of the power block and storage capacity could still be enhanced if the stability limit could be extended well above 600 °C. Yet, temperatures above 600 °C lead to the formation of toxic gases (e.g., NO_x) and corrosive decomposition products in the salt, which are potentially harmful to, e.g., the container materials [4,5]. Additionally, it has been demonstrated that contact of molten salt with alloy materials (e.g., Inconel 625, 45# carbon steel) is related to the evolution of NO and NO₂ [6,7]. These toxic gases cannot be released into the environment without further gas treatment [8]. The chemical nature of solar salt has been intensively studied, and there is general agreement on a decomposition mechanism with two reaction steps. Initially, the nitrate anion (NO₃⁻) will decompose to form a nitrite ion (NO₂⁻) under the evolution of oxygen (O₂) (Equation (1)).

$$NO_3^- \rightleftharpoons NO_2^- + 0.5O_2 \tag{1}$$

At temperatures beyond 565 °C, the NO_2^- -ion will decompose to form oxide ion species (e.g., $O_2^{2^-}$, O_2^- , O^{2^-}) under the evolution of nitrous gases (e.g., NO, NO₂, N₂O).

The following equilibrium reactions (Equations (2) and (3)) represent the most likely possibility for the second degradation step of solar salt at elevated temperatures [9,10].

$$2\mathrm{NO}_2^- \rightleftharpoons \mathrm{O}^{2-} + 2\mathrm{NO} + 0.5\mathrm{O}_2 \tag{2}$$

$$2NO_2^- \rightleftharpoons O^{2-} + N_2 + 1.5O_2 \tag{3}$$

So far, the first decomposition step of NO_3^- -anions (Equation (1)) has been proven valid [11,12]. For the second decomposition step, several reaction mechanisms were suggested, and, for solar salt above 600 °C, the majority of them can be described by a combination of Equations (2) and (3) [13–16]. Equation (2) is considered to include the temperature-dependent gas–gas equilibrium reaction (Equation (4)), which lies on the side of NO for temperatures above 300 °C [17].

$$2NO + 0.5O_2 \rightleftharpoons 2NO_2 \tag{4}$$

Equation (3) is understood as a subordinated decomposition reaction related to Equation (2), although Yang et al. [6] reported that it is favorable from a thermodynamic perspective. However, in the studies of Wright et al. [9] and Olivares et al. [18], the N₂ emission was measured to be an order of magnitude less than the emission of NO. Owing to this fact, Equation (2) is understood as the primary reaction path for nitrite decomposition in the presented work. This reaction generally leads to the formation of corrosive oxide ions coupled with the release of nitrous gases. The exact stoichiometry and mechanism, however, still need to be confirmed experimentally.

The authors believe that the whole potential of solar salt as a TES medium, in terms of its maximum operating temperature, has not yet been exploited. The main reason for this limitation is the usage of a system configuration where the hot and cold tanks of the TES system are openly connected to ambient air. In this case, NO_3^- and NO_2^- concentrations equilibrate as a function of the present oxygen partial pressure, according to Equation (1) [2,19]. However, nitrite decomposition (Equation (2)) is not stabilized since nitrous gases are constantly flushed out of the tanks [8,20,21]. Consequently, oxide ion formation can thermodynamically never reach equilibrium and should continue to increase during the lifetime of the plant to an unacceptable level. This can potentially result in aggravated corrosion, which is a crucial factor hindering TES with nitrate salts by moving to higher operating temperatures [22–24].

Retaining reactive gases such as O_2 and NO or NO_2 in the system would effectively prevent the decomposition of the nitrate salt, which has been partly demonstrated previously [25].

In this study, the presence of nitric oxide (NO) in the purge gas was proven to reduce the rate of O^{2-} -formation significantly [26,27]. Yet, a fully stabilized solar salt system with a constant oxide ion concentration at 620 °C has not been presented in the literature. It has been suggested that transport limitations and corrosive side reactions may have affected the solar salt chemistry, leading to misinterpretation of chemical equilibria, especially on small-scale experiments (e.g., sub-kg scale). In their kinetic study, Nissen and Meeker [11] have already revealed that it is necessary to eliminate oxygen (and nitrite) mass transport effects in order to achieve reproducible data, but they assumed that there were no errors in the thermodynamic equilibrium data. However, in a more recent study [28], it was found that above 600 °C, all of the present thermodynamic datasets for solar salt are most likely afflicted by decomposition reactions or mass transport limitations and do not reflect a thermodynamic equilibrium. In consequence, the interpretation of those results leads to false thermodynamic predictions, especially on the high-temperature properties of solar salt. However, the authors suggested that the data of Sötz et al. [12] generated at temperatures below 550 °C are in fact applicable for elevated temperatures if side reactions are reduced to a minimum. With this study, by more careful experimental design improvements, the requirements for generating data without side reactions were met. These include the replacement of metal components of test rigs previously utilized for the generation of high-temperature thermodynamic data with a fully ceramic experimental setup. Additionally, experimental design improvements involved the appropriate selection of process parameters (e.g., purge gas). A new experimental series with an improved setup up to 620 °C and a thermodynamic evaluation is presented. For the first time, the experiments demonstrate the impact of several nitrous gas species (NO, NO₂, or N₂O) as well as N₂ on the oxide ion-producing reaction up to 620 °C to identify the most relevant reactions for the stabilization of solar salt.

2. Material and Methods

Solar salt (60 wt% NaNO₃, 40 wt% KNO₃) was produced by stoichiometric mixing of NaNO₃ (Merck, purity > 99%) and KNO₃ (Merck, purity > 99%). For each experiment, an autoclave test rig (described elsewhere [25]) was loaded with 150 g of solar salt contained in an Al_2O_3 crucible. The in-house setup (see Figure 1a) was designed in such a way that only the lower part of the autoclave is heated. Salt creeping up the crucible walls will solidify in the cold part and fall back into molten salt. The reported setup was optimized by substituting stainless steel components with full ceramic (Al_2O_3) components (see Figure 1b). The autoclave test rig is temperature controlled with a maximum deviation of ± 4 °C. To fix the atmospheric composition, the salt is purged with a constant gas flow (100 mL/min) adjusted by calibrated flow meters (EL-Flow; Bronkhorst high-tech B.V., AK Ruurlo, Netherlands). To avoid concentration gradients in the molten salt, every experiment is stirred at 60 rpm if not mentioned otherwise. After melting the salt mixture at $300 \,^{\circ}\text{C}$ under a flow of synthetic air (5.0 grade, Linde Gas), the auto sampling unit (detailed picture in [25]) is mounted onto the autoclave test rig. Subsequently, the desired purge gas flow is adjusted by mixing O_2 , N_2 , and a reference gas containing 2000 ppm NO (NO₂, N_2O) in N_2 (all 5.0-grade Linde gas). The concentrations of O_2 (vol%), CO_2 (ppm), NO_2 (ppm), and NO (ppm) in the exhaust gas are continuously measured with the Emerson X-SREAM analyzer (Model XEGP, Emerson Electric Co., St. Louis, USA). The salt is heated to the target temperature (e.g., 600 °C, 620 °C). Upon reaching the target temperature, the first salt sample is collected (t = 0 h). Over the course of the isothermal experiments (approx. 1200 h, ± 2 °C), salt samples are extracted and analyzed by wet chemistry to monitor salt composition. To investigate whether oxide ion formation is limited by mass transport, the agitator speed is adjusted between 0, 60 (default speed), and 120 rpm.

To reveal the ion content of the salt samples, ion chromatography (IC; Metrohm model 883 Basic IC plus) was utilized. About 125 mg of the salt sample was dissolved in ultrapure water (conductivity < $0.055 \,\mu$ Scm⁻¹) and analyzed. As a result, the content of nitrate and nitrite is given in absolute values based on a standardized calibration of the IC method. A detailed description of the experimental procedure and calibration is given elsewhere [28]. The oxide ion contents were determined by automated acid base titration (Metrohm Titrando 800, Herisau, Switzerland) under an inert purge gas of N_2 (5.0-grade Linde gas). This technique is based on the reaction of basic oxide ions (e.g., O^{2-}) in water to form two hydroxide ions (HO⁻). By titration of HCl solution (0.01 M) until neutrality, the amount of hydroxide ion can be determined. A detailed description is given in our previous work [27]. The limit of detection (LOD) for oxide ions, represented as O^{2-} in this work, was below 0.01 mol% (20 ppm) with regard to salt composition. The measuring errors of nitrate and nitrite content were $\pm 0.3\%$ and $\pm 0.9\%$, respectively. For the detection of oxide ions, the relative error at the LOD was $\pm 14\%$, which is the maximum deviation and is applied below the limit of quantification (LOQ > 0.07 mol%). Above the LOQ, the error was as low as 2% and is shown as error bars for the oxide data points in the plots of this work. For nitrate and nitrite, the error bars lay within the symbol size. Cation concentrations of all experiments were monitored and remained unchanged over time and hence are not part of the discussion. Anion concentrations are given and discussed in relative molar percentage (mol%), where the sum of all anions detected (NO₃⁻, NO₂⁻, O²⁻) is equal to 100%.



Figure 1. (a) Schematic image of the autoclave test rig with inside view of different components. Hot section indicated by orange arrows. (b) Anion content over time of solar salt stored at 620 °C, purged with synthetic air (closed symbols), and purged with synthetic air and 200 ppm NO (half open symbols). Equilibrium composition is marked as horizontal lines. Picture of metal stirrer (red) and ceramic stirrer (blue). Arrow with color transition from red to blue indicate the direction of salt composition change with the optimization of the setup. * Red data points are republished (Reprinted/adapted with permission from Ref. [26], 2020, International Solar Energy Society).

Equilibrium levels were calculated from anion content after the reaction quotient (ratio between educt and product) obtained a stable value. For NO_3^- and NO_2^- (Equation (1)), this is the case after approximately 300 h. Oxide formation rates are often afflicted with a strong error, especially if a corrosion reaction cannot be excluded [28]. It has been shown in a different study [27] that nitrous gases stabilize the molten salt, and an established oxide equilibrium allows comparison between different experiments. The O^{2-} equilibrium (Equation (2)) takes approximately 500 h to be attained. After the respective time, the median of the remaining data points is calculated and displayed as horizontal lines in the graphs, which are defined as equilibrium composition.

3. Results and Discussion

The principle of oxide ion formation has been the subject of many studies using molten nitrate salts for thermal energy storage. Unfortunately, despite decades of research, there is no general agreement about one single reaction to describe the oxide formation in molten nitrate salt. Missing data on the equilibrium composition of solar salt at elevated temperatures prevents sophisticated predictions of the long-term salt composition development, which is necessary for next-generation nitrate salt TES. In subsequent sections, the optimized setup is introduced and its effect on the salt composition is evaluated. Further, the role of N₂ gas in the stabilization of solar salt is discussed. To generate insight into the role of nitrous gases, for the first time, equilibrium data for solar salt purged with NO₂ and N₂O are presented. At 620 °C, the potential boundaries for the stabilization of molten salt with NO purge gas are introduced. Finally, the generated data are evaluated from a thermodynamic perspective, and process implications are made.

3.1. Setup Optimization

In the above-mentioned studies, with increasing operating temperatures, the authors experienced a significant alteration of the test rig, in particular the corrosion of the metal agitator unit. Corrosion reactions involve redox reactions between nitrate/nitrite ions and the alloying elements Fe, Cr, and Ni, leading to an increase in the impurity levels (e.g., chromate ($CrO_4^{2^-}$) ions) in the molten salt but also changes to the decomposition mechanism [27,29]. Consequently, the metal agitator (Figure 1) was exchanged for a full ceramic (γ -Al₂O₃) 3D-printed propeller to prevent side reactions and, at the same time, increase mixing efficiency by geometry optimization. To identify any changes due to the optimized setup, this study comprises two experiments with identical parameter sets to two experiments already published [26]. Figure 1 displays the results of salt composition over time of two experiments with metallic (red, previous work [25]) and inert ceramic (blue, this work) propeller setups.

Closed symbols in Figure 1 depict the data of experiments under a synthetic air (20% O_2) atmosphere at 620 °C. The nitrate and nitrite content of both experiments attain a steady state after about 300 h, but for the experiment with the ceramic stirrer (blue), the NO_2^- content (11.9 mol%) is significantly lower compared to the data in red (13.5 mol%) gained with the metallic stirrer. The oxide ion concentrations increased in both experiments, as expected because the purge gas did not contain the gases (e.g., NO) necessary to obtain an oxide ion equilibrium.

A similar result was found in the experiment with a purge gas of 20% O_2 and 200 ppm of NO (rest N_2). The concentration of NO_3^- and NO_2^- (88.5 mol%, 11.5 mol%) for the optimized setup (blue) reveals a lower amount of the decomposition product compared to the red dataset (86.2 mol%, 13.7 mol%). In the case of the oxide ion concentration (in red), the equilibrium concentration was measured to be 0.1 mol%; albeit, a slow increase is still visible. Using the ceramic setup, the oxide ion concentration (in blue) stabilizes at 0.045 mol% under identical conditions.

This outcome is noteworthy in various aspects. The optimized setup not only stabilized the conditions for the molten salt to reach equilibrium in all reaction steps but also significantly decreased the fraction of decomposed salt due to side reactions with metallic components, specifically a reduction of up to 50% in the concentration of oxide ions. If the degree of salt decomposition is defined by the fraction of decomposition products (NO₂⁻, O^{2-}) versus pure nitrate salt, our results become clearer. With this definition, it can be stated that the improvements to the experimental setup led to a lowering of the degree of salt decomposition by 16%. This result can be explained by the reduction in side reactions, which in the former publications led to higher decomposition product formation. Without corrosion reactions, the concentrations of NO₂⁻ and O²⁻ (in steady state) present the pure chemistry of solar salt at 620 °C and are now applicable for thermodynamic calculations. Consequently, solar salt appears to be more stable under these conditions than suggested by previous investigations. The next section includes results on the potential impact of nitrogen gas on the oxide ion producing a reaction in molten solar salt.

3.2. Salt Stabilization without N₂

In the before-mentioned study of Sötz et al. [26], an equilibrium description was developed based on experimental data and an intensive literature review. It was found that the entirety of the published reaction mechanisms diverges in the fraction of nitrogen produced in the course of the oxide ion formation. Based on comparing the listed thermodynamic enthalpies and experimental results, a closed agreement for the following reaction equation (Equation (5)) was found.

$$2NO_2^- \rightleftharpoons O^{2-} + 0.5NO + 1.25O_2 + 0.75N_2 \tag{5}$$

Because of the high stability of nitrogen at the prevailing conditions (1 atm, 620 °C), the relevance of the nitrogen molecule in the stabilization of the molten salt is still questionable.

To prove the effect of nitrogen on the oxide ion equilibrium position, a set of storage experiments without nitrogen but with argon in the purge gas were performed in this study. It is emphasized that this investigation was conducted prior to the system optimization. Thus, this dataset is directly comparable to the published data of Sötz [26]. The result of the anion composition development over time in comparison to the equilibrium values (red lines) of the reference study is shown in Figure 2.





For all experiments, the same partial pressure of oxygen (0.2 atm) was present in the purge gas. Consequently, the nitrate–nitrite equilibriums at 600 °C and 620 °C were expected to be identical to the published values from Sötz [26]. As can be seen in Figure 2 (top and middle graphs), three out of the four experiments align well with the published data performed in the presence of nitrogen gas (red line). Solely the experiment performed at 620 °C in 20% O₂ with argon showed a shift of the equilibrium composition towards the product side of Equation (1) with 78.9 \pm 0.9 mol% nitrate and 20.4 \pm 0.5 mol% nitrite compared to the reference at the same partial pressure of oxygen (86.4 mol% and 13.5 mol%). Additionally, the same salt samples contained significant amounts of chromate ions (up to 0.5 ± 0.1 mol%), which is a known indicator for the presence of corrosion reactions during the experiment [24]. This deviation can most likely be ascribed to more severe corrosion reactions of the salt with a metal stirrer compared to the other experiments. In the bottom graph of Figure 2, the oxide ion content is depicted. The experiment purged with 200 ppm NO (20% O_2 in argon) shows stable oxide ion concentrations after 700 h and is close to the published data at 620 °C (0.10 ± 0.08 mol%). At 600 °C, the data with argon purge are above the published results ($0.06 \pm 0.04 \text{ mol}\%$) (dotted red line).

At 600 °C, another study [27] performed in the same test rig is available for comparison. Here, after the regeneration of solar salt with identical experimental conditions, an oxide ion concentration of 0.11 ± 0.02 mol% was obtained, which is above even the result at 620 °C

 $(0.10 \pm 0.08 \text{ mol}\%)$. These findings indicate that impurities and corrosion side reactions inflict the oxide ion data with a significant error and at such a low concentration that data need careful analysis. However, the results allow for a couple of conclusions concerning the stabilization of solar salt. Firstly, the corrosion reaction did alter the nitrate–nitrite equilibrium and clearly demonstrates the necessity of the optimization of the experimental setup. Secondly, it was found that nearly equivalent oxide ion equilibrium values could be achieved with and without the presence of nitrogen in the purge gas.

The latter result is in contradiction to the oxide equilibrium in Equation (5) where NO, O_2 , and N_2 are absolutely required for the stabilization of the nitrite decomposition. In consequence, the postulated equilibrium description (Equation (5)) does not reflect the present reaction mechanism of the experiments discussed in this paper. However, the detection of N_2 during the thermal decomposition of nitrate salt in several studies [9,18] remains; therefore, it is likely that the decomposition of nitrite proceeds under NO (Equation (2)) as well as N_2 (Equation (3)) emissions. From a thermodynamic perspective, Yang et al. [6] stated that N_2 evolution (Equation (3)) is more favorable than NO evolution. Thus, the reverse direction of Equation (3), a regeneration of the salt with N_2 , is unlikely and can be understood as an irreversible reaction path in the prevailing conditions. Consequently, a stable oxide ion concentration over time, as shown in Figure 2, is only feasible if the irreversibly produced oxide ions (as in Equation (3)) are compensated by NO regeneration through Equation (2).

Apart from N_2 and NO, the gases NO_2 and N_2O were also detected to be reaction products of nitrate salt decomposition [9,18]. The next part of the study focuses on answering which nitrous gas species is the most relevant in controlling the stabilization of solar salt at elevated temperatures.

3.3. Impact of NO, NO₂, and N₂O

The following set of experiments was performed with 20% O₂ and 200 ppm NO and NO₂ or N₂O in N₂ at 600 °C or 620 °C. To accelerate the equilibration process, the initial conditions were modified by either adding nitrite salt (10 mol%), purging with pure nitrogen, or overheating (630 °C) the salt. However, the modifications did not affect the final equilibrium composition of solar salt and are comparable to each other, as has been stated by Nissen and Meeker [11]. To reveal the influence of the different nitrous gases on the equilibrium composition, especially the oxide ion concentration, the anion concentrations over time of the respective experiments are summarized in Figure 3.

The equilibrium concentrations for nitrate as well as for nitrite for experiments at 600 °C and at 620 °C are in close agreement. A thermodynamic evaluation and equilibrium data are given in the upcoming Section 3.5.

In the bottom graph of Figure 3, the oxide ion concentration evolution over time of the different experiments is shown. It is immediately visible that the oxide ion concentration increases constantly (1E-06 mol%/h) for molten salt purged with 200 ppm N_2O and that it did not reach an equilibrium state. In order to obtain oxide equilibrium from the opposing side in the 600 °C experiment (Figure 3, blue cross), the NO₂ purge gas was subsequently simply switched on after 300 h to initially increase oxide ion formation. In comparison to solar salt purged with N_2O , the oxide content without nitrous gases after 300 h was at 0.090 \pm 0.002 mol%, whereas with N₂O purge gas after 300 h, it was significantly less at 0.045 \pm 0.008 mol%. For experiments purged with 200 ppm NO and NO₂ at 600 °C (light blue), the oxide equilibrium state was approached from initially higher values of oxide ion, which subsequently became reduced via regeneration reactions (Equation (2)). In particular, with NO₂, the regeneration was quicker than with NO (Figure 3, dashed line: 0.032 ± 0.008 mol%) and led to the lowest oxide ion content (Figure 3, dash dot: 0.016 ± 0.002 mol%) under these conditions. The same trend is visible for the experiments at 620 °C, where the oxide equilibrium of salt purged with NO₂ (0.029 \pm 0.002 mol%) is slightly below that purged with NO ($0.045 \pm 0.002 \text{ mol}\%$).



Figure 3. Anion content over time of solar salt stored at 600 °C (light blue) and 620 °C (dark blue) then purged with 20% O_2 and 200 ppm of either NO, NO₂, or N₂O. Horizontal lines mark the equilibrium content of the respective experiment.

Based on these experiments, it was found that the stabilizing effect of N₂O (20% O₂ with 200 ppm N₂O) on solar salt is significantly lower compared to that of NO and NO₂. However, with respect to the nitrate–nitrite equilibrium, similar results for all of the NO_x gases (at the same temperatures) were obtained. It is concluded that all NO_x gas species (200 ppm) reduce the extent of the nitrite decomposition (Equation (2)), which allows for equilibration of the nitrate–nitrite reactions without the impact of oxide ion formation. This is the first evidence for the suggestion in the literature [26,28] that above 600 °C, nitrite decomposition needs to be suppressed to achieve a proper thermodynamic nitrate–nitrite equilibrium (see Section 3.5, Equation (7)). When comparing 200 ppm of NO and NO₂, both lead to stable oxide ion concentrations at 600 °C and 620 °C, whereas NO₂ gives lower oxide ion values than NO.

Interestingly, a remarkable difference when analyzing the composition of the waste gas of molten salt purged with NO and NO₂ was detectable. The raw data are found in the supplementary section, exemplary for two of the previously discussed experiments at 620 °C with NO or NO₂ purge gas (Figure S2). To validate the extent of the temperature-dependent gas–gas reaction (Equation (4)) of NO, O₂, and NO₂, as mentioned in the introduction, a blank experiment without salt at 620 °C and different NO_x concentrations of 200–1200 ppm was performed (Figure S2). For an inlet gas containing 200 ppm NO, 20 \pm 5 ppm was oxidized to NO₂, whereas from an initial value of 200 ppm NO₂, 50 \pm 5 ppm was reduced to NO after passing the hot chamber. During every molten salt experiment, the measured concentrations of NO or NO₂ in the exhaust gas typically settle at a steady value after a few hundred hours, which is considered in the following discussion. The measured composition thereby correlates with the originally set purge gas composition (e.g., 200 ppm). With 200 ppm NO purged molten salt (620 °C, 20% O₂), a value of 174 \pm 6 ppm NO and

21 ± 5 ppm NO₂ was measured (t = 700-1000 h). In contrast, the gas composition for molten salt (620 °C, 20% O₂) purged with 200 ppm NO₂ contained 108 ± 5 ppm NO and 81 ± 5 ppm NO₂ (t = 800-1100 h), which is not in agreement with the blank experiment (Figure S2). However, the total NO_x concentration (NO and NO₂ combined) measured matches that of the supply gas, which ensures no net consumption of nitrous gas species during the experiments.

In general, solar salt with a constant composition of nitrate, nitrite, and oxide ions was achieved with NO and NO₂. This state is only feasible when forward and reverse reactions (Equations (1) and (2)) occur at an equal rate. In other words, the decomposition of solar salt is stopped by the simultaneous regeneration of the decomposition products (NO_2^-, O^{2^-}) with O₂ and NO or NO₂. This state is defined as an equilibrium where the reactant concentration is constant, including the consumption and emission of gases. With NO purge, this was the case, and the exhaust gas composition was almost the same as the incoming gas (200 ppm NO) with some partial oxidation to NO₂. In this regard, the temperature-dependent gas–gas reaction (Equation (4)) of NO, O₂, and NO₂ comes into play and was validated in a blank experiment without salt. In the hot reaction chamber (620 °C), NO gas is stable but cools down (25 °C) on its way to the gas analyzer, and consequently suffers from oxidation to NO₂, which corresponds to the measured concentration of 26 \pm 5 ppm NO₂. Without the consumption of NO_x gas after passing the molten salt, it is reasonable to assume that an equilibrium state was attained.

In the case of NO₂, 107 ± 5 ppm NO is found after leaving the reaction vessel with molten salt, which is significantly more than expected from the blank experiment (50 ppm, Figures S1 and S2). In the following, a potential reaction mechanism is suggested to explain the outcome of the experiments purged with NO₂. NO₂ gas is known to react with the nitrite ion and form nitrate according to the following reaction in Equation (6) [30].

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \tag{6}$$

Because the concentration of nitrite is typically two orders of magnitude higher (see Figure 3) than oxide, it is statistically more likely for the NO₂ molecule to react with a nitrite ion than an oxide ion. In general, it is believed that reactions such as in Equation (6) but also the reverse direction of the equilibrium reactions in Equations (1) and (2) are dominantly occurring at a liquid–gas interface. This is because gas solubility in molten salts is typically low due to the lack of intermolecular interactions [31]. After the reaction of NO₂ at the liquid–gas interface, NO molecules are subsequently formed via Equation (6). It is reasonable to assume that a regeneration reaction of oxide ions (Equation (2)) with NO, which is produced directly at the reaction interface, is more effective compared to NO, which is obstructed by gas diffusion towards the reaction interface. This hypothesis could explain why NO₂ purge gas shows better performance compared to NO in the stabilization of solar salt at 600 and 620 °C.

3.4. Boundaries for Solar Salt Stabilization

The next set of experiments was performed to identify potential boundary conditions for the stabilization of solar salt with 200 ppm NO at 600 °C and 620 °C. Boundary conditions are defined as critical process parameters that, under equilibration such as those of solar salt in terms of stable nitrate, nitrite, and oxide ion content, are no longer feasible. Thereby, the effect of higher nitrite concentrations (achieved by a reduction in the oxygen partial pressure) on the position of the nitrite oxide equilibrium was investigated. At the same time, 200 ppm NO was not varied to isolate the effect of the nitrite concentration on the nitrite–oxide equilibrium. The results of the salt composition data are summarized in Figure 4.



Solar Salt at 600 °C with NO purge

Figure 4. Anion content over time of solar salt stored at 600 $^{\circ}$ C (light blue) purged with 200 ppm NO in N₂ and 20% (data from Figure 3, not shown for clarity), 10%, or 5% O₂. Horizontal lines mark the equilibrium content of the respective experiment.

Both experiments attained nitrate–nitrite equilibrium after 300 h (Figure 4, top and middle), and this equilibrium composition was extracted for thermodynamic evaluation (Table 1). An oxide ion equilibrium was accomplished with 5% and 10% O₂ (200 ppm NO), at 0.06 ± 0.01 mol% and 0.055 ± 0.008 mol%.

With these results, it becomes clear that the content of NO_2^- changes the position of the oxide ion equilibrium, according to Equation (2). However, the relation is not exactly as written in the reaction mechanism (Equation (2)) because the oxide to nitrite ratio theoretically should be constant at a single temperature, which is not reflected by the experimental data (see Table 1). This behavior can potentially be explained by the strong regeneration of NO and the resultant low equilibrium concentration of oxide ions, in which case detection is hardly possible without a significant error. Still, the combined data from Figures 3 and 4 are the first to link the oxygen and NO_x partial pressure with a stable oxide ion concentration at 600 and 620 °C. The results are summarized in Section 3.5. and are recommended to be used for the modeling of salt composition evolution in any solar salt-based system operating under similar conditions.

To challenge the stabilization of solar salt with 200 ppm NO, a set of experiments at 620 °C was performed. As a reference, for solar salt without stabilization, the reaction chamber was purged with 100% N₂. Additionally, the mixing velocity was varied, and in another experiment, the effect of a pressurized system (1 bar overpressure) on the stabilization of solar salt at 620 °C was investigated. The data are summarized in Figure 5.

Temp. [°C]	P _{O2} [atm]	c _{NOx} [ppm]	$\frac{\begin{bmatrix} NO_2^- \end{bmatrix}}{\begin{bmatrix} NO_3^- \end{bmatrix}}$ $[mol \cdot mol^{-1}]$	ln(K ₁)	$\frac{[O^{2-}]}{[NO_2^-]}$ [mol·mol ⁻¹]	$\frac{[O^{2-}]}{h}$ [mol·h ⁻¹]	Source
600	0.2		$1.12 imes 10^{-1}$	-2.9955	-	-	Bonk [25] & Sötz [26]
	0.2	200 (NO)	$1.00 imes10^{-1}$	-3.1016	$6.56 imes10^{-3}$	-	Sötz [26]
	0.2	200 (NO)	$1.30 imes 10^{-1}$	-3.1756	$3.72 imes 10^{-3}$	-	This work
	0.2	200 (NO ₂)	$9.18 imes10^{-2}$	-3.1928	$1.90 imes 10^{-3}$	-	This work
	0.2	$200 (N_2 O)$	$8.85 imes 10^{-2}$	-3.2300	-	$1 imes 10^{-6}$	This work
	0.1	200 (NO)	$1.24 imes10^{-1}$	-3.2389	$4.99 imes10^{-3}$	-	This work
	0.05	200 (NO)	$1.87 imes10^{-1}$	-3.1743	$3.84 imes10^{-3}$	-	This work
620 _	0.2		$1.56 imes 10^{-1}$	-2.6624	-	-	Sötz et al. [26]
	0.2		$1.36 imes10^{-1}$	-2.8030	-	$2 imes 10^{-6}$	This work
	0.2	200 (NO)	$1.56 imes10^{-1}$	-2.6601	$7.40 imes10^{-3}$	-	Sötz et al. [26]
	0.2	200 (NO)	$1.30 imes10^{-1}$	-2.8448	$3.87 imes 10^{-3}$	-	This work
	0.2	200 (NO)	$1.22 imes 10^{-1}$	-2.9064	$4.10 imes10^{-3}$	-	This work
	0.2	200 (NO ₂)	$1.18 imes 10^{-1}$	-2.9390	$2.60 imes 10^{-3}$	-	This work
	Additional experimental design modifications						
	0	0	-	-	-	$8 imes 10^{-6}$	This work (pure N2)
	0.2	200 (NO)	$1.23 imes 10^{-1}$	-2.9037	-	$6 imes 10^{-7}$	This work ($\overline{1}$ bar rel.)
	0.2	200 (NO)	$1.28 imes10^{-1}$	-2.8639	-	$7 imes 10^{-7}$	This work (120 rpm)
	0.05	200 (NO)	$3.01 imes10^{-1}$	-2.6988	-	6×10^{-7}	This work (0 rpm)

Table 1. Equilibrium nitrite to nitrate ratios and extracted $\ln(K_1)$ values as well as oxide to nitrite ratios at 600 °C and 620 °C. Oxid ion formation rate (mol%/h) is given for experiments not in equilibrium.



Figure 5. Anion content over time of solar salt stored at 620 °C. Purge gas was pure nitrogen (red color), 20% O_2 (blue color), 20% O_2 200 ppm NO and 120 rpm mixing velocity (green color), 10% 100 ppm NO 1 bar overpressure (orange color), and 5% O_2 200 ppm and 0 rpm (purple color). Linear regression fit of the oxide ion formation severs as a guide to the eye with the respective slope (*m*).

The system purged with pure N_2 shows the continuous decomposition of nitrate and the formation of nitrite and oxide ions. Experiments purged with oxygen attain a stable nitrate and nitrite composition after 500 h. With 5% O_2 at 1200 h, fluctuations of the nitrate

and nitrite content are visible and originate from pressure built up in the chamber due to the clogging of a waste gas filter with salt powder. Despite the presence of nitrous gases in the gas stream, no stable oxide ion concentration was attained over the course of the different experiments. At 620 °C and 5% O₂ (200 ppm NO), oxide ion concentration increased over 3000 h. In the case of an accelerated mixing velocity (120 rpm), there was no significant difference in the nitrate–nitrite equilibrium compared to the reference (with identical purge gas) present (see Table 1), but the oxide ion composition did not reach a stable value within 1000 h.

Despite the fact that none of the experiments reached an oxide ion equilibrium, a close examination of the oxide ion formation in Figure 5 (bottom right) gives insights into the effect of the parameter variation. The equilibrium values for the nitrate, nitrite, and oxide ions of the experiment from Section 3.3. (Figure 3) at 620 °C (20% O₂, 200 ppm NO) are shown as dashed blue lines for comparison. At the start of the experiment, the oxide formation rates of NO purged experiments under atmospheric pressure (Figure 5, green and purple color; *t*: 0–75 h) are fast and close to those of the experiment purged with 20% oxygen (blue color). Hereafter, the rates decrease and are approximated with the linear regression fit. Interestingly, the pressurized experiment (orange color) did not show the same behavior but remained low and constant over 1000 h. In this case, the final oxide composition is close to the equilibrium composition of the reference (dotted blue line), which could indicate that the experiment was not long enough to reach a stable oxide ion composition.

The current data highlight the importance of proper gas phase management for the stabilization of solar salt at 620 °C. As shown in Figure 5, in addition to the temperature, the mixing velocity, the present pressure, and the specific overlaying gas, the atmosphere is crucial for the equilibration process. Thereby, the dominant factor for the oxide ion formation rate is the presence of nitrous gases rather than mixing velocity. Pressurizing the test rig seems to have had a positive effect on the stabilization of the molten salt because the oxide ion formation was immediately reduced to a low rate. These results could be explained by the equilibrium in Equation (2). Here, the oxide ion formation correlates with the emission of NO gas molecules, which in turn is suppressed if an external pressure, e.g., 1 bar overpressure, is applied, but further studies are necessary for final proof. Additionally, oxide formation rates with the same NO partial pressure are quite similar (Figure 5, bottom right: 6×10^{-6} mol%/h) and are not affected by the nitrite ion concentration. This finding agrees with the result of the previously mentioned study [28], where the oxide formation rate did not correlate with the nitrite concentration but with the temperature. In addition, in a similar way, the oxide ion equilibrium levels show a weak impact on the nitrite concentration (Figure 4). As already mentioned, it seems likely that reactions with oxide species and NO mainly take place at the liquid gas interface and should correlate with the surface to bulk ratio. Due to the 100 g scale of the experiments, the surface to bulk ratio is larger compared to a TES tank and even increases during the experiments from 12% to 25% due to sample extraction. Still, no significant effect of this change on the salt composition was found, probably because the mixing of the salt was sufficient to prevent any mass transport limitations. However, without mixing (Figure 5, purple color), oxide ion concentration increased for over 3000 h, which could indicate the presence of a mass transport limitation in the regeneration of oxide ions with nitrous gases. Especially at a larger scale, where the surface to bulk ratio becomes orders of magnitude smaller (e.g., in a TES tank), such mass transport effects could have an effect on the salt's stability.

3.5. Thermodynamic Evaluation

In the previous study [28], the equilibrium values of nitrate and nitrite at temperatures above 600 °C were postulated to be afflicted with a significant error because of oxide ion formation. It was mentioned that solar salt purged with NO gas counters this effect by the regeneration of decomposition products in the molten salt. To compare the thermodynamic data of different studies, a van't Hoff diagram is typically used, which consists of the natural

logarithm of the equilibrium constant (K_1) plotted against the inverse of the temperature. According to Equation (7), the slope of a linear regression of the temperature-dependent equilibrium constants allows for the extraction of Gibb's free energy (ΔG_R).

$$\ln K_1 = -\frac{\Delta G_R}{RT}; \text{ with } K_1 = \frac{[\text{NO}_2^-]}{[\text{NO}_3^-]} P_{\text{O}_2}^{0.5}$$
(7)

Figure 6 gives the nitrate–nitrite equilibrium data of several studies in comparison to the new set of data of this study (see Table 1) for 600 °C (0.00115 K⁻¹) to 620 °C (0.00112 K⁻¹). For completeness, all generated data are summarized in Table 1. For experiments where an oxide ion equilibrium was attained, the nitrite to oxide ion ratio is given. Further studies may relate this ratio to the oxide equilibrium constant (K_2) and NO_x partial pressure, according to Equation (8).

$$K_2 \sim \frac{\left\lfloor O^{2-} \right\rfloor}{\left[NO_2^- \right]^y} P_{NO_x}^y \tag{8}$$



Figure 6. van't Hoff plots of nitrate and nitrite equilibrium individual data points (column 4, Table 1) obtained in this work and shown in Figures 1–4, as well as literature data from Steinbrecher et al. 2021, 2023and Sötz et al. 2010, 2020, 2020a for comparison. Color code indicates oxygen partial pressure of the individual experiments. Reprinted/adapted with permission from Ref. [27] 2021, MDPI, [12] 2019, Elsevier B.V., [32] 2020 Elsevier B.V., [26], 2020, International Solar Energy Society, [28] 2023, Elsevier B.V.)

The rate of oxide formation for experiments without stable anion content over time is given in mol% per h.

The solid line in Figure 6 is reprinted from the literature data of Sötz et al. 2020 [32] and presents an upper boundary for the nitrate–nitrite equilibrium composition. This study was performed with 1 g scale sample volumes and uncontrolled salt decomposition, or more precisely, strong oxide ion formation. In a recent study [28], it was shown that above 600 °C, also at a 100 g scale, oxide ion formation leads to a shift of the equilibrium position to the nitrite side and higher values of $\ln(K_1)$ (Equation (7)). The dotted line is extrapolated from low-temperature data from another study by Sötz et al. 2019 [12] without measurable

amounts of oxide ions. This line is interpreted as the ideal nitrate-nitrite equilibrium composition, without the influence of oxide ion formation and without mass transport effects (at a mg sample scale). The entire dataset presented herewith (red symbols), which was performed in an experimental setup with a reduced corrosion impact, now, indeed, shows a significant shift towards lower values of $ln(K_1)$ compared to the published data with steel components (black symbols). Consequently, the present paper confirms that solar salt is more stable than previous studies suggested, and the reported reaction enthalpy $(\Delta H = 95 \text{ kJ/mol})$ and entropy ($\Delta S = 85 \text{ J/molK}$) published by Sötz [12] are also accurate for 600 and 620 °C. Another verification of this concept is given with the experiment performed at 620 °C and 20% oxygen (without NO). Here, the $ln(K_1)$ value is the second highest (-2.8030) of the study because oxide ion formation occurred unopposed. The experiment with the highest $ln(K_1)$ value of -2.6988 was performed without mixing at 5% oxygen and 200 ppm NO. Even though oxide formation was reduced due to the low concentration of oxygen and the eliminated stirrer, nitrite regeneration, the reverse direction of Equation (1), was probably limited by oxygen mass transport, which is known to have an impact on the reaction rate [11]. This result supports the theory that a molten solar salt system that suffers either from mass transport issues, oxide formation, or both will give $ln(K_1)$ values above the ideal equilibrium line (Figure 6, dotted black line).

The investigation carried out here leads to at least five major factors that determine the stability of solar salt at temperatures beyond 600 $^{\circ}$ C:

- Corrosion reactions lead to increased salt decomposition and reduce solar salt stability.
- Nitrogen gas has a subordinate role in the stabilization of solar salt.
- Nitrous gases' impact on salt stability increases from N₂O to NO to NO₂.
- At 600 °C, solar salt is stable over time when in contact with 200 ppm NO and an oxygen partial pressure of at least 0.05 atm.
- At 620 °C, the surface to volume ratio seems to become of increasing importance, and for stabilization, a higher concentration of NO_x gas is advisable.

The presented data are highly relevant for large-scale TES units as well as for any corrosion study performed at temperatures where oxide formation can be expected (e.g., 600 °C). Figure 6 can serve as a stability indicator for solar salt. More precisely, the nitratenitrite equilibrium data of this study are understood as the benchmark for a stable salt composition. It was shown that any deviation towards larger values of $ln(K_1)$ indicates the presence of congruent reactions. With this information, simple monitoring of the anion composition will give deep insight into the long-term behavior (e.g., stability, corrosivity) of any solar salt-based system.

4. Conclusions

One goal of this study was to obtain molten solar salt with stable oxide ion concentrations at 620 °C. By the successful practical exclusion of corrosion side reactions with metallic components, a solar salt equilibrium, in terms of a stable nitrite and oxide ion composition, was attained compared to previously published work. In addition, the fraction of the decomposition product in the equilibrium state at 620 °C was reduced by 16%, proving solar salt to be more stable than previously anticipated. Nitrogen gas was identified as having a subordinate role in the stabilization of molten salt and seemingly not taking part in a regeneration reaction. Concerning the different nitrous gas species, their positive impact on salt stability was found to increase in the order of N_2O to NO to NO₂. Mass transport limitations were not proven with either an increased mixing velocity or excess pressure. However, for static molten salt, indications were found that, at a larger scale, where the surface to bulk ratio becomes smaller, this effect might come into play. This is because regeneration reactions are thought to primarily occur at the liquid–gas interface, whereas decomposition is considered a bulk reaction. In summary, the combined set of data is significant for use in the development of high-temperature TES systems and molten salt heat transfer applications, where parameters such as surface to bulk ratio and mass transport change substantially. With this study, we deliver the first extended set of solar salt

equilibrium data that are inevitably required in the future to understand and quantify the corrosiveness of molten salt under certain atmospheric conditions. With this knowledge, the operation of a solar salt-based TES unit at temperatures above 600 °C is realizable if the salt and gas phase compositions are monitored and controlled carefully.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/en16145241/s1, Figure S1: Blank experiment in the autoclave test rig at 620 °C without molten salt, purged with 20% O₂ and different concentrations of NO₂ (left) and NO (right). NO_x (cNO + cNO₂) concentration measured from the exhaust gas versus the input gas concentration; Figure S2: Concentration over time of NO and NO₂ in the exhaust gas of the purged reaction chamber containing molten solar salt. Experiment purged with 200 ppm NO₂, 20% O₂ (left) and 100% N₂ purged for the first 100 h, subsequently switched to purge gas with 200 ppm NO, 20% O₂ (100–1000 h; right).

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References

- 1. Bauer, T.; Odenthal, C.; Bonk, A. Molten Salt Storage for Power Generation. Chem. Ing. Tech. 2021, 93, 534–546. [CrossRef]
- Tracey, T.R. Conceptual Design of Advanced Central Receiver Power System; Final Report; Martin Marietta Corp.: Denver, CO, USA, 1978.
- Pacheco, J.E.; Bradshaw, R.W.; Dawson, D.B.; De la Rosa, W.; Gilbert, R.; Goods, S.H. Final Test and Evaluation Results from the Solar Two Project; SAND2002-0120; Sandia National Laboratories (SNL-NM): Albuquerque, NM, USA; Sandia National Laboratories (SNL-CA): Livermore, CA, USA, 2002.
- Bauer, T.; Pfleger, N.; Laing, D.; Steinmann, W.-D.; Eck, M.; Kaesche, S. 20—High-Temperature Molten Salts for Solar Power Application. In *Molten Salts Chemistry*; Lantelme, F., Groult, H., Eds.; Elsevier: Oxford, UK, 2013; pp. 415–438.
- Durth, M.; Prieto, C.; Rodriguez-Sanchez, A.; Patino-Rodriguez, D.; Cabeza, L.F. Effects of sodium nitrate concentration on thermophysical properties of solar salts and on the thermal energy storage cost. *Sol. Energy* 2019, *182*, 57–63. [CrossRef]
- Yang, C.; Wei, X.; Wang, W.; Lin, Z.; Ding, J.; Wang, Y.; Yang, J. NO_x emissions and the component changes of ternary molten nitrate salts in thermal energy storage process. *Appl. Energy* 2016, 184, 346–352. [CrossRef]
- Wei, X.; Yang, C.; Lu, J.; Wang, W.; Ding, J. The mechanism of NO_x emissions from binary molten nitrate salts contacting nickel base alloy in thermal energy storage process. *Appl. Energy* 2017, 207, 265–273. [CrossRef]
- Wei, X.L.; Wang, Y.; Peng, Q.; Yang, J.P.; Yang, X.X.; Ding, J. NO_x emissions and NO₂⁻ formation in thermal energy storage process of binary molten nitrate salts. *Energy* 2014, 74, 215–221. [CrossRef]
- 9. Wright, S.; Tran, T.; Chen, C.; Olivares, R.I.; Sun, S. Thermal stability of potassium and sodium nitrate molten salt mixtures above 500 °C. In Proceedings of the Ninth International Conference on Molten Slags, Fluxes and Salts, Beijing, China, 27–30 May 2012.
- Bradshaw, R.W.; Siegel, N.P. Molten nitrate salt development for thermal energy storage in parabolic trough solar power systems. In Proceedings of the ASME 2008 2nd International Conference on Energy Sustainability Collocated with the Heat Transfer, Fluids Engineering, and 3rd Energy Nanotechnology Conferences, American Society of Mechanical Engineers, Jacksonville, FL, USA, 10–14 August 2008; pp. 631–637.
- 11. Nissen, D.A.; Meeker, D.E. Nitrate/nitrite chemistry in sodium nitrate-potassium nitrate melts. *Inorg. Chem.* **1983**, *22*, 716–721. [CrossRef]
- 12. Sötz, V.A.; Bonk, A.; Forstner, J.; Bauer, T. Microkinetics of the reaction NO₃⁻ ≓ NO₂⁻ + 0.5 O₂ in molten sodium nitrate and potassium nitrate salt. *Thermochim. Acta* **2019**, *678*, 178301. [CrossRef]

- 13. Abe, O.; Utsunomiya, T.; Hoshino, Y. Acid—Base and redox reactions in fused sodium nitrite. *Thermochim. Acta* **1984**, *74*, 131–141. [CrossRef]
- 14. Stern, K.H. High temperature properties and decomposition of inorganic salts part 3, nitrates and nitrites. *J. Phys. Chem. Ref. Data* **1972**, *1*, 747–772. [CrossRef]
- Xianwei, H.; Yue, L.; Zongxin, Y.; Bingliang, G.; Zhongning, S.; Zhaowen, W. Thermal stability of sodium nitrate–sodium nitrite melts: A Raman spectra study. *Spectrosc. Lett.* 2018, *51*, 350–355. [CrossRef]
- 16. Laue, W.; Thiemann, M.; Scheibler, E.; Wiegand, K.W. Nitrates and nitrites. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2000.
- 17. Tsukahara, H.; Ishida, T.; Mayumi, M. Gas-phase oxidation of nitric oxide: Chemical kinetics and rate constant. *Nitric Oxide* **1999**, *3*, 191–198. [CrossRef]
- Olivares, R.I. The thermal stability of molten nitrite/nitrates salt for solar thermal energy storage in different atmospheres. *Sol. Energy* 2012, *86*, 2576–2583. [CrossRef]
- Villada, C.; Bonk, A.; Bauer, T.; Bolivar, F. High-temperature stability of nitrate/nitrite molten salt mixtures under different atmospheres. *Appl. Energy* 2018, 226, 107–115. [CrossRef]
- Bauer, T.; Pfleger, N.; Breidenbach, N.; Eck, M.; Laing, D.; Kaesche, S. Material aspects of Solar Salt for sensible heat storage. *Appl. Energy* 2013, 111, 1114–1119. [CrossRef]
- Bonk, A.; Braun, M.; Hanke, A.; Forstner, J.; Rückle, D.; Kaesche, S.; Sötz, V.A.; Bauer, T. Influence of Different Atmospheres on Molten Salt Chemistry and Its Effect on Steel Corrosion; SolarPACES; AIP Publishing: Santigo, Chile, 2017; p. 090003.
- Summers, K.; Chidambaram, D. Corrosion in Molten Salts for Solar Thermal Power. *Electrochem. Soc. Interface* 2021, 30, 63–66. [CrossRef]
- 23. Fernandez, A.G.; Cabeza, L.F. Molten salt corrosion mechanisms of nitrate based thermal energy storage materials for concentrated solar power plants: A review. *Sol. Energy Mater. Sol. Cells* **2019**, *194*, 160–165. [CrossRef]
- 24. Federsel, K.; Wortmann, J.; Ladenberger, M. High-temperature and corrosion behavior of nitrate nitrite molten salt mixtures regarding their application in concentrating solar power plants. *Energy Procedia* **2015**, *69*, 618–625. [CrossRef]
- 25. Bonk, A.; Braun, M.; Sotz, V.A.; Bauer, T. Solar Salt—Pushing an old material for energy storage to a new limit. *Appl. Energy* **2020**, 262, 114535. [CrossRef]
- 26. Sötz, V.A.; Bonk, A.; Steinbrecher, J.; Bauer, T. Defined purge gas composition stabilizes molten nitrate salt—Experimental prove and thermodynamic calculations. *Sol. Energy* 2020, 211, 453–462. [CrossRef]
- Steinbrecher, J.; Bonk, A.; Sötz, V.A.; Bauer, T. Investigation of Regeneration Mechanisms of Aged Solar Salt. *Materials* 2021, 14, 5664. [CrossRef] [PubMed]
- Steinbrecher, J.; Hanke, A.; Braun, M.; Bauer, T.; Bonk, A. Stabilization of Solar Salt at 650 °C—Thermodynamics and practical implications for thermal energy storage systems. *Sol. Energy Mater. Sol. Cells* 2023, 258, 112411. [CrossRef]
- 29. Bonk, A.; Rückle, D.; Kaesche, S.; Braun, M.; Bauer, T. Impact of Solar Salt aging on corrosion of martensitic and austenitic steel for concentrating solar power plants. *Sol. Energy Mater. Sol. Cells* **2019**, 203, 110162. [CrossRef]
- 30. White, S.H.; Twardoch, U.M. Study of the Interactions of Molten Sodium Nitrate-Potassium Nitrate 50 mol% Mixture with Water Vapor and Carbon Dioxide in Air; Final report; Sandia National Labs.: Livermore, CA, USA; EIC Labs., Inc.: Newton, MA, USA, 1981.
- 31. Tomkins, R.P.T.; Bansal, N.P. (Eds.) Gases in Molten Salts; Elsevier: Morristown, NJ, USA, 1991.
- Sötz, V.A.; Bonk, A.; Bauer, T. With a view to elevated operating temperatures in thermal energy storage—Reaction chemistry of Solar Salt up to 630 °C. Sol. Energy Mater. Sol. Cells 2020, 212, 110577. [CrossRef]

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