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Thermodynamic Feasibility Analysis of a Novel Water-Splitting Cycle

Author
Hennessy, Brian Philip

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Thermodynamic Feasibility Analysis of a Novel Water-Splitting Cycle

A thesis submitted in partial satisfaction

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in Chemical Engineering

by

Brian Philip Hennessy

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ABSTRACT OF THE THESIS

Thermodynamic Feasibility Analysis

of a Novel Water-Splitting Cycle

by

Brian Philip Hennessy

Master of Science in Chemical Engineering

University of California, Los Angeles, 2014

Professor Vasilios I. Manousiouthakis, Chair

This paper analyzes the thermodynamic feasibility of three reactions, one undesirable side reaction, and a flash separation for a water-splitting cycle. The thermodynamic feasibility of each reaction was analyzed using both an equilibrium constant based approach and through solution of the associated Gibbs free energy minimization problem. The thermodynamic feasibility of each reaction was determined at a variety of feed conditions, temperatures, and pressures. Future research will be conducted to determine optimal conditions at which to run the cycle to produce pure hydrogen and oxygen efficiently.

The thesis of Brian Philip Hennessy is approved.

James F. Davis

Selim M. Senkan

Vasilios I. Manousiouthakis, Committee Chair

University of California, Los Angeles

2014

DEDICATION

I would like to dedicate this work to my parents whose support throughout my life has allowed me to reach where I am today.

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a_i	number of atoms of element i in the system
$C_{p_j}^{(k)}$	constant pressure heat capacity of species j in phase k
$\hat{f}_j^{(k)}$	fugacity of species j
$f_j^{o(k)}$	reference fugacity of species j
F	flow rate of inlet to flash separator
G	total Gibbs free energy for all phases
$G^{(k)}$	total Gibbs free energy for phase k
$G_j^{(k)}$	Gibbs free energy for species j in phase k
$G_j^{o(k)}$	standard state molar Gibbs free energy of species j in phase k
$\Delta G_{f_j}^{(k)}$	Gibbs free energy of formation of species j in phase k
ΔG_r^o	Gibbs free energy of reaction r
$\Delta H_{f_j}^{o(k)}$	standard state enthalpy of formation for species j in phase k
ΔH_j^{fus}	enthalpy of fusion of species j
ΔH_j^{vap}	enthalpy of vaporization of species j
K_r	equilibrium constant for reaction r
L	flow rate of liquid stream outlet from flash separator
$\mu_j^{(k)}$	chemical potential of species j in phase k
$n^{(k)}$	total moles in phase k
$n_j^{(k)}$	moles of component j in phase k

$n_j^{0(k)}$	initial moles of component j in phase k
NC	number of components (species) in the system
NE	number of elements in the system
NP	number of phases in the system
P	pressure of the system
P^o	reference pressure
P_j	partial pressure of species j
R	ideal gas constant
$\Delta S_{f_j}^{o(k)}$	standard state entropy of formation for species j in phase k
T	temperature of the system
T_j^{fus}	melting point of species j at standard pressure
T_j^{vap}	boiling point of species j at standard pressure
ν_j	stoichiometric coefficient for species j
ν_{ij}	stoichiometric coefficient quantifying number of atoms of element i in a molecule of component j
V	flow rate of vapor stream outlet from flash separator
$x_j^{(k)}$	mole fraction of species j in phase k
x_j	liquid phase mole fraction of species j
y_j	vapor phase mole fraction of species j
z_j	mole fraction of species j in inlet to flash separator
γ_j	activity coefficient of species j in the liquid phase

$\hat{\phi}_j$	fugacity coefficient of species j in the gas phase
ξ_r	extent of reaction r

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1. Introduction

In recent years, society has become more aware of the environmental consequences of, such energy consuming human activities as, commuting, traveling, shipping, and vehicular transportation. Since the last century, fossil fuels have been used as the main energy source for these activities, [1]; however, their use has been associated with the global climate change phenomenon, [2], due to the emissions of greenhouse effect gases resulting from vehicles using such fuels. In addition, the use of fossil fuels has a limited horizon, as they are non-renewable resources, [1], and energy insecurity implications, given their concentration in unstable parts of the world. Along with the oil crisis of 1973 and the recent one in the late 2000's, the aforesaid reasons have pushed the development of renewable energy sources as an answer to tackle the present energy challenges. One such renewable energy resource is the Sun. Concentrated Solar Power (CSP) technologies allow the exploitation of the sun's energy to produce electricity or to power high temperature processes generating fuels and other chemicals, [3]. An appealing fuel candidate, that can replace fossil fuels, is hydrogen, which can be efficiently converted to energy in fuel cells, [3]. Hydrogen is currently mass produced largely from natural gas, for applications such as petroleum refining and ammonia production, [2, 3], as well as welding, metal fabrication, and other industrial processes [2]. Research and development has also been carried out for the development of new processes to mass produce hydrogen for fueling purposes, [4−7]. Hydrogen produced from fossil fuel based energy resources is often characterized as “black”, and is not considered a renewable fuel. It is thus highly desirable that hydrogen be produced via CSP technologies, since CSP produced hydrogen would become a sustainable, clean, and economically appealing fuel, [1], [3], and thus be characterized as “green”.

A primary route for the renewable production of hydrogen is water splitting. The separation of water into its constituents, hydrogen and oxygen, can be performed by different methods. One water splitting method is through electrolysis, where the electricity required could come from green energy sources, such as CSP. The disadvantage of this production method is its high energy cost, [8]. Another water splitting method is through the use of multiple reactions, each running at different temperatures, constituting so-called thermochemical cycles. The temperatures required for these processes are lower than those required for the thermal decomposition of water, and can be readily provided by CSP technology. The production of hydrogen through CSP thermochemical cycles has been demonstrated, [1, 9 −11], especially in sunbelt regions, [11, 12], and represents a means of transportability and long-term storage capability of solar energy, [9, 10, 13].

According to [8], which provides a concise chronology of the development of thermochemical cycles, they were first introduced, for hydrogen production, by [14, 15] in the 1960's. Since then, more than 100 different cycles have been studied, [16], along with analyses of the general thermodynamics for such processes, [17, 18]. However, the considered energy sources at that time were nuclear reactors, with a temperature limit of 1000 ^{o}C, [19]; although, replacing nuclear energy by solar energy to power the hydrogen thermochemical cycles was researched in the 1970's, [20 −22], this research activity was halted, until more recently in the early 2000's, [10, 23].

Water-splitting thermochemical cycles (WSTCs) for hydrogen production can be divided into three types: direct, two-step, and multi-step. The direct or one-step WSTC, also known as thermolysis, is an endothermic reaction that dissociates water into gaseous hydrogen and oxygen; furthermore, the temperatures required for this process are reported to be 2000 ^{o}C (2273.15 K),

by [11, 13], 2226.85 ^{o}C to 2726.85 ^{o}C (2500 K to 3000 K) by [24], and 2526.85 ^{o}C (2800 K) by [1, 25]. Direct WSTC has three main disadvantages: low yields, difficult oxygen, hydrogen separation process, and expensive reactor materials. For the low hydrogen yield, [25] states that carrying out thermolysis at 2526.85 ^{o}C (2800 K) leads only to 17% hydrogen yield at 0.01 bar. Then, the *in situ* separation of hydrogen and oxygen, to avoid their recombination, is a technological drawback as stated by [2, 8, 13, 25]. Finally, the reactor to run direct WSTC requires extremely exotic materials, [2], to be able to run the reaction at the high temperatures previously mentioned, [13]. Now, the two-step WSTC implements endothermic and exothermic reactions to dissociate water at temperatures lower than direct WSTC, which vary depending on the chemical species used from 1726.85 ^{o}C to 2226.85 ^{o}C (2000 K to 2500 K) by [2] and above 1300 ^{o}C (1573.15 K) by [1, 9]. Two-step WSTCs typically use metal oxides that undergo redox reactions to produce the hydrogen and oxygen from water, [10, 11]. The first step is an endothermic reduction of the oxide, also known as activation step, where heat is required to be supplied to carry out the reaction; then, the second step, or hydrolysis, is an exothermic oxidation of the reduced oxide which by reacting with water, in steam form, generates hydrogen and regenerates the initial oxide, [2, 9, 26], where the temperature for hydrolysis has been reported to be below 1000 ^{o}C (1273.15 K) by [1], below 799.85 ^{o}C (1073 K) by [2], and 500 ^{o}C to 800 ^{o}C (773.15 K to 1073.15 K) by [8]. According to [3, 8], a WSTC for hydrogen production, using solar energy as the energy source, was first proposed by [26] using the redox system Fe_3O_4/FeO. This was followed up by multiple other research teams that developed two-step cycles, with different redox pairs, such as [11, 24, 27 −34]. Lastly, a multi-step WSTC typically consists of a main endothermic reaction, followed by a series of reactions, either endothermic or exothermic, that output hydrogen and oxygen while regenerating the chemical species used in the

first endothermic step. The highest temperature reported for multi-step WSTCs is 1266.85 ^{o}C (1500 K), [2]. The disadvantage of multi-step WSTCs is that incorporating more reaction steps can potentially lead to higher capital costs and lower thermal efficiencies, [2]. Examples of these cycles are the Westinghouse cycle [35], the sulphur iodine cycle [36] and the methanol-sulphuric acid water splitting cycle [37].

As stated before, most of the current research on WSTCs has been done considering CSP technology as the energy source for the highly endothermic step of the process as reported by [9, 38, 39] and [8], based on [40, 41], stating that temperatures of 2000 ^{o}C (2273.15 K) can be achieved, and [10] reporting that current developments in solar optics lead to CSP technology reaching temperatures of 1726.85 ^{o}C (2000 K) for solar-to-thermal conversion. The aim for any CSP WSTC is to have the maximum temperature of the cycle at a feasible and cost effective level, while minimizing the number of reaction steps, [2].

1.1. Proposed Thermochemical Cycle Description

In this work, a novel thermochemical water splitting cycle for the production of hydrogen and oxygen from water is studied; particularly, the thermodynamic feasibility of the chemical reactions involved in the cycle are analyzed on an individual basis, in order to provide the operating conditions for each reaction. The proposed cycle is categorized as a three-step cycle that is based on the thermal decomposition of sodium carbonate $\left(Na_2CO_3\right)$ at temperatures higher than 1131.25 K (melting point of sodium carbonate). The chemical species involved in the cycle are: water $\left(H_2O\right)$, oxygen $\left(O_2\right)$, hydrogen $\left(H_2\right)$, sodium $\left(Na\right)$, sodium carbonate $\left(Na_2CO_3\right)$, sodium hydroxide $\left(NaOH\right)$, and carbon dioxide $\left(CO_2\right)$. The chemical reactions of the cycle are:

$$2Na_2CO_{3(\ell)} \overset{K_{R1}(T)}{\rightleftarrows} 4Na_{(g)} + 2CO_{2(g)} + O_{2(g)} \tag{R1}$$

$$4Na_{(l)} + 4H_2O_{(g)} \overset{K_{R2}(T)}{\rightleftarrows} 4NaOH_{(l)} + 2H_{2(g)} \tag{R2}$$

$$4NaOH_{(\ell)} + 2CO_{2(g)} \overset{K_{R3}(T)}{\rightleftarrows} 2Na_2CO_{3(\ell)} + 2H_2O_{(g)} \tag{R3}$$

which lead to the overall water decomposition reaction:

$$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{R4}$$

Next, a brief description of the proposed cycle is provided. Figure 1 illustrates a schematic diagram of the cycle's unit operations and their interconnections, illustrating that only water is fed into the cycle while hydrogen, oxygen, and water are the outputs. First, Reactor 1 is fed with an inert gas, such as He or Ar, and Na_2CO_3 which undergoes thermal decomposition at temperatures equal to and above its melting point. The heat required for this endothermic reaction can be supplied by many different means. If the heat source is concentrated solar power, then the proposed cycle is a renewable hydrogen (and oxygen) production process, and the produced hydrogen is "green". As seen in reaction (R1), Na_2CO_3 decomposes into three gaseous products: Na, O_2, and CO_2. The operating conditions at which these products are obtained from reaction (R1) are riddled with discrepancies in the literature. Additionally, a potential reaction between Na and O_2 could also take place, leading to the formation of sodium oxide, as follows:

$$4Na_{(g)} + O_{2(g)} \overset{K_{R5}(T)}{\rightleftarrows} 2Na_2O_{(s\,or\,l)} \tag{R5}$$

Then, provided reaction (R1) is carried out, without reaction (R5) proceeding, the gaseous products of the sodium carbonate decomposition are cooled down to a temperature level below the boiling point of sodium so as to liquefy the sodium, and are then sent to a vapor-liquid

equilibrium flash unit in order to separate the liquid Na from the gaseous O_2, CO_2, and Ar. Next, the liquid Na is directed to Reactor 2 where it is reacted with excess H_2O in steam form, as shown in reaction (R2), while the remaining O_2, CO_2, and Ar stream is sent to Reactor 3. The steam excess in Reactor 2 serves to control this highly exothermic reaction producing H_2 and liquid $NaOH$. The hydrogen is readily separated as an output of the cycle while the remaining liquid $NaOH$ is directed towards Reactor 3 where it reacts exothermically with the O_2, CO_2, and Ar stream. The Na_2CO_3 regenerated in reaction (R3) is separated from the gaseous O_2, H_2O, Ar mixture, and is fed into Reactor 1 to start over the process of thermal decomposition. The O_2, H_2O, Ar mixture is cooled down, so as to liquefy the H_2O. The resulting two phase mixture is then separated in a vapor liquid equilibrium flash, producing a gaseous O_2, Ar mixture, and liquid H_2O product, which can be externally recycled to the cycle's H_2O feed. The gaseous O_2, Ar mixture is then fed into another separator (e.g. pressure swing adsorber), to yield two products: Ar noble gas that is recycled to Reactor 1, and pure O_2 which becomes the cycle's pure O_2 product.

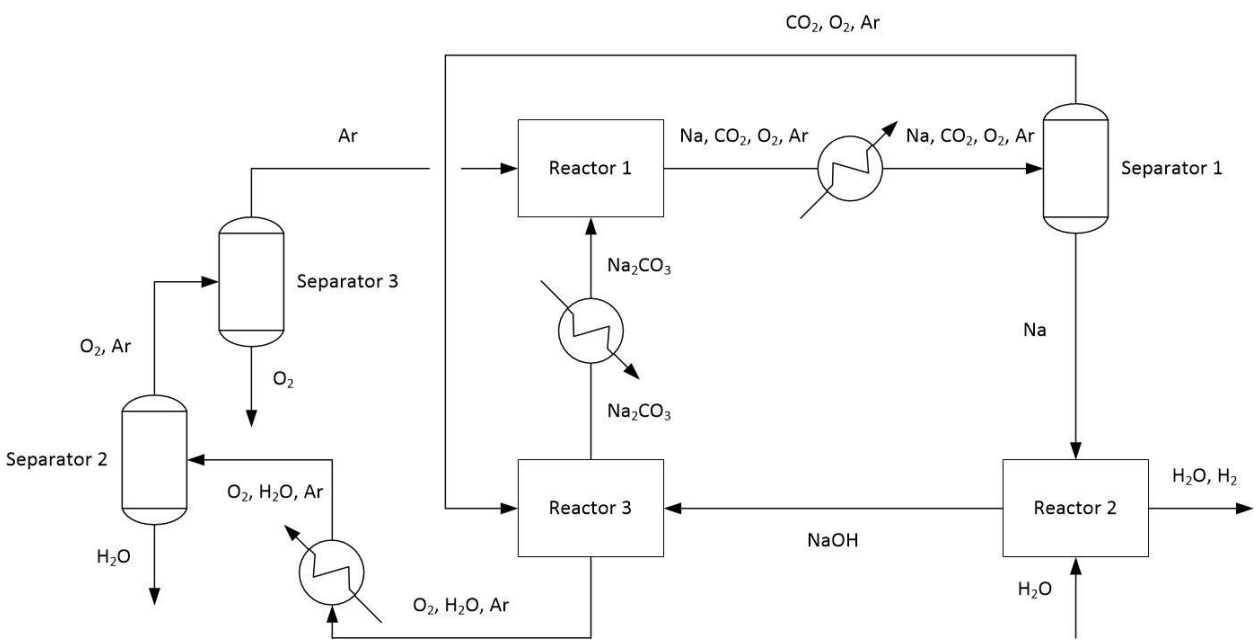

Figure 1 - Basic schematic of the proposed sodium carbonate-based WSTC

Although the above reactions have been studied and utilized in different fields, they have not been used together as intended in the above cycle. Therefore, the cycle's operating conditions such as temperature, pressure, gas composition, dilution (use of inert sweep gas) for the reactions have not been determined. Thus the aim of this work is to establish the theoretical thermodynamic feasibility of the cycle's reactions through rigorous reaction equilibrium calculations, and also through the use of the Gibbs free energy minimization method. As a result, this work will provide the aforementioned operating condition ranges over which the reactions are feasible for each unit operation. Additionally, it will be shown that the potential occurrence of reaction (R5) is negligible under the considered conditions, and therefore (R5) should not be considered as a reaction taking place in the cycle.

2. Conceptual Framework and Solution Approach

2.1. Thermodynamic Data Literature Review

In this work, the Gibbs free energy of formation was used both for calculation of the equilibrium constant for each of the reactions and the Gibbs minimization problem. The Gibbs free energy of each species was calculated using the following method, [42] – p. 491-4:

1. Start with the standard Gibbs free energy of formation for the species in its phase at standards conditions.
2. If the species is not already in the correct phase, integrate the heat capacity from standard temperature to its melting or boiling temperature, which will become the new "current temperature", otherwise proceed to step 6 and take the standard temperature to be the "current temperature."
3. Use the enthalpy of formation to transition phases.
4. If the species is still not in the correct phase, integrate the heat capacity from the "current temperature" to the next transition temperature, which will become the new "current temperature."
5. Repeat Steps 3 and 4 until the species is in the correct phase.
6. If the species is in the correct phase, integrate the heat capacity from the "current temperature" to the reaction temperature.

Equations (1) through (9) show the Gibbs free energy calculation using all standard and reaction phases.

Equation (1) gives the formula for the calculation of Gibbs free energy for a species that is a solid in its standard state and is also a solid at the reaction conditions.

$$G_j^{(s)}(T) = \left(\Delta H_{f_j}^{o(s)}\left(T^o\right) + \int_{T^o}^{T} C_{p_j}^{(s)} dT\right) - T\left(\Delta S_{f_j}^{o(s)}\left(T^o\right) + \int_{T^o}^{T} \frac{C_{p_j}^{(s)}}{T} dT\right) \quad (1)$$

Equation (2) gives the formula for the calculation of Gibbs free energy for a species that is a solid in its standard state and is a liquid at the reaction conditions.

$$G_j^{(l)}(T)=\left[\begin{array}{l}\left(\Delta H_{f_j}^{o(s)}\left(T^o\right)+\int_{T^o}^{T_j^{fus}} C_{p_j}^{(s)}dT+\Delta H_j^{fus}+\int_{T_j^{fus}}^{T} C_{p_j}^{(l)}dT\right)+\\ -T\left(\Delta S_{f_j}^{o(s)}\left(T^o\right)+\int_{T^o}^{T_j^{fus}} \frac{C_{p_j}^{(s)}}{T}dT+\frac{\Delta H_j^{fus}}{T_j^{fus}}+\int_{T_j^{fus}}^{T} \frac{C_{p_j}^{(l)}}{T}dT\right)\end{array}\right] \tag{2}$$

Equation (3) gives the formula for the calculation of Gibbs free energy for a species that is a solid in its standard state and is a gas at the reaction conditions.

$$G_j^{(g)}(T)=\left[\begin{array}{l}\left(\Delta H_{f_j}^{o(s)}\left(T^o\right)+\int_{T^o}^{T_j^{fus}} C_{p_j}^{(s)}dT+\Delta H_j^{fus}+\int_{T_j^{fus}}^{T_j^{vap}} C_{p_j}^{(l)}dT+\Delta H_j^{vap}+\int_{T_j^{vap}}^{T} C_{p_j}^{(g)}dT\right)+\\ -T\left(\Delta S_{f_j}^{o(s)}\left(T^o\right)+\int_{T^o}^{T_j^{fus}} \frac{C_{p_j}^{(s)}}{T}dT+\frac{\Delta H_j^{fus}}{T_j^{fus}}+\int_{T_j^{fus}}^{T_j^{vap}} \frac{C_{p_j}^{(l)}}{T}dT+\frac{\Delta H_j^{vap}}{T_j^{vap}}+\int_{T_j^{vap}}^{T} \frac{C_{p_j}^{(g)}}{T}dT\right)\end{array}\right] \tag{3}$$

Equation (4) gives the formula for the calculation of Gibbs free energy for a species that is a liquid in its standard state and is a solid at the reaction conditions.

$$G_j^{(s)}(T)=\left[\begin{array}{l}\left(\Delta H_{f_j}^{o(l)}\left(T^o\right)+\int_{T^o}^{T_j^{fus}} C_{p_j}^{(l)}dT+\Delta H_j^{fus}+\int_{T_j^{fus}}^{T} C_{p_j}^{(s)}dT\right)+\\ -T\left(\Delta S_{f_j}^{o(l)}\left(T^o\right)+\int_{T^o}^{T_j^{fus}} \frac{C_{p_j}^{(l)}}{T}dT+\frac{\Delta H_j^{fus}}{T_j^{fus}}+\int_{T_j^{fus}}^{T} \frac{C_{p_j}^{(s)}}{T}dT\right)\end{array}\right] \tag{4}$$

Equation (5) gives the formula for the calculation of Gibbs free energy for a species that is a liquid in its standard state and is also a liquid at the reaction conditions.

$$G_j^{(l)}(T)=\left(\Delta H_{f_j}^{o(l)}\left(T^o\right)+\int_{T^o}^{T} C_{p_j}^{(l)}dT\right)-T\left(\Delta S_{f_j}^{o(l)}\left(T^o\right)+\int_{T^o}^{T} \frac{C_{p_j}^{(l)}}{T}dT\right) \tag{5}$$

Equation (6) gives the formula for the calculation of Gibbs free energy for a species that is a liquid in its standard state and is a gas at the reaction conditions.

$$G_j^{(g)}(T)=\left[\begin{array}{l}\left(\Delta H_{f_j}^{o(l)}\left(T^o\right)+\int_{T^o}^{T_j^{vap}} C_{p_j}^{(l)}dT+\Delta H_j^{vap}+\int_{T_j^{vap}}^{T} C_{p_j}^{(g)}dT\right)+\\ -T\left(\Delta S_{f_j}^{o(l)}\left(T^o\right)+\int_{T^o}^{T_j^{vap}} \frac{C_{p_j}^{(l)}}{T}dT+\frac{\Delta H_j^{vap}}{T_j^{vap}}+\int_{T_j^{vap}}^{T} \frac{C_{p_j}^{(g)}}{T}dT\right)\end{array}\right] \tag{6}$$

Equation (7) gives the formula for the calculation of Gibbs free energy for a species that is a gas in its standard state and is a solid at the reaction conditions.

$$G_j^{(s)}(T)=\left[\begin{array}{l}\left(\Delta H_{f_j}^{o(g)}\left(T^o\right)+\int_{T^o}^{T_j^{vap}} C_{p_j}^{(g)}dT+\Delta H_j^{vap}+\int_{T_j^{vap}}^{T_j^{fus}} C_{p_j}^{(l)}dT+\Delta H_j^{fus}+\int_{T_j^{fus}}^{T} C_{p_j}^{(s)}dT\right)+\\ -T\left(\Delta S_{f_j}^{o(g)}\left(T^o\right)+\int_{T^o}^{T_j^{vap}} \frac{C_{p_j}^{(g)}}{T}dT+\frac{\Delta H_j^{vap}}{T_j^{vap}}+\int_{T_j^{vap}}^{T_j^{fus}} \frac{C_{p_j}^{(l)}}{T}dT+\frac{\Delta H_j^{fus}}{T_j^{fus}}+\int_{T_j^{fus}}^{T} \frac{C_{p_j}^{(s)}}{T}dT\right)\end{array}\right] \tag{7}$$

Equation (8) gives the formula for the calculation of Gibbs free energy for a species that is a gas in its standard state and is a liquid at the reaction conditions.

$$G_j^{(l)}(T)=\left[\begin{array}{l}\left(\Delta H_{f_j}^{o(g)}\left(T^o\right)+\int_{T^o}^{T_j^{vap}} C_{p_j}^{(g)}dT+\Delta H_j^{vap}+\int_{T_j^{vap}}^{T} C_{p_j}^{(l)}dT\right)+\\ -T\left(\Delta S_{f_j}^{o(g)}\left(T^o\right)+\int_{T^o}^{T_j^{vap}} \frac{C_{p_j}^{(g)}}{T}dT+\frac{\Delta H_j^{vap}}{T_j^{vap}}+\int_{T_j^{vap}}^{T} \frac{C_{p_j}^{(l)}}{T}dT\right)\end{array}\right] \tag{8}$$

Equation (9) gives the formula for the calculation of Gibbs free energy for a species that is a gas in its standard state and is a gas at the reaction conditions.

$$G_j^{(g)}(T)=\left(\Delta H_{f_j}^{o(g)}\left(T^o\right)+\int_{T^o}^{T} C_{p_j}^{(g)}dT\right)-T\left(\Delta S_{f_j}^{o(g)}\left(T^o\right)+\int_{T^o}^{T} \frac{C_{p_j}^{(g)}}{T}dT\right) \tag{9}$$

The Gibbs free energy of formation at the reaction temperature was then calculated by subtracting the value of the Gibbs free energy at the reaction temperature of the molecules corresponding to the constituent elements of each species in stoichiometric amounts, from the Gibbs free energy at the reaction temperature of the considered species. The values of these Gibbs free energies are calculated using the method described above. An example of the

calculation of the Gibbs free energy of formation at the reaction temperature T is given in equation (10) below:

$$\Delta G_{f_{H_2O}}^{(g)}(T) = G_{H_2O}^{(g)}(T) - G_{H_2}^{(g)}(T) - \frac{1}{2} G_{O_2}^{(g)}(T) \tag{10}$$

The Gibbs free energy of the various reactions in this paper was also calculated. This was done by adding the Gibbs free energies for the products, calculated using equations (1) though (9), multiplied by their stoichiometric coefficients and subtracting the Gibbs free energies for the reactants multiplied by their stoichiometric coefficients, as shown by equation (11).

$$\Delta G_r^o(T) = \sum_{products} \nu_j \left(G_j^{(k)}(T) \right) - \sum_{reactants} \nu_j \left(G_j^{(k)}(T) \right) \tag{11}$$

As an example, for the reaction $aA_{(\alpha)} + bB_{(\beta)} \rightleftarrows cC_{(\gamma)} + dD_{(\delta)}$, the Gibbs free energy of the reaction was calculated as shown by equation (12).

$$\Delta G_r^o(T) = c\left[G_C^{(\gamma)}(T) \right] + d\left[G_D^{(\delta)}(T) \right] - a\left[G_A^{(\alpha)}(T) \right] - b\left[G_B^{(\beta)}(T) \right] \tag{12}$$

Heat capacity data, to be used in the calculation of the Gibbs free energy, was gathered from multiple sources for this work. Coefficient data is presented in Table 2 in Appendix A from [43], [44], and [45] in the form:

$$C_p = A + B \cdot T + C \cdot T^2 + D \cdot T^3 + E \cdot T^4 + F \cdot T^5 + G \cdot T^6 + \frac{H}{T^2} \tag{13}$$

Data from [43] was used in the calculations since it is the most up-to-date information, it contained information for all species, and it gave results very similar to that given by the other sources for species for which heat capacity data were available from more than one source.

2.2. Sodium Carbonate Decomposition Literature Review

Sodium carbonate decomposition data from the literature vary. [46] in 1905 presented data suggesting that carbonate decomposition begins at about 700 ^{o}C (973 K) and the carbonate decomposition pressure does not exceed 1 Torr until about 950 ^{o}C (1223 K). In their experimental apparatus, [47] employed a loosely fitting, thin-walled, transparent quartz sleeve which was open at both ends to protect the reactor against the fluxing action of hot alkali. This low cost protective sleeve is expendable and can be replaced as needed. Such a sleeve was also used by [48] in their study of carbon detection in sodium metal, along with a quartz wool plug placed just downstream of the sleeve but still within the hot zone of the furnace to prevent sodium oxide migration into the cooler end zone where it might recombine with CO_2. A loose quartz wool plug was also used in the downstream end of the protective sleeve. The sample boat was also made of quartz. These same authors identify 1100 ^{o}C as a temperature at which they can attain complete carbon recovery (in the form of CO_2 dry-ice) from sodium carbonate. This is significantly inconsistent with work by [49], who in 1908 identified 1350 ^{o}C as the sodium carbonate's decomposition temperature, namely the temperature at which the decomposition pressure of the substance is one atmosphere. There is also a discrepancy between these values and those from [46] and [47] by about 200 ^{o}C. [50] in 2001 used thermogravimetric analysis (with argon sweeping gas and a heating rate of 10 ^{o}C per minute) to show that the continuous removal of CO_2 leads to appreciable decomposition of Na_2CO_3 starting at about 1120 ^{o}C, and that at 1200 ^{o}C 20% of the carbonate is decomposed. If the reactor is closed (no gaseous product removal), only 9% of the initial carbonate was decomposed at 1200 ^{o}C. In these same experiments [50] Nickel and Platinum crucibles were used to carry out reactions of sodium

carbonate and sodium hydroxide at temperatures ranging from 1000 ^{o}C up to 1200 ^{o}C. In 2001, [51] also studied carbonate decomposition using DTA and DSC. They found a loss of 26% at 1200 ^{o}C when using a heating rate of 10 ^{o}C per minute, a platinum crucible, and argon as the sweeping gas with a flow of 5 x 10^{-5} m^3/min; however, they did not specify the time lapsed for the reaction. Also, they suggested a two reaction mechanism for the decomposition (first, oxide formation, then, oxide decomposition) with reaction oxide formation being the rate limiting step. No kinetics for carbonate decomposition were identified.

[52] discussed the results of the kinetics of the thermal decomposition of sodium carbonate obtained by [53] and how they are supported by other researchers' findings. Two main conclusions were drawn by [53]:

1) The decomposition of sodium carbonate becomes appreciable only at temperatures above its melting point, which is 1127 K.
2) The decomposition mechanism takes place in two steps:

$$Na_2CO_{3(l)} \overset{K_{R6}(T)}{\rightleftarrows} Na_2O_{(dissolved)} + CO_{2(g)} \tag{R6}$$

$$Na_2O_{(dissolved)} \overset{K_{R7}(T)}{\rightleftarrows} 2Na_{(g)} + \frac{1}{2}O_{2(g)} \tag{R7}$$

Furthermore, [53] applied the transpiration method to measure the rate of decomposition of the sodium carbonate using different carrier gases such as helium, argon, and carbon dioxide; a discussion on the transpiration method and the carbonate decomposition vapor pressure is provided later and supports the idea of employing different inert gases for these tests. In these measurements, each sweep gas had different results: helium had no effect on the rate of decomposition of sodium carbonate, determined as loss of weight with time; carbon dioxide slowed down the decomposition rate when compared to that obtained by helium; finally, argon

produced a lower decomposition rate than that of helium as it is more viscous than helium. [53] performed the decomposition reaction in helium at 1173 K and measured the weight loss of the sodium carbonate melt versus time. It is shown that 90% of the sodium carbonate melt sample was lost during a five (5) hour period of time.

The data points of the experiment showed two different slopes: a *steep slope* from time zero to 2.5 hours and another slope closer to zero from 2.5 hours to 5 hours. Thus, [53] fitted the experimental data assuming the two step reaction mechanism shown above and that the first reaction step is first order while the second step is zero order; also, they assumed $K_1 > K_2$. The results of these measurements indicate that equilibrium is reached very rapidly and that the equilibrium concentration of sodium oxide in the melt is small; the former is in agreement with [54] who estimated the equilibrium concentration of sodium oxide at 1200 K to be approximately 0.45% by weight.

[54] considered a two-step reaction mechanism for the decomposition of sodium carbonate and provided an expression for the equilibrium constant of both reactions as a function of temperature. Equation (14) gives the equilibrium constant for reaction (R6) while equation (15) gives the equilibrium constant for reaction (R7), where K is dimensionless and T is in Kelvin.

$$\log K_{R6} = 6.4 - \frac{16600}{T} \tag{14}$$

$$\log K_{R7} = 14.7 - \frac{29900}{T} \tag{15}$$

[55] and [56] performed research on the vaporization of sodium oxide, and they found out, through theoretical calculations and experimental measurements, that when heating up sodium oxide in vacuum (Knudsen effusion experiment) it vaporizes by decomposition to the

gaseous elements with no substantive presence of a gaseous sodium oxide. The experimentally obtained equilibrium constants and corresponding temperatures and decomposition pressures of the sodium oxide decomposition reaction are compared to those obtained from [54] in Table 1.

Table 1 - Sodium oxide decomposition equilibrium constant, temperature, and pressure

Temperature (K)	Vaporization time in effusion cell (hours), [55]	Equilibrium constant K, [55]	Equilibrium constant K, [53]	Decomposition Pressure (Torr), [55]	Decomposition Pressure (Torr), [53]
1000	20.35	6.3096×10^{-16}	6.3096×10^{-16}	0.46	0.46
1250	0.37	6.0256×10^{-10}	1.2589×10^{-10}	6.99	9.90
1450	0.17	1.1722×10^{-6}	7.9433×10^{-8}	29.3	53.29

The temperatures shown in the above table are those measured in the [56] experiments. Furthermore, the reason of the differences between the values provided by the two sources might be the fact that, in calculating the reaction equilibrium constant, [54] did not consider the phase transition enthalpies of the sodium oxide and of the sodium. Based on the above information, it can be concluded that the sodium oxide decomposition is fast, which is consistent with [57] that in 1951 presented theoretical calculations demonstrating that at 1000 K, gaseous Na_2O is unstable and dissociates.

[58] described that, in the molten carbonate literature, the vapor pressure of an alkali carbonate is an indicator of the stability of the melt, which is considered as the irreversible loss of alkali species in a flowing gas environment. Then, these authors described the work by [59] on the characterization of high temperature vapor employing the transpiration method. The basic premise of the transpiration method is that a carrier gas sweeps the vapor species released from the molten alkali carbonate dissociation process, while weight measurements of the carbonate are taken as a function of time and a quantitative analysis of the species in the carrier gas is performed. Some important notes on this procedure, as they related to this project, are the fact

that the crucible where the molten alkali carbonate is heated is an alumina $\left(Al_2O_3\right)$ crucible; also, [59] suggested performing several runs with different flow rates of the carrier gas as well as the chemical species of the gas in order to estimate several vapor-liquid equilibria between the molten alkali carbonate and the possible chemical species in the dissociated vapor. This means that the choice of carrier gas flow rate and chemical nature of the gas can have an effect on which species are formed as the decomposition of the molten salt takes place. Finally, the transpiration method can take place in high pressure or vacuum.

2.3. Equilibrium Constant Method

In order to calculate the concentrations of the species of a particular reaction at equilibrium, it is required to first calculate the standard state molar Gibbs free energy at the particular temperature at which the reaction is to be carried out. Consider the following definitions from [60] – p. 442 regarding the standard states for the fugacity in gaseous and condensed phases:

Gases: the standard state is the pure gas at the reaction temperature and at a pressure such that the fugacity is one (1) atm of pressure. Setting the standard state fugacity $f_j^{o(g)} = 1$ has the advantage of making the activity numerically equal to the fugacity.

Liquids and solids: the standard state is the pure substance at the reaction temperature and at the pressure of one (1) atm.

Given the change in standard state molar Gibbs free energy for the reaction, as calculated using equation (11), the definition of the equilibrium constant, from [42] – p. 490, is:

$$K_r \triangleq \exp\left[\frac{-\Delta G_r^o}{RT}\right] \Leftrightarrow \ln K_r \triangleq \frac{-\Delta G_r^o}{RT} \tag{16}$$

Furthermore, the equilibrium constant for a reaction $aA_{(\alpha)} + bB_{(\beta)} \rightleftarrows cC_{(\gamma)} + dD_{(\delta)}$ can be written as:

$$K_r = \frac{\left(\frac{\hat{f}_C^{(\gamma)}}{f_C^{o(\gamma)}}\right)^c \left(\frac{\hat{f}_D^{(\delta)}}{f_D^{o(\delta)}}\right)^d}{\left(\frac{\hat{f}_A^{(\alpha)}}{f_A^{o(\alpha)}}\right)^a \left(\frac{\hat{f}_B^{(\beta)}}{f_B^{o(\beta)}}\right)^b} \tag{17}$$

Then, from [60] – p. 462-3, the fugacity ratio, $\left(\frac{\hat{f}_j^{(k)}}{f_j^{o(k)}}\right)$, of a pure condensed phase, assuming incompressibility, is close to unity except for very high pressures.

Now, consider the following definitions from [60] – p. 259, 456 for the fugacity coefficient and equilibrium constant respectively:

$$\hat{\phi}_i = \frac{\hat{f}_j}{P_j} \tag{18}$$

$$K_r = \prod \hat{f}_j^{\nu_j} = \prod \left(P_j \hat{\phi}_j\right)^{\nu_j} \tag{19}$$

Then, assuming $\hat{\phi}_j \cong 1$ for low to moderate pressures, implies that:

$$K_r = \prod P_j^{\nu_j} = \prod \left(P y_j\right)^{\nu_j} = P^{\Sigma \nu_j} \prod y_j^{\nu_j} = P^{\nu} \prod y_j^{\nu_j} \tag{20}$$

which allows expression of the equilibrium constant in terms of partial pressures or vapor mole fractions at equilibrium, with $\nu \triangleq \sum_i \nu_i$.

2.4. WSTC Reactions' Equilibrium Constant Calculations

The following assumptions are considered before calculating the equilibrium constants for reactions (R1)−(R3) and (R5): all sodium species are either a gas or a liquid, i.e. there is no coexistence of these species in both gas and liquid phases; no pressure dependence on heat

capacities since gases are treated as ideal gases and liquid/solid heat capacities are considered independent of pressure; the melting point of species has no pressure dependence. In addition, the following assumptions are made with regard to the calculation of the sodium carbonate and sodium oxide constant-pressure heat capacities: sodium carbonate is never considered to be a gas, and only considered to be a solid or liquid, since no information regarding a boiling point is available, nor heat of vaporization values; the latter also applies to sodium oxide which is only considered to be either a solid or a liquid.

Furthermore, with regard to reaction (R1), the normal boiling point of sodium is 1155.95 K at pressure equal to one (1) bar; therefore, the boiling point of sodium at pressures less than one (1) bar will be lower, and thus, the sodium will be in gaseous form even for the melting point of carbonate being 1131.25 K. Therefore, even at the melting point of sodium carbonate, which is 25 K lower than the boiling point of sodium, it is guaranteed that the sodium will be vapor as long as the pressure is appropriately lower than one (1) bar.

Now, consider reaction (R1) and define $n_{Na_2CO_3}^{0(l)}$ to be the initial moles of sodium carbonate, x_i to be the liquid mole fraction of species i, y_i to be the vapor mole fraction of species i, ξ_1 to be the extent of the reaction, and $\alpha = \frac{moles\, inert}{n_{Na_2CO_3}^{0(l)}}$ to be the molar feed ratio of an inert species (such as Ar) to Na_2CO_3. Then for reaction (R1) the following initial conditions hold:

$$\left\{\begin{array}{ll} v_{Na_2CO_3} = -2 & n^{0(l)}_{Na_2CO_3} = n^{0(l)}_{Na_2CO_3} \\ v_{Na} = 4 & n^{0(g)}_{Na} = 0 \cdot n^{0(l)}_{Na_2CO_3} \\ v_{CO_2} = 2 & n^{0(g)}_{CO_2} = 0 \cdot n^{0(l)}_{Na_2CO_3} \\ v_{O_2} = 1 & n^{0(g)}_{O_2} = 0 \cdot n^{0(l)}_{Na_2CO_3} \\ v_{Ar} = 0 & n^{0(g)}_{Ar} = \alpha n^{0(l)}_{Na_2CO_3} \\ \sum v_i = 5 & \end{array}\right\} \overset{n_j = n_j^0 + v_j \xi_1}{\Rightarrow} \left\{\begin{array}{l} n^{(l)}_{Na_2CO_3\,Na_2CO_3} = n^{0(l)}_{Na_2CO_3} - 2\xi_1 \\ n^{(g)}_{Na} = 0 \cdot n^{0(l)}_{Na_2CO_3} + 4\xi_1 \\ n^{(g)}_{CO_2} = 0 \cdot n^{0(l)}_{Na_2CO_3} + 2\xi_1 \\ n^{(g)}_{O_2} = 0 \cdot n^{0(l)}_{Na_2CO_3} + \xi_1 \\ n^{(g)}_{Ar} = \alpha n^{0(l)}_{Na_2CO_3} + 0 \cdot \xi_1 \\ n_{total} = (1+\alpha) n^{0(l)}_{Na_2CO_3} + 5\xi_1 \end{array}\right\} \tag{21}$$

When the reaction reaches equilibrium, the following relations must hold:

$$\left\{\begin{array}{ll} x_{Na_2CO_3} = 1 & y_{Na_2CO_3} = 0 \\ x_{Na} = 0 & y_{Na} = \dfrac{4\xi_1}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1} \\ x_{NCO_2} = 0 & y_{CO_2} = \dfrac{2\xi_1}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1} \\ x_{O_2} = 0 & y_{O_2} = \dfrac{\xi_1}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1} \\ x_{Ar} = 0 & y_{Ar} = \dfrac{\alpha n^{0(l)}_{Na_2CO_3}}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1} \\ n^{(l)} = n^{0(l)}_{Na_2CO_3} - 2\xi_1 & n^{(g)} = \alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1 \end{array}\right\} \tag{22}$$

where $\left\{\begin{array}{l} 1 = x_{Na_2CO_3} + x_{Na} + x_{CO_2} + x_{O_2} + x_{Ar} \\ 1 = y_{Na_2CO_3} + y_{Na} + y_{CO_2} + y_{O_2} + y_{Ar} \\ P = P_{Na_2CO_3} + P_{Na} + P_{CO_2} + P_{O_2} + P_{Ar} \end{array}\right\}$ and $0 \le \xi_1 \le \dfrac{n^{0(l)}_{Na_2CO_3}}{2}$. Then, the equilibrium constant is:

$$K_{R1}(T) = \frac{\left(\dfrac{\hat{f}^{(g)}_{Na}}{f^{o(g)}_{Na}}\right)^4 \left(\dfrac{\hat{f}^{(g)}_{CO_2}}{f^{o(g)}_{CO_2}}\right)^2 \left(\dfrac{\hat{f}^{(g)}_{O_2}}{f^{o(g)}_{O_2}}\right)}{\left(\dfrac{\hat{f}^{(l)}_{Na_2CO_3}}{f^{o(l)}_{Na_2CO_3}}\right)^2} = \frac{\left(\dfrac{y_{Na}\hat{\phi}_{Na}P}{P^{\circ}}\right)^4 \left(\dfrac{y_{CO_2}\hat{\phi}_{CO_2}P}{P^{\circ}}\right)^2 \left(\dfrac{y_{O_2}\hat{\phi}_{O_2}P}{P^{\circ}}\right)}{\left(x_{Na_2CO_3}\gamma_{Na_2CO_3}\right)^2} \tag{23}$$

Further simplification of equation (23) yields equation (24).

$$K_{R1}(T) = \frac{\left(y_{Na}\hat{\phi}_{Na}\right)^4 \left(y_{CO_2}\hat{\phi}_{CO_2}\right)^2 \left(y_{O_2}\hat{\phi}_{O_2}\right)}{\left(x_{Na_2CO_3}\gamma_{Na_2CO_3}\right)^2}\left(\frac{P}{P^\circ}\right)^7 \tag{24}$$

Assuming $P^\circ = 1bar$; $\hat{\phi}_i = 1 \quad \forall i = Na, CO_2, O_2$; $\gamma_{Na_2CO_3} = 1$, equation (24) reduces further to yield:

$$K_{R1}(T) = y_{Na}^4 y_{CO_2}^2 y_{O_2}\left(\frac{P}{P^\circ}\right)^7 \tag{25}$$

Substituting the expressions for the vapor mole fractions into the equilibrium constant give:

$$K_{R1}(T) = \left(\frac{4\xi_1}{\alpha n_{Na_2CO_3}^{0(l)} + 7\xi_1}\right)^4 \left(\frac{2\xi_1}{\alpha n_{Na_2CO_3}^{0(l)} + 7\xi_1}\right)^2 \left(\frac{\xi_1}{\alpha n_{Na_2CO_3}^{0(l)} + 7\xi_1}\right)\left(\frac{P}{P^\circ}\right)^7 \tag{26}$$

Defining carbonate conversion as $\zeta_1 \triangleq \frac{2\xi_1}{n_{Na_2CO_3}^{0(l)}}$, then yields equations (27) and (28):

$$K_{R1}(T) = 8\left(\frac{\zeta_1}{\alpha + 3.5\zeta_1}\right)^7 \left(\frac{P}{P^\circ}\right)^7 \qquad 0 \le \zeta_1 \le 1 \tag{27}$$

$$\zeta_1 = \begin{cases} \alpha\left(\left(\frac{8}{K_{R1}(T)}\right)^{\frac{1}{7}}\left(\frac{P}{P^\circ}\right)^1 - 3.5\right)^{-1} & if\ \frac{P}{P^\circ} > (\alpha + 3.5)\left(\frac{K_{R1}(T)}{8}\right)^{\frac{1}{7}} \\ 1 & if\ \frac{P}{P^\circ} \le (\alpha + 3.5)\left(\frac{K_{R1}(T)}{8}\right)^{\frac{1}{7}} \end{cases} \tag{28}$$

Consider next reaction (R2), with sodium as the limiting reactant, and define $n_{Na}^{0(l)}$ to be the initial moles of sodium, x_i to be the liquid mole fraction of species i, y_i to be the vapor mole fraction of species i, ξ_2 to be the extent of the reaction, and $\beta = \frac{n_{H_2O}^{0(g)}}{n_{Na}^{0(l)}} \ge 1$ to be the molar

feed ratio of H_2O (reactant in excess) to Na (limiting reactant). The initial conditions of this reaction are given by (29) and the equilibrium concentrations are given by (30),

$$\left\{\begin{array}{ll} v_{Na} = -4 & n_{Na}^{0(l)} = n_{Na}^{0(l)} \\ v_{H_2O} = -4 & n_{H_2O}^{0(g)} = \beta n_{Na}^{0(l)} \\ v_{NaOH} = 4 & n_{NaOH}^{0(l)} = 0 \cdot n_{Na}^{0(l)} \\ v_{H_2} = 2 & n_{H_2}^{0(g)} = 0 \cdot n_{Na}^{0(l)} \\ \sum v_i = -2 & \end{array}\right\} \overset{n_j = n_j^0 + v_j \xi_2}{\Rightarrow} \left\{\begin{array}{l} n_{Na}^{(l)} = n_{Na}^{0(l)} - 4\xi_2 \\ n_{H_2O}^{(l)} = \beta n_{Na}^{0(l)} - 4\xi_2 \\ n_{NaOH}^{(l)} = 0 \cdot n_{Na}^{0(l)} + 4\xi_2 \\ n_{H_2}^{(g)} = 0 \cdot n_{Na}^{0(l)} + 2\xi_2 \\ n_{total} = (1+\beta) n_{Na}^{0(l)} - 2\xi_2 \end{array}\right\} \tag{29}$$

$$\left\{\begin{array}{ll} x_{Na} = \dfrac{n_{Na}^{0(l)} - 4\xi_2}{n_{Na}^{0(l)}} & y_{Na} = 0 \\ x_{H_2O} = 0 & y_{H_2O} = \dfrac{\beta n_{Na}^{0(l)} - 4\xi_2}{\beta n_{Na}^{0(l)} - 2\xi_2} \\ x_{NaOH} = \dfrac{4\xi_2}{n_{Na}^{0(l)}} & y_{NaOH} = 0 \\ x_{H_2} = 0 & y_{H_2} = \dfrac{2\xi_2}{\beta n_{Na}^{0(l)} - 2\xi_2} \\ n^{(l)} = n_{Na}^{0(l)} & n^{(g)} = \beta n_{Na}^{0(l)} - 2\xi_2 \end{array}\right\} \tag{30}$$

where $\left\{\begin{array}{l} 1 = x_{Na} + x_{H_2O} + x_{NaOH} + x_{H_2} \\ 1 = y_{Na} + y_{H_2O} + y_{NaOH} + y_{H_2} \\ P = P_{Na} + P_{H_2O} + P_{NaOH} + P_{H_2} \end{array}\right\}$ and $0 \le \xi_2 \le \dfrac{n_{Na}^{0(l)}}{4}$. Then, the equilibrium constant is given by equation (31):

$$K_{R2}(T) = \frac{\left(\dfrac{\hat{f}_{NaOH}^{(l)}}{f_{NaOH}^{o(l)}}\right)^4 \left(\dfrac{\hat{f}_{H_2}^{(g)}}{f_{H_2}^{o(g)}}\right)^2}{\left(\dfrac{\hat{f}_{Na}^{(l)}}{f_{Na}^{o(l)}}\right)^4 \left(\dfrac{\hat{f}_{H_2O}^{(g)}}{f_{H_2O}^{o(g)}}\right)^4} = \frac{\left(x_{NaOH}\gamma_{NaOH}\right)^4 \left(\dfrac{y_{H_2}\hat{\phi}_{H_2}P}{P^\circ}\right)^2}{\left(x_{Na}\gamma_{Na}\right)^4 \left(\dfrac{y_{H_2O}\hat{\phi}_{H_2O}P}{P^\circ}\right)^4} \tag{31}$$

Further reduction of equation (31) yields:

$$K_{R2}(T) = \frac{\left(x_{NaOH}\gamma_{NaOH}\right)^4 \left(y_{H_2}\hat{\phi}_{H_2}\right)^2}{\left(x_{Na}\gamma_{Na}\right)^4 \left(y_{H_2O}\hat{\phi}_{H_2O}\right)^4} \left(\frac{P}{P^\circ}\right)^{-2} \tag{32}$$

Assuming $P^\circ = 1bar$; $\hat{\phi}_i = 1 \quad \forall i = H_2O, H_2$; $\gamma_i = 1 \quad \forall i = Na, NaOH$, this reduces further to:

$$K_{R2}(T) = \frac{x_{NaOH}^4 y_{H_2}^2}{x_{Na}^4 y_{H_2O}^4} \left(\frac{P}{P^\circ}\right)^{-2} \tag{33}$$

Substituting the expressions for the liquid and vapor mole fractions into the equilibrium constant give:

$$K_{R2}(T) = \frac{\left(\frac{4\xi_2}{n_{Na}^{0(l)}}\right)^4 \left(\frac{2\xi_2}{\beta n_{Na}^{0(l)} - 2\xi_2}\right)^2}{\left(\frac{n_{Na}^{0(l)} - 4\xi_2}{n_{Na}^{0(l)}}\right)^4 \left(\frac{\beta n_{Na}^{0(l)} - 4\xi_2}{\beta n_{Na}^{0(l)} - 2\xi_2}\right)^4} \left(\frac{P}{P^\circ}\right)^{-2} \tag{34}$$

which can be reduced to:

$$K_{R2}(T) = \frac{2^{10}\,\xi_2^6 \left(\beta n_{Na}^{0(l)} - 2\xi_2\right)^2}{\left(n_{Na}^{0(l)} - 4\xi_2\right)^4 \left(\beta n_{Na}^{0(l)} - 4\xi_2\right)^4} \left(\frac{P}{P^\circ}\right)^{-2} \tag{35}$$

Defining sodium conversion as $\zeta_2 \triangleq \frac{4\xi_2}{n_{Na}^{0(l)}}$, then yields:

$$K_{R2}(T) = \frac{\zeta_2^6 \left(2\beta - \zeta_2\right)^2}{16\left(1-\zeta_2\right)^4 \left(\beta - \zeta_2\right)^4} \left(\frac{P}{P^\circ}\right)^{-2} \qquad 0 \le \zeta_2 \le 1 \tag{36}$$

$$\frac{P}{P^\circ} = \frac{\zeta_2^3 \left(2\beta - \zeta_2\right)}{4\sqrt{K_{R2}(T)}\left(1-\zeta_2\right)^2 \left(\beta - \zeta_2\right)^2} \qquad 0 \le \zeta_2 \le 1 \tag{37}$$

Consider next reaction (R3) and define $n_{NaOH}^{0(l)}$ to be the initial moles of sodium hydroxide, x_i to be the liquid mole fraction of species i, y_i to be the vapor mole fraction of species i, ξ_3 to

be the extent of the reaction, and $\alpha = \dfrac{moles\, inert}{n_{NaOH}^{0(l)}}$ to be the molar feed ratio of an inert species (such as Ar) to $NaOH$, where the actual mass of inert is the same as in reaction (R1). Then the initial conditions and equilibrium concentrations are given by equations (38) and (39) respectively.

$$\left\{\begin{array}{ll} \nu_{NaOH} = -4 & n_{NaOH}^{0(l)} = n_{NaOH}^{0(l)} \\ \nu_{CO_2} = -2 & n_{CO_2}^{0(g)} = \frac{1}{2} n_{NaOH}^{0(l)} \\ \nu_{Na_2CO_3} = 2 & n_{Na_2CO_3}^{0(l)} = 0 \cdot n_{NaOH}^{0(l)} \\ \nu_{H_2O} = 2 & n_{H_2O}^{0(g)} = 0 \cdot n_{NaOH}^{0(l)} \\ \nu_{Ar} = 0 & n_{Ar}^{0(g)} = \alpha n_{NaOH}^{0(l)} \\ \sum \nu_i = -2 & \end{array}\right\} \overset{n_j = n_j^0 + \nu_j \xi_3}{\Rightarrow} \left\{\begin{array}{l} n_{NaOH}^{(l)} = n_{NaOH}^{0(l)} - 4\xi_3 \\ n_{CO_2}^{(g)} = \frac{1}{2} n_{NaOH}^{0(l)} - 2\xi_3 \\ n_{Na_2CO_3}^{(l)} = 0 \cdot n_{NaOH}^{0(l)} + 2\xi_3 \\ n_{H_2O}^{(g)} = 0 \cdot n_{NaOH}^{0(l)} + 2\xi_3 \\ n_{Ar}^{(g)} = \alpha n_{NaOH}^{0(l)} + 0 \cdot \xi_3 \\ n_{total} = (1.5 + \alpha) n_{NaOH}^{0(l)} - 2\xi_3 \end{array}\right\} \tag{38}$$

$$\left\{\begin{array}{ll} x_{NaOH} = \dfrac{n_{NaOH}^{0(l)} - 4\xi_3}{n_{NaOH}^{0(l)} - 2\xi_3} & y_{NaOH} = 0 \\ x_{CO_2} = 0 & y_{CO_2} = \dfrac{\frac{1}{2} n_{NaOH}^{0(l)} - 2\xi_3}{\left(\frac{1}{2} + \alpha\right) n_{NaOH}^{0(l)}} \\ x_{Na_2CO_3} = \dfrac{2\xi_3}{n_{NaOH}^{0(l)} - 2\xi_3} & y_{Na_2CO_3} = 0 \\ x_{H_2O} = 0 & y_{H_2O} = \dfrac{2\xi_3}{\left(\frac{1}{2} + \alpha\right) n_{NaOH}^{0(l)}} \\ x_{Ar} = 0 & y_{Ar} = \dfrac{\alpha n_0^{NaOH}}{\left(\frac{1}{2} + \alpha\right) n_{NaOH}^{0(l)}} \\ n^{(l)} = n_{NaOH}^{0(l)} - 2\xi_3 & n^{(g)} = \left(\frac{1}{2} + \alpha\right) n_{NaOH}^{0(l)} \end{array}\right\} \tag{39}$$

where $\begin{Bmatrix} 1 = x_{NaOH} + x_{CO_2} + x_{Na_2CO_3} + x_{H_2O} + x_{Ar} \\ 1 = y_{NaOH} + y_{CO_2} + y_{Na_2CO_3} + y_{H_2O} + x_{Ar} \\ P = P_{NaOH} + P_{CO_2} + P_{Na_2CO_3} + P_{H_2O} + P_{Ar} \end{Bmatrix}$ and $0 \le \xi_3 \le \frac{n_{NaOH}^{0(l)}}{4}$. The equilibrium constant is given by equation (40) which can be reduced to give equation (41):

$$K_{R3}(T) = \frac{\left(\frac{\hat{f}_{Na_2CO_3}^{(l)}}{f_{Na_2CO_3}^{o(l)}}\right)^2 \left(\frac{\hat{f}_{H_2O}^{(g)}}{f_{H_2O}^{o(g)}}\right)^2}{\left(\frac{\hat{f}_{NaOH}^{(l)}}{f_{NaOH}^{o(l)}}\right)^4 \left(\frac{\hat{f}_{CO_2}^{(g)}}{f_{CO_2}^{o(g)}}\right)^2} = \frac{\left(x_{Na_2CO_3}\gamma_{Na_2CO_3}\right)^2 \left(\frac{y_{H_2O}\hat{\phi}_{H_2O}P}{P^\circ}\right)^2}{\left(x_{NaOH}\gamma_{NaOH}\right)^4 \left(\frac{y_{CO_2}\hat{\phi}_{CO_2}P}{P^\circ}\right)^2} \tag{40}$$

$$K_{R3}(T) = \frac{\left(x_{Na_2CO_3}\gamma_{Na_2CO_3}\right)^2 \left(y_{H_2O}\hat{\phi}_{H_2O}\right)^2}{\left(x_{NaOH}\gamma_{NaOH}\right)^4 \left(y_{CO_2}\hat{\phi}_{CO_2}\right)^2} \tag{41}$$

Assuming $P^\circ = 1bar$; $\hat{\phi}_i = 1 \quad \forall i = H_2O, CO_2$; $\gamma_i = 1 \quad \forall i = Na_2CO_3, NaOH$, equation (41) becomes:

$$K_{R3}(T) = \frac{x_{Na_2CO_3}^2 y_{H_2O}^2}{x_{NaOH}^4 y_{CO_2}^2} \tag{42}$$

Substituting the expressions for the liquid and vapor mole fractions into the equilibrium constant give:

$$K_{R3}(T) = \frac{\left(\frac{2\xi_3}{n_{NaOH}^{0(l)} - 2\xi_3}\right)^2 \left(\frac{2\xi_3}{\left(\frac{1}{2}+\alpha\right)n_{NaOH}^{0(l)}}\right)^2}{\left(\frac{n_{NaOH}^{0(l)} - 4\xi_3}{n_{NaOH}^{0(l)} - 2\xi_3}\right)^4 \left(\frac{\frac{1}{2}n_{NaOH}^{0(l)} - 2\xi_3}{\left(\frac{1}{2}+\alpha\right)n_{NaOH}^{0(l)}}\right)^2} \Rightarrow \tag{43}$$

which can be reduced to:

$$K_{R3}(T) = \frac{(2\xi_3)^4 \left(n_{NaOH}^{0(l)} - 2\xi_3\right)^2}{\left(n_{NaOH}^{0(l)} - 4\xi_3\right)^4 \left(\frac{1}{2} n_{NaOH}^{0(l)} - 2\xi_3\right)^2} \tag{44}$$

Defining sodium hydroxide conversion as $\zeta_3 \triangleq \frac{4\xi_3}{n_{NaOH}^{0(l)}}$, then yields:

$$K_{R3}(T) = \frac{\frac{1}{16}\zeta_3^4 (2-\zeta_3)^2}{(1-\zeta_3)^6} \qquad 0 \le \zeta_3 \le 1 \tag{45}$$

$$\frac{(\zeta_3)^2 (2-\zeta_3)}{(1-\zeta_3)^3} = 4\sqrt{K_{R3}(T)} \tag{46}$$

A potential side reaction that may take place during reaction (R1) is the formation of Na_2O from the combination of reaction (R1) gaseous products Na and O_2. Consequently, the equilibrium constant for reaction (R5), the sodium oxide formation, is derived by itself and then followed by the equilibrium constant derivation of the coupling of reactions (R1) and (R5).

Consider reaction (R5) only and define $n_{Na}^{0(g)}$ to be the initial moles of sodium, x_i to be the liquid to solid mole fraction of species i, y_i to be the vapor mole fraction of species i, ξ_5 to be the extent of the reaction, $\alpha = \frac{moles\, inert}{n_{Na}^{0(g)}}$ to be the molar feed ratio of an inert species (such as Ar) to Na, and $\beta = \frac{n_{O_2}^{0(g)}}{n_{Na}^{0(g)}} \ge 1/4$ to be the molar feed ratio of O_2 (reactant in excess) to Na (limiting reactant), Then the initial conditions are:

$$\left\{\begin{array}{ll} v_{Na} = -4 & n_{Na}^{0(g)} = n_{Na}^{0(g)} \\ v_{O_2} = -1 & n_{O2}^{0(g)} = \beta n_{Na}^{0(g)} \\ v_{Na_2O} = 2 & n_{Na_2O}^{0(x)} = 0 \cdot n_{Na}^{0(g)} \\ v_{Ar} = 0 & n_{Ar}^{0(g)} = \alpha n_{Na}^{0(g)} \\ \sum v_i = -3 & \end{array}\right\} \overset{n_j = n_j^0 + v_j \xi_5}{\Rightarrow} \left\{\begin{array}{l} n_{Na}^{(g)} = n_{Na}^{0(g)} - 4\xi_5 \\ n_{O_2}^{(g)} = \beta n_{Na}^{0(g)} - \xi_5 \\ n_{Na_2O}^{(x)} = 0 \cdot n_{Na}^{0(g)} + 2\xi_5 \\ n_{Ar}^{(g)} = \alpha n_{Na}^{0(g)} + 0 \cdot \xi_5 \\ n_{total} = \left(1 + \alpha + \beta\right) n_{Na}^{0(g)} - 3\xi_5 \end{array}\right\} \tag{47}$$

Equilibrium concentrations are given by equation (48) where Na_2O is either a solid or liquid, represented by (x).

$$\left\{\begin{array}{ll} x_{Na} = 0 & y_{Na} = \dfrac{n_{Na}^{0(g)} - 4\xi_5}{\left(1 + \alpha + \beta\right) n_{Na}^{0(g)} - 5\xi_5} \\ x_{O_2} = 0 & y_{O_2} = \dfrac{\beta n_{Na}^{0(g)} - \xi_5}{\left(1 + \alpha + \beta\right) n_{Na}^{0(g)} - 5\xi_5} \\ x_{Na_2O} = \dfrac{2\xi_5}{2\xi_5} = 1 & y_{Na_2O} = 0 \\ x_{Ar} = 0 & y_{Ar} = \dfrac{\alpha n_{Na}^{0(g)}}{\left(1 + \alpha + \beta\right) n_{Na}^{0(g)} - 5\xi_5} \\ n^{(x)} = 2\xi_5 & n^{(g)} = \left(1 + \alpha + \beta\right) n_{Na}^{0(g)} - 5\xi_5 \end{array}\right\} \tag{48}$$

where $\left\{\begin{array}{l} 1 = x_{Na_2O} + x_{Na} + x_{O_2} + x_{Ar} \\ 1 = y_{Na_2O} + y_{Na} + y_{O_2} + y_{Ar} \\ P = P_{Na_2O} + P_{Na} + P_{O_2} + P_{Ar} \end{array}\right\}$ and $0 \le \xi_5 \le \dfrac{n_{Na}^{0(g)}}{4}$ $\left(\beta \ge \dfrac{1}{4}\right)$. Then, the equilibrium constant is:

$$K_{R5}\left(T\right) = \frac{\left(\dfrac{\hat{f}_{Na_2O}^{(x)}}{f_{Na_2O}^{o(x)}}\right)^2}{\left(\dfrac{\hat{f}_{Na}^{o(g)}}{f_{Na}^{(g)}}\right)^4 \left(\dfrac{\hat{f}_{O_2}^{o(g)}}{f_{O_2}^{(g)}}\right)} = \frac{\left(x_{Na_2O}\gamma_{Na_2O}\right)^2}{\left(\dfrac{y_{Na}\hat{\phi}_{Na}P}{P^{\circ}}\right)^4 \left(\dfrac{y_{O_2}\hat{\phi}_{O_2}P}{P^{\circ}}\right)} \tag{49}$$

which can be reduced to:

$$K_{\mathrm{R}5}(T)=\frac{\left(x_{Na_2O}\gamma_{Na_2O}\right)^2}{\left(y_{Na}\hat{\phi}_{Na}\right)^4\left(y_{O_2}\hat{\phi}_{O_2}\right)}\left(\frac{P}{P^{\circ}}\right)^{-5} \tag{50}$$

Assuming $P^{\circ}=1bar$; $\hat{\phi}_i=1 \quad \forall i=Na,O_2$; $\gamma_i=1 \quad \forall i=Na_2O$; $x_{Na_2O}=1$:

$$K_{R5}(T)=\frac{1}{y_{Na}^4 y_{O_2}}\left(\frac{P}{P^{\circ}}\right)^{-5} \tag{51}$$

Substituting the expressions for the liquid and vapor mole fractions into the equilibrium constant give:

$$K_{R5}(T)=\frac{1}{\left(\frac{n_{Na}^{0(g)}-4\xi_5}{(1+\alpha+\beta)n_{Na}^{0(g)}-5\xi_5}\right)^4\left(\frac{\beta n_{Na}^{0(g)}-\xi_5}{(1+\alpha+\beta)n_{Na}^{0(g)}-5\xi_5}\right)}\left(\frac{P}{P^{\circ}}\right)^{-5} \tag{52}$$

which reduces to:

$$K_{R5}(T)=\frac{\left((1+\alpha+\beta)n_{Na}^{0(g)}-5\xi_5\right)^5}{\left(n_{Na}^{0(g)}-4\xi_5\right)^4\left(\beta n_{Na}^{0(g)}-\xi_5\right)}\left(\frac{P}{P^{\circ}}\right)^{-5} \tag{53}$$

Defining sodium conversion as $\zeta_5 \triangleq \frac{4\xi_5}{n_{Na}^{0(g)}}$, then yields:

$$K_{R5}(T)=\frac{\left(4(1+\alpha+\beta)-5\zeta_5\right)^5}{2^8\left(1-\zeta_5\right)^4\left(4\beta-\zeta_5\right)}\left(\frac{P}{P^{\circ}}\right)^{-5} \tag{54}$$

$$\frac{P}{P^{\circ}}=\left[\frac{\left(4(1+\alpha+\beta)-5\zeta_5\right)^5}{2^8 K_{R5}(T)\left(1-\zeta_5\right)^4\left(4\beta-\zeta_5\right)}\right]^{\frac{1}{5}} \tag{55}$$

Now, if both reaction (R1) and (R5) are coupled, that is the gaseous Na and O_2 output by reaction (R1) are allowed to react and form Na_2O, as in reaction (R5), then the equilibrium constants for both coupled reactions are derived as follows. Consider reaction (R1) and define

$n_{Na_2CO_3}^{0(l)}$ to be the initial moles of sodium carbonate, x_i to be the liquid mole fraction of species i, y_i to be the vapor mole fraction of species i, ξ_1 to be the extent of reaction (R1), ξ_5 to be the extent of the reaction (R5), $\alpha = \dfrac{moles\, inert}{n_{Na_2CO_3}^{0(l)}}$ to be the molar feed ratio of an inert species (such as Ar) to Na_2CO_3. Then the initial conditions for the combined reactions are:

$$\left\{\begin{array}{ll} \nu_{Na_2CO_3} = -2 & n_{Na_2CO_3}^{0(l)} = n_{Na_2CO_3}^{0(l)} \\ \nu_{Na} = 4 & n_{Na}^{0(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} \\ \nu_{CO_2} = 2 & n_{CO_2}^{0(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} \\ \nu_{O_2} = 1 & n_{O_2}^{0(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} \\ \nu_{Ar} = 0 & n_{Ar}^{0(g)} = \alpha n_{Na_2CO_3}^{0(l)} \\ \sum \nu_i = 5 & \\ \nu_{Na} = -4 & n_{Na}^{0(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} \\ \nu_{O_2} = -1 & n_{O_2}^{0(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} \\ \nu_{Na_2O} = 2 & n_{Na_2O}^{0(x)} = 0 \cdot n_{Na_2CO_3}^{0(l)} \\ \sum \nu_i = -3 & \end{array}\right\} \overset{n_j = n_j^0 + \nu_j \xi_r}{\Rightarrow} \left\{\begin{array}{l} n_{Na_2CO_3}^{(l)} = n_{Na_2CO_3}^{0(l)} - 2\xi_1 \\ n_{Na}^{(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} + 4\xi_1 - 4\xi_5 \\ n_{CO_2}^{(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} + 2\xi_1 \\ n_{O_2}^{(g)} = 0 \cdot n_{Na_2CO_3}^{0(l)} + \xi_1 - \xi_5 \\ n_{Ar}^{(g)} = \alpha n_{Na_2CO_3}^{0(l)} + 0 \cdot \xi_1 \\ n_{Na_2O}^{(x)} = 0 \cdot n_{Na_2CO_3}^{0(l)} + 2\xi_5 \\ n_{total} = (1+\alpha) n_{Na_2CO_3}^{0(l)} + 5\xi_1 - 3\xi_5 \end{array}\right\} \tag{56}$$

The equilibrium concentrations for the combined reactions are:

$$\left\{\begin{array}{ll} x_{Na_2CO_3} = \dfrac{n^{0(l)}_{Na_2CO_3} - 2\xi_1}{n^{0(l)}_{Na_2CO_3} - 2\xi_1 + 2\xi_5} & y_{Na_2CO_3} = 0 \\ x_{Na_2O} = \dfrac{2\xi_5}{n^{0(l)}_{Na_2CO_3} - 2\xi_1 + 2\xi_5} & y_{Na_2O} = 0 \\ x_{Na} = 0 & y_{Na} = \dfrac{4\xi_1 - 4\xi_5}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1 - 5\xi_5} \\ x_{CO_2} = 0 & y_{CO_2} = \dfrac{2\xi_1}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1 - 5\xi_5} \\ x_{O_2} = 0 & y_{O_2} = \dfrac{\xi_1 - \xi_5}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1 - 5\xi_5} \\ x_{Ar} = 0 & y_{Ar} = \dfrac{\alpha n^{0(l)}_{Na_2CO_3}}{\alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1 - 5\xi_5} \\ n^{(l)} = n^{0(l)}_{Na_2CO_3} - 2\xi_1 + 2\xi_5 & n^{(g)} = \alpha n^{0(l)}_{Na_2CO_3} + 7\xi_1 - 5\xi_5 \end{array}\right\} \tag{57}$$

where $\left\{\begin{array}{l} 1 = x_{Na_2CO_3} + x_{Na} + x_{CO_2} + x_{O_2} + x_{Ar} + x_{Na_2O} \\ 1 = y_{Na_2CO_3} + y_{Na} + y_{CO_2} + y_{O_2} + y_{Ar} + y_{Na_2O} \\ P = P_{Na_2CO_3} + P_{Na} + P_{CO_2} + P_{O_2} + P_{Ar} + P_{Na_2O} \end{array}\right\}$ and $0 \le \xi_1 \le \dfrac{n^{0(l)}_{Na_2CO_3}}{2}$, $0 \le \xi_5 \le \xi_1 \le \dfrac{n^{0(l)}_{Na_2CO_3}}{2}$.

Then, the equilibrium constant for reaction (R1) is:

$$K_{R1}(T) = \frac{\left(\dfrac{\hat{f}^{(g)}_{Na}}{f^{o(g)}_{Na}}\right)^4 \left(\dfrac{\hat{f}^{(g)}_{CO_2}}{f^{o(g)}_{CO_2}}\right)^2 \left(\dfrac{\hat{f}^{(g)}_{O_2}}{f^{o(g)}_{O_2}}\right)}{\left(\dfrac{\hat{f}^{(l)}_{Na_2CO_3}}{f^{o(l)}_{Na_2CO_3}}\right)^2} = \frac{\left(\dfrac{y_{Na}\hat{\phi}_{Na}P}{P^{\circ}}\right)^4 \left(\dfrac{y_{CO_2}\hat{\phi}_{CO_2}P}{P^{\circ}}\right)^2 \left(\dfrac{y_{O_2}\hat{\phi}_{O_2}P}{P^{\circ}}\right)}{\left(x_{Na_2CO_3}\gamma_{Na_2CO_3}\right)^2} \tag{58}$$

which can be reduced to:

$$K_{R1}(T) = \frac{\left(y_{Na}\hat{\phi}_{Na}\right)^4 \left(y_{CO_2}\hat{\phi}_{CO_2}\right)^2 \left(y_{O_2}\hat{\phi}_{O_2}\right)}{\left(x_{Na_2CO_3}\gamma_{Na_2CO_3}\right)^2} \left(\frac{P}{P^{\circ}}\right)^7 \tag{59}$$

Assuming $P^{\circ} = 1bar$; $\hat{\phi}_i = 1 \quad \forall i = Na, CO_2, O_2$; $\gamma_{Na_2CO_3} = 1$ equation (59) reduces to equation (60).

$$K_{R1}\left(T\right)=\frac{y_{Na}^{4}y_{CO_2}^{2}y_{O_2}}{x_{Na_2CO_3}^{2}}\left(\frac{P}{P^{\circ}}\right)^{7} \tag{60}$$

Then, the equilibrium constant for reaction (R5) is:

$$K_{R5}\left(T\right)=\frac{\left(\frac{\hat{f}_{Na_2O}^{(x)}}{f_{Na_2O}^{o(x)}}\right)^{2}}{\left(\frac{\hat{f}_{Na}^{(g)}}{f_{Na}^{o(g)}}\right)^{4}\left(\frac{\hat{f}_{O_2}^{(g)}}{f_{O_2}^{o(g)}}\right)}=\frac{\left(x_{Na_2O}\gamma_{Na_2O}\right)^{2}}{\left(\frac{y_{Na}\hat{\phi}_{Na}P}{P^{\circ}}\right)^{4}\left(\frac{y_{O_2}\hat{\phi}_{O_2}P}{P^{\circ}}\right)} \tag{61}$$

which can be reduced to:

$$K_{R5}\left(T\right)=\frac{\left(x_{Na_2O}\gamma_{Na_2O}\right)^{2}}{\left(y_{Na}\hat{\phi}_{Na}\right)^{4}\left(y_{O_2}\hat{\phi}_{O_2}\right)}\left(\frac{P}{P^{\circ}}\right)^{-5} \tag{62}$$

Assuming $P^{\circ}=1bar$; $\hat{\phi}_i=1 \quad \forall i=Na,O_2$; $\gamma_{Na_2O}=1$, then:

$$K_{R5}\left(T\right)=\frac{x_{Na_2O}^{2}}{y_{Na}^{4}y_{O_2}}\left(\frac{P}{P^{\circ}}\right)^{-5} \tag{63}$$

Substituting the expressions for the vapor and liquid mole fractions in reaction (R1) equilibrium constant then yields:

$$K_{R1}\left(T\right)=\frac{\left(\frac{4\xi_1-4\xi_5}{\alpha n_{Na_2CO_3}^{0(l)}+7\xi_1-5\xi_5}\right)^{4}\left(\frac{2\xi_1}{\alpha n_{Na_2CO_3}^{0(l)}+7\xi_1-5\xi_5}\right)^{2}\left(\frac{\xi_1-\xi_5}{\alpha n_{Na_2CO_3}^{0(l)}+7\xi_1-5\xi_5}\right)}{\left(\frac{n_{Na_2CO_3}^{0(l)}-2\xi_1}{n_{Na_2CO_3}^{0(l)}-2\xi_1+2\xi_5}\right)^{2}}\left(\frac{P}{P^{\circ}}\right)^{7} \tag{64}$$

which reduces to:

$$K_{R1}\left(T\right)=2^{10}\frac{\xi_1^{2}\left(\xi_1-\xi_5\right)^{5}}{\left(n_{Na_2CO_3}^{0(l)}-2\xi_1\right)^{2}}\frac{\left(n_{Na_2CO_3}^{0(l)}-2\xi_1+2\xi_5\right)^{2}}{\left(\alpha n_{Na_2CO_3}^{0(l)}+7\xi_1-5\xi_5\right)^{7}}\left(\frac{P}{P^{\circ}}\right)^{7} \tag{65}$$

Normalizing the extents of reaction of (R1) and (R5) as $\zeta_1 \triangleq \frac{2\xi_1}{n_{Na_2CO_3}^{0(l)}}$ and $\zeta_5 \triangleq \frac{2\xi_5}{n_{Na_2CO_3}^{0(l)}}$ then yields:

$$K_{R1}(T) = 2^{10}\frac{\zeta_1^2(\zeta_1-\zeta_5)^5}{(1-\zeta_1)^2}\frac{(1-\zeta_1+\zeta_5)^2}{(2\alpha+7\zeta_1-5\zeta_5)^7}\left(\frac{P}{P^\circ}\right)^7 \qquad 0\le\zeta_1\le 1 \qquad 0\le\zeta_5\le\zeta_1\le 1 \quad (66)$$

Substituting the expressions for the vapor and liquid mole fractions in reaction (R5) equilibrium constant then yields:

$$K_{R5}(T) = \frac{\left(\frac{2\xi_5}{n_{Na_2CO_3}^{0(l)}-2\xi_1+2\xi_5}\right)^2}{\left(\frac{4\xi_1-4\xi_5}{\alpha n_{Na_2CO_3}^{0(l)}+7\xi_1-5\xi_5}\right)^4\left(\frac{\xi_1-\xi_5}{\alpha n_{Na_2CO_3}^{0(l)}+7\xi_1-5\xi_5}\right)}\left(\frac{P}{P^\circ}\right)^{-5} \quad (67)$$

which reduces to:

$$K_{R5}(T) = \frac{1}{2^6}\frac{\xi_5^2}{(\xi_1-\xi_5)^5}\frac{\left(\alpha n_0^{Na_2CO_3}+7\xi_1-5\xi_5\right)^5}{\left(n_0^{Na_2CO_3}-2\xi_1+2\xi_5\right)^2}\left(\frac{P}{P^\circ}\right)^{-5} \quad (68)$$

Applying again the above normalizations then yields:

$$K_{R5}(T) = \frac{1}{2^8}\frac{\zeta_5^2}{(\zeta_1-\zeta_5)^5}\frac{(2\alpha+7\zeta_1-5\zeta_5)^5}{(1-\zeta_1+\zeta_5)^2}\left(\frac{P}{P^\circ}\right)^{-5} \qquad 0\le\zeta_1\le 1 \qquad 0\le\zeta_5\le\zeta_1\le 1 \quad (69)$$

It then holds that:

$$K_{R1}(T)\cdot K_{R5}(T) = 2^2\frac{\zeta_1^2\zeta_5^2}{(1-\zeta_1)^2}\frac{1}{(2\alpha+7\zeta_1-5\zeta_5)^2}\left(\frac{P}{P^\circ}\right)^2 \quad (70)$$

Taking the square root of each side yields:

$$\sqrt{K_{R1}(T)\cdot K_{R5}(T)} = 2\frac{\zeta_1\zeta_5}{(1-\zeta_1)}\frac{1}{(2\alpha+7\zeta_1-5\zeta_5)}\left(\frac{P}{P^\circ}\right) \quad (71)$$

Further algebra leads to:

$$\zeta_5 = \frac{\sqrt{K_{R1}(T)\cdot K_{R5}(T)}\,(2\alpha+7\zeta_1)(1-\zeta_1)}{\left[2\zeta_1\left(\frac{P}{P^\circ}\right)+5\sqrt{K_{R1}(T)\cdot K_{R5}(T)}\,(1-\zeta_1)\right]} \tag{72}$$

Let $K=\sqrt{K_{R1}(T)\cdot K_{R5}(T)}$ and substituting equation (72) for ζ_5 into equation (66) yields:

$$K_{R1}(T) = \frac{\frac{2^{10}\zeta_1^2}{(1-\zeta_1)^2}\left[\left(\frac{2\zeta_1^2\left(\frac{P}{P^\circ}\right)+5K\zeta_1(1-\zeta_1)-K(2\alpha+7\zeta_1)(1-\zeta_1)}{2\zeta_1\left(\frac{P}{P^\circ}\right)+5K(1-\zeta_1)}\right)^5 \cdot \left(\frac{\left[2\zeta_1\left(\frac{P}{P^\circ}\right)+5K(1-\zeta_1)-2\zeta_1^2\left(\frac{P}{P^\circ}\right)+ -5K\zeta_1(1-\zeta_1)+K(2\alpha+7\zeta_1)(1-\zeta_1)\right]}{2\zeta_1\left(\frac{P}{P^\circ}\right)+5K(1-\zeta_1)}\right)^2\right]}{\left(\frac{\left[4\alpha\zeta_1\left(\frac{P}{P^\circ}\right)+10K\alpha(1-\zeta_1)+14\zeta_1^2\left(\frac{P}{P^\circ}\right)+ +35K\zeta_1(1-\zeta_1)-5K(2\alpha+7\zeta_1)(1-\zeta_1)\right]}{2\zeta_1\left(\frac{P}{P^\circ}\right)+5K(1-\zeta_1)}\right)^7}\left(\frac{P}{P^\circ}\right)^7 \tag{73}$$

Rearrangement of equation (73) gives equation (74).

$$K_{R1}(T) = \frac{2^{10}\left(\left(\frac{P}{P^\circ}\right)-K\left(\frac{1}{\zeta_1}-1\right)\left(1+\frac{\alpha}{\zeta_1}\right)\right)^5\left(\left(\frac{P}{P^\circ}\right)+K\left(1+\frac{5+2\alpha}{2\zeta_1}\right)\right)^2}{\left(7+\frac{2\alpha}{\zeta_1}\right)^7} \tag{74}$$

The above equation must be solved numerically in order to produce the value of ζ_1 at a given temperature. This ζ_1 value is then used in equation (72) to find the value for ζ_5.

The equilibrium constant expressions for reactions (R1) to (R3) and (R5) are solved numerically by fixing temperature (T), conversion (ζ_r), and molar ratios (α, β), and solving for the equilibrium pressure (P). Then, pressure values are obtained for a select range of temperatures, conversions, and molar ratios which are shown in the results section.

2.5. Gibbs Free Energy Minimization Method

Consider the following optimization problem:

$$\left\{\begin{array}{lll} \pi \triangleq \min\limits_{x \in R^n} & f(x) & \\ s.t. & h_i(x) = 0 & \forall i = 1, m \\ & g_j(x) \le 0 & \forall j = 1, p \end{array}\right\} \tag{75}$$

Assuming closedness and boundedness of the feasible region, differentiability of the functions involved in defining the optimization objective and its constraints, and regularity of all feasible points, ensures the existence of a minimum, and that the following necessary conditions of optimality must hold, [61] – p. 314:

$$\left\{\begin{array}{ll} \dfrac{\partial f(x)}{\partial x} + \sum\limits_{i=1}^{m} \lambda_i \dfrac{\partial h_i(x)}{\partial x} + \sum\limits_{j=1}^{p} \omega_j \dfrac{\partial g_j(x)}{\partial x} = 0 & \\ h_i(x) = 0 & \forall i = 1, m \\ \omega_j g_j(x) = 0 & \forall j = 1, p \\ g_j(x) \le 0 & \forall j = 1, p \\ \omega_j \ge 0 & \forall j = 1, p \end{array}\right\} \tag{76}$$

The identification of phase and reaction equilibrium conditions for a system that is at constant temperature and pressure, and involves multiple species and possibly multiple phases, can be

identified through the minimization of the system's total Gibbs free energy at constant temperature and pressure. This minimization problem can be stated as follows:

$$\left\{ \begin{array}{l} \pi\left(T,P,\left\{a_i\right\}_{i=1}^{NE}\right) \hat{=} \min\limits_{\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}} \quad G\left(T,P,\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}\right) \\ \qquad\qquad s.t. \quad a_i - \sum\limits_{k}^{NP}\sum\limits_{j}^{NC} \nu_{ij} n_j^{(k)} = 0 \quad \forall i = 1, NE \\ \qquad\qquad\qquad n_j^{(k)} \geq 0 \quad \forall j = 1, NC; \ \forall k = 1, NP \end{array} \right\} \tag{77}$$

However the total Gibbs free energy of the system $G\left(T,P,\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}\right)$ can be expressed in terms of the total Gibbs free energies $G^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}\right)$ of the individual phases as follows:

$$G\left(T,P,\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}\right) = \sum_{k=1}^{NP} G^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}_{j=1}^{NC}\right) \tag{78}$$

However the total Gibbs free energy $G^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}\right)$ of phase k can be expressed in terms of the partial molar properties of the species comprising the phase as follows:

$$G^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}_{j=1}^{NC}\right) = \sum_{p=1}^{NC} n_p^{(k)} \left(\frac{\partial G^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}_{j=1}^{NC}\right)}{\partial n_p^{(k)}} \right) \qquad \forall k = 1, NP \tag{79}$$

Then,

$$G\left(T,P,\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}\right) = \sum_{k=1}^{NP}\sum_{p=1}^{NC} n_p^{(k)} \left(\frac{\partial G^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}_{j=1}^{NC}\right)}{\partial n_p^{(k)}} \right) \tag{80}$$

However, the partial molar Gibbs free energy of species p in phase k is equal to the chemical potential of species p in phase k, [42] – p. 526, i.e.

$$\mu_p^{(k)}\left(T,P,\left\{x_j^{(k)}\right\}_{j=1}^{NC}\right) \triangleq \frac{\partial G^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}_{j=1}^{NC}\right)}{\partial n_p^{(k)}} \quad \forall p=1,NC; \quad \forall k=1,NP \tag{81}$$

where $x_j^{(q)} \triangleq \dfrac{n_j^{(q)}}{\sum_{p=1}^{NC} n_p^{(q)}} \quad \forall j=1,NC; \forall q=1,NP$ is the mole fraction of species j in phase q.

Then, as shown in Ref. [62],

$$G\left(T,P,\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}\right) = \sum_{k=1}^{NP}\sum_{p=1}^{NC} n_p^{(k)}\mu_p^{(k)}\left(T,P,\left\{x_j^{(k)}\right\}_{j=1}^{NC}\right) \tag{82}$$

The overall Gibbs free energy minimization problem then becomes:

$$\left\{\begin{array}{ll} \pi\left(T,P,\{a_i\}_{i=1}^{NE}\right) \triangleq \min\limits_{\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})},\left\{x_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}} & \sum_{k=1}^{NP}\sum_{p=1}^{NC} n_p^{(k)}\mu_p^{(k)}\left(T,P,\left\{x_j^{(k)}\right\}_{j=1}^{NC}\right) \\ s.t. \quad a_i - \sum_{k}^{NP}\sum_{j}^{NC}\nu_{ij}n_j^{(k)} = 0 & \forall i=1,NE \\ x_j^{(k)}\left[\sum_{p=1}^{NC} n_p^{(k)}\right] - n_j^{(k)} = 0 & \forall j=1,NC; \quad \forall k=1,NP \\ n_j^{(k)} \geq 0 & \forall j=1,NC; \quad \forall k=1,NP \end{array}\right\} \tag{83}$$

Under the assumptions of feasible region closedness, and boundedness; differentiability of the functions involved in defining the optimization objective and its constraints; and regularity of all feasible points, the following necessary conditions of optimality must hold:

$$
\left\{
\begin{array}{l}
\left[
\begin{array}{l}
\dfrac{\partial\left[\sum_{k=1}^{NP}\sum_{p=1}^{NC} n_p^{(k)}\mu_p^{(k)}\left(T,P,\left\{x_j^{(k)}\right\}_{j=1}^{NC}\right)\right]}{\partial n_l^{(q)}} + \\
+\sum_{i=1}^{NE}\lambda_i \dfrac{\partial\left(a_i - \sum_{k}^{NP}\sum_{j}^{NC}\nu_{ij}n_j^{(k)}\right)}{\partial n_l^{(q)}} \\
+\sum_{k=1}^{NP}\sum_{j=1}^{NC}\tau_{jk}\dfrac{\partial\left(x_j^{(k)}\left[\sum_{p=1}^{NC}n_p^{(k)}\right]-n_j^{(k)}\right)}{\partial n_l^{(q)}} + \sum_{k=1}^{NP}\sum_{j=1}^{NC}\omega_{jk}\dfrac{\partial\left(-n_j^{(k)}\right)}{\partial n_l^{(q)}}
\end{array}
\right] = 0 \quad \forall l = 1, NC; \quad \forall q = 1, NP \\
\left[
\begin{array}{l}
\dfrac{\partial\left[\sum_{k=1}^{NP}\sum_{p=1}^{NC} n_p^{(k)}\mu_p^{(k)}\left(T,P,\left\{x_j^{(k)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_l^{(q)}} + \\
+\sum_{i=1}^{NE}\lambda_i \dfrac{\partial\left(a_i - \sum_{k}^{NP}\sum_{j}^{NC}\nu_{ij}n_j^{(k)}\right)}{\partial x_l^{(q)}} + \\
+\sum_{k=1}^{NP}\sum_{j=1}^{NC}\tau_{jk}\dfrac{\partial\left(x_j^{(k)}\left[\sum_{p=1}^{NC}n_p^{(k)}\right]-n_j^{(k)}\right)}{\partial x_l^{(q)}} + \sum_{k=1}^{NP}\sum_{j=1}^{NC}\omega_{jk}\dfrac{\partial\left(-n_j^{(k)}\right)}{\partial x_l^{(q)}}
\end{array}
\right] = 0 \quad \forall l = 1, NC; \quad \forall q = 1, NP \\
a_i - \sum_{k}^{NP}\sum_{j}^{NC}\nu_{ij}n_j^{(k)} = 0 \quad \forall i = 1, NE \\
x_j^{(k)}\left[\sum_{p=1}^{NC}n_p^{(k)}\right] - n_j^{(k)} = 0 \quad \forall j = 1, NC; \quad \forall k = 1, NP \\
\omega_{jk}n_j^{(k)} = 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP \\
-n_j^{(k)} \le 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP \\
\omega_{jk} \ge 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP
\end{array}
\right\} \quad (84)
$$

$$
\left\{
\begin{array}{l}
\left[
\begin{array}{l}
\dfrac{\partial\left[\sum_{p=1}^{NC} n_p^{(q)} \mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial n_l^{(q)}} - \sum_{i=1}^{NE} \lambda_i \dfrac{\partial\left[\sum_{j}^{NC} \nu_{ij} n_j^{(q)}\right]}{\partial n_l^{(q)}} + \\
+\sum_{j=1}^{NC} \tau_{jq} \dfrac{\partial\left(x_j^{(q)}\left[\sum_{p=1}^{NC} n_p^{(q)}\right] - n_j^{(q)}\right)}{\partial n_l^{(q)}} - \sum_{j=1}^{NC} \omega_{jq} \dfrac{\partial n_j^{(q)}}{\partial n_l^{(q)}}
\end{array}
\right] = 0 \quad \forall l = 1, NC; \quad \forall q = 1, NP \\
\left[
\begin{array}{l}
\dfrac{\partial\left[\sum_{p=1}^{NC} n_p^{(q)} \mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_l^{(q)}} - \sum_{i=1}^{NE} \lambda_i \dfrac{\partial\left[\sum_{j}^{NC} \nu_{ij} n_j^{(q)}\right]}{\partial x_l^{(q)}} + \\
+\sum_{j=1}^{NC} \tau_{jq} \dfrac{\partial\left(x_j^{(q)}\left[\sum_{p=1}^{NC} n_p^{(q)}\right] - n_j^{(q)}\right)}{\partial x_l^{(q)}} - \sum_{j=1}^{NC} \omega_{jq} \dfrac{\partial n_j^{(q)}}{\partial x_l^{(q)}}
\end{array}
\right] = 0 \quad \forall l = 1, NC; \quad \forall q = 1, NP \\
a_i - \sum_{k}^{NP} \sum_{j}^{NC} \nu_{ij} n_j^{(k)} = 0 \quad \forall i = 1, NE \\
x_j^{(k)}\left[\sum_{p=1}^{NC} n_p^{(k)}\right] - n_j^{(k)} = 0 \quad \forall j = 1, NC; \quad \forall k = 1, NP \\
\omega_{jk} n_j^{(k)} = 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP \\
-n_j^{(k)} \le 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP \\
\omega_{jk} \ge 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP
\end{array}
\right\}
\tag{85}
$$

$$
\left\{
\begin{array}{l}
\mu_l^{(q)}\left(T,P,\left\{n_j^{(q)}\right\}_{j=1}^{NC}\right) - \sum_{i=1}^{NE} \lambda_i \nu_{il} + \sum_{j=1}^{NC} \tau_{jq} x_j^{(q)} - \tau_{lq} - \omega_{lq} = 0 \quad \forall l = 1, NC; \quad \forall q = 1, NP \\
\sum_{p=1}^{NC} n_p^{(q)} \dfrac{\partial\left[\mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_l^{(q)}} + \tau_{lq}\left[\sum_{p=1}^{NC} n_p^{(q)}\right] = 0 \qquad \forall l = 1, NC; \quad \forall q = 1, NP \\
a_i - \sum_{k}^{NP} \sum_{j}^{NC} \nu_{ij} n_j^{(k)} = 0 \quad \forall i = 1, NE \\
x_j^{(k)}\left[\sum_{p=1}^{NC} n_p^{(k)}\right] - n_j^{(k)} = 0 \quad \forall j = 1, NC; \quad \forall k = 1, NP \\
\omega_{jk} n_j^{(k)} = 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP \\
-n_j^{(k)} \le 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP \\
\omega_{jk} \ge 0 \qquad \forall j = 1, NC; \quad \forall k = 1, NP
\end{array}
\right\}
\tag{86}
$$

$$\left\{\begin{array}{ll}
\mu_l^{(q)}\left(T,P,\left\{n_j^{(q)}\right\}_{j=1}^{NC}\right)-\sum_{i=1}^{NE}\lambda_i\nu_{il}+\sum_{j=1}^{NC}\tau_{jq}x_j^{(q)}-\tau_{lq}-\omega_{lq}=0 & \forall l=1,NC;\quad \forall q=1,NP \\
\tau_{lq}=-\sum_{p=1}^{NC}x_p^{(q)}\dfrac{\partial\left[\mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_l^{(q)}} & \forall l=1,NC;\quad \forall q=1,NP \\
a_i-\sum_{k}^{NP}\sum_{j}^{NC}\nu_{ij}n_j^{(k)}=0 & \forall i=1,NE \\
x_j^{(k)}\left[\sum_{p=1}^{NC}n_p^{(k)}\right]-n_j^{(k)}=0 & \forall j=1,NC;\quad \forall k=1,NP \\
\omega_{jk}n_j^{(k)}=0 & \forall j=1,NC;\quad \forall k=1,NP \\
-n_j^{(k)}\le 0 & \forall j=1,NC;\quad \forall k=1,NP \\
\omega_{jk}\ge 0 & \forall j=1,NC;\quad \forall k=1,NP
\end{array}\right\} \tag{87}$$

The above suggests that $\forall l=1,NC$; $\forall q=1,NP$ such that $n_l^{(q)}>0$, it holds that $\omega_{lq}=0$. In addition, the quantity $\sum_{i=1}^{NE}\lambda_i\nu_{il}$ does not depend on q, $\forall l=1,NC$. Thus if $\sum_{j=1}^{NC}\tau_{jq}x_j^{(q)}-\tau_{lq}$ also does not depend on q, $\forall l=1,NC$ such that $n_l^{(q)}>0$, then:

$$\mu_l^{(q)}\left(T,P,\left\{n_j^{(q)}\right\}_{j=1}^{NC}\right)=\mu_l^{(k)}\left(T,P,\left\{n_j^{(q)}\right\}_{j=1}^{NC}\right)\ \forall l=1,NC;\ \forall k=1,NP;\ \forall q=1,NP \tag{88}$$

such that $n_l^{(q)}>0$. Verification of the above condition is easier to pursue, when it is brought in the form shown below.

$$\left\{\begin{aligned}
&\sum_{j=1}^{NC}\tau_{jq}x_j^{(q)}-\tau_{lq}=\sum_{j=1}^{NC}\tau_{jq}x_j^{(q)}-\tau_{lq}\sum_{j=1}^{NC}x_j^{(q)}=\sum_{j=1}^{NC}\left(\tau_{jq}-\tau_{lq}\right)x_j^{(q)}= \\
&=\sum_{j=1}^{NC}\left(-\sum_{p=1}^{NC}x_p^{(q)}\frac{\partial\left[\mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_j^{(q)}}+\sum_{p=1}^{NC}x_p^{(q)}\frac{\partial\left[\mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_l^{(q)}}\right)x_j^{(q)}= \\
&=\sum_{j=1}^{NC}\sum_{p=1}^{NC}x_p^{(q)}x_j^{(q)}\left[\frac{\partial\left[\mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_l^{(q)}}-\frac{\partial\left[\mu_p^{(q)}\left(T,P,\left\{x_j^{(q)}\right\}_{j=1}^{NC}\right)\right]}{\partial x_j^{(q)}}\right]
\end{aligned}\right\} \tag{89}$$

Considering the standard state of a species at temperature T to be the state of that species in pure form, at that temperature T, at $P^o=1bar$, and in an ideal gas, liquid, or solid phase, then the chemical potential of species j can be written as, [42] – p.526:

$$\mu_j^{(k)}\left(T,P,\left\{n_j^{(k)}\right\}_{(j,k)=(1,1)}^{(NC,\mathrm{NP})}\right)=G_j^{o(k)}\left(T\right)+RT\ln\frac{\hat{f}_j^{(k)}}{f_j^{o(k)}} \tag{90}$$

When $G_j^{o(k)}$ is defined to have a value of zero for all elements in their standard phase at $P^o=1bar$ and T, $G_j^{o(k)}\left(T\right)=\Delta G_{f_j}^{o(k)}\left(T\right)$, [63] – p. 395. Then the following holds, [62]:

$$G\left(T,P,\left\{n_p^{(k)}\right\}_{(p,k)=(1,1)}^{(NC,\mathrm{NP})}\right)=\sum_{k=1}^{NP}\sum_{j=1}^{NC}n_j^{(k)}\mu_j^{(k)}\left(T,P,\left\{x_p^{(k)}\right\}_{j=1}^{NC}\right)=\sum_{k}^{NP}\sum_{j}^{NC}n_j^{(k)}\left(\Delta G_{f_j}^{o(k)}\left(T\right)+RT\ln\frac{\hat{f}_j^{(k)}}{f_j^{o(k)}}\right) \tag{91}$$

For an ideal mixture, the above fugacity ratios simplify as follows [63] – p. 638:

$$\frac{\hat{f}_j^{(g)}}{f_j^{o(g)}}=y_jP=\frac{n_j^{(g)}}{\sum_l^{NC}n_l^{(g)}}P \tag{92}$$

$$\frac{\hat{f}_j^{(l)}}{f_j^{o(l)}}=x_j=\frac{n_j^{(l)}}{\sum_l^{NC}n_l^{(l)}} \tag{93}$$

$$\frac{\hat{f}_j^{(s)}}{f_j^{o(s)}} = 1 \tag{94}$$

In turn, this implies that for a gas-liquid-solid ideal mixture the following holds:

$$G = \sum_j^{NC} n_j^{(g)} \left[\Delta G_{f_j}^{o(g)}(T) + RT \ln\left(y_j P\right) \right] + \sum_j^{NC} n_j^{(l)} \left[\Delta G_{f_j}^{o(l)}(T) + RT \ln\left(x_j\right) \right] + \sum_j^{NC} n_j^{(s)} \Delta G_{f_j}^{o(s)}(T) \tag{95}$$

Rearranging gives:

$$G = \sum_j^{NC} n_j^{(g)} \Delta G_{f_j}^{o(g)}(T) + n_j^{(l)} \Delta G_{f_j}^{o(l)}(T) + n_j^{(s)} \Delta G_{f_j}^{o(s)}(T) + RT \left[n_j^{(g)} \ln\left(y_j P\right) + n_j^{(l)} \ln\left(x_j\right) \right] \tag{96}$$

In this case, the total Gibbs free energy minimization problem becomes:

$$\left\{ \begin{array}{l} \pi\left(T, P, \{a_i\}_{i=1}^{NE}\right) \triangleq \min\limits_{\left\{n_j^{(g)}\right\}_1^{NC}, \left\{n_j^{(l)}\right\}_1^{NC}, \left\{n_j^{(s)}\right\}_1^{NC}} \sum_j^{NC} \left[\begin{array}{l} n_j^{(g)} \Delta G_{f_j}^{o(g)}(T) + n_j^{(l)} \Delta G_{f_j}^{o(l)}(T) + \\ + n_j^{(s)} \Delta G_{f_j}^{o(s)}(T) + \\ + RT \left[\begin{array}{l} n_j^{(g)} \ln\left(\dfrac{n_j^{(g)}}{\sum_l^{NC} n_l^{(g)}} P \right) + \\ + n_j^{(l)} \ln\left(\dfrac{n_j^{(l)}}{\sum_l^{NC} n_l^{(l)}} \right) \end{array} \right] \end{array} \right] \\ \qquad s.t. \quad a_i - \sum_k^{NP} \sum_j^{NC} \nu_{ij} n_j^{(k)} = 0 \quad \forall i = 1, NA \\ \qquad\qquad n_j^{(g)} \geq 0;\ n_j^{(l)} \geq 0;\ n_j^{(s)} \geq 0 \qquad \forall j = 1, NC \end{array} \right\} \tag{97}$$

2.6. WSTC Gibbs Free Energy Minimization Calculations

The general Gibbs minimization problem can be applied to the species in each reactor and solved to find the equilibrium concentrations of those species without specifying the exact

reactions taking place. Application of the general problem to the species present in reactor 1 yields the following:

$$\left\{\begin{array}{ll}
\nu \triangleq \min\limits_{n^{(l)}_{Na_2CO_3},n^{(s)}_{Na_2O},n^{(g)}_{Na},n^{(g)}_{CO_2},n^{(g)}_{O_2},n^{(g)}_{Ar}} & n^{(l)}_{Na_2CO_3}\Delta G^{o(l)}_{f_{Na_2CO_3}}(T)+n^{(s)}_{Na_2O}\Delta G^{o(s)}_{f_{Na_2O}}(T)+n^{(g)}_{Na}\Delta G^{o(g)}_{f_{Na}}(T)+ \\
 & +n^{(g)}_{CO_2}\Delta G^{o(g)}_{f_{CO_2}}(T)+n^{(g)}_{O_2}\Delta G^{o(g)}_{f_{O_2}}(T)+n^{(g)}_{Ar}\Delta G^{o(g)}_{f_{Ar}}(T)+ \\
 & +RT\left(\begin{array}{l}
n^{(l)}_{Na_2CO_3}\ln\left(\dfrac{n^{(l)}_{Na_2CO_3}}{n^{(l)}_{Na_2CO_3}}\right)+ \\
+n^{(g)}_{Na}\ln\left(\dfrac{n^{(g)}_{Na}}{n^{(g)}_{Na}+n^{(g)}_{CO_2}+n^{(g)}_{O_2}+n^{(g)}_{Ar}}P\right)+ \\
+n^{(g)}_{CO_2}\ln\left(\dfrac{n^{(g)}_{CO_2}}{n^{(g)}_{Na}+n^{(g)}_{CO_2}+n^{(g)}_{O_2}+n^{(g)}_{Ar}}P\right)+ \\
+n^{(g)}_{O_2}\ln\left(\dfrac{n^{(g)}_{O_2}}{n^{(g)}_{Na}+n^{(g)}_{CO_2}+n^{(g)}_{O_2}+n^{(g)}_{Ar}}P\right)+ \\
+n^{(g)}_{Ar}\ln\left(\dfrac{n^{(g)}_{Ar}}{n^{(g)}_{Na}+n^{(g)}_{CO_2}+n^{(g)}_{O_2}+n^{(g)}_{Ar}}P\right)+
\end{array}\right) \\
s.t. & a_{Na}-\left(2n^{(l)}_{Na_2CO_3}+2n^{(s)}_{Na_2O}+n^{(g)}_{Na}\right)=0 \\
 & a_{C}-\left(n^{(l)}_{Na_2CO_3}+n^{(g)}_{CO_2}\right)=0 \\
 & a_{O}-\left(3n^{(l)}_{Na_2CO_3}+n^{(s)}_{Na_2O}+2n^{(g)}_{CO_2}+2n^{(g)}_{O_2}\right)=0 \\
 & a_{Ar}-\left(n^{(g)}_{Ar}\right)=0 \\
 & n^{(l)}_{Na_2CO_3}\geq 0 \\
 & n^{(s)}_{Na_2O}\geq 0 \\
 & n^{(g)}_{Na}\geq 0 \\
 & n^{(g)}_{CO_2}\geq 0 \\
 & n^{(g)}_{O_2}\geq 0 \\
 & n^{(g)}_{Ar}\geq 0
\end{array}\right\} \quad (98)$$

The necessary conditions of optimality can be used on the Gibbs minimization problem to prove that it gives the same results as calculations involving the equilibrium constant. Take, for

example, a reactor that causes reaction (R1) to proceed. Application of the Gibbs minimization problem derived in (77) to this case gives:

$$\left\{\begin{array}{ll} \nu = \min\limits_{n^{(l)}_{Na_2CO_3}, n^{(g)}_{Na}, n^{(g)}_{CO_2}, n^{(g)}_{O_2}} & G\left(T, P, n^{(l)}_{Na_2CO_3}, n^{(g)}_{Na}, n^{(g)}_{CO_2}, n^{(g)}_{O_2}\right) \\ s.t. & a_{Na} - \left(2n^{(l)}_{Na_2CO_3} + n^{(g)}_{Na}\right) = 0 \\ & a_C - \left(n^{(l)}_{Na_2CO_3} + n^{(g)}_{CO_2}\right) = 0 \\ & a_O - \left(3n^{(l)}_{Na_2CO_3} + 2n^{(g)}_{CO_2} + 2n^{(g)}_{O_2}\right) = 0 \\ & n^{(l)}_{Na_2CO_3} \geq 0 \\ & n^{(g)}_{Na} \geq 0 \\ & n^{(g)}_{CO_2} \geq 0 \\ & n^{(g)}_{O_2} \geq 0 \end{array}\right\} \tag{99}$$

Assuming a minimum exists, application of the necessary conditions of optimality, shown by (76), to this problem yields the following:

$$
\left\{
\begin{array}{l}
\dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{Na_2CO_3}^{(l)}} - 2\lambda_{Na} - \lambda_C - 3\lambda_O - \omega_{Na_2CO_3} = 0 \\
\dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{Na}^{(g)}} - \lambda_{Na} - \omega_{Na} = 0 \\
\dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{CO_2}^{(g)}} - \lambda_C - 2\lambda_O - \omega_{CO_2} = 0 \\
\dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{O_2}^{(g)}} - 2\lambda_O - \omega_{O_2} = 0 \\
a_{Na} - \left(2n_{Na_2CO_3}^{(l)} + n_{Na}^{(g)}\right) = 0 \\
a_C - \left(n_{Na_2CO_3}^{(l)} + n_{CO_2}^{(g)}\right) = 0 \\
a_O - \left(3n_{Na_2CO_3}^{(l)} + 2n_{CO_2}^{(g)} + 2n_{O_2}^{(g)}\right) = 0 \\
\omega_{Na_2CO_3} n_{Na_2CO_3}^{(l)} = 0 \\
\omega_{Na_2} n_{Na}^{(g)} = 0 \\
\omega_{CO_2} n_{CO_2}^{(g)} = 0 \\
\omega_{O_2} n_{O_2}^{(g)} = 0 \\
-n_{Na_2CO_3}^{(l)} \le 0 \\
-n_{Na}^{(g)} \le 0 \\
-n_{CO_2}^{(g)} \le 0 \\
-n_{O_2}^{(g)} \le 0 \\
\omega_{Na_2CO_3} \ge 0 \\
\omega_{Na_2} \ge 0 \\
\omega_{CO_2} \ge 0 \\
\omega_{O_2} \ge 0
\end{array}
\right\}
\tag{100}
$$

Since all species must be present at equilibrium for this decomposition, even if in very small amounts, $\omega_i = 0 \;\; \forall i$. This allows the problem presented in (100) to be reduced to:

$$\left\{\begin{array}{l}\dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{Na_2CO_3}^{(l)}}-2\lambda_{Na}-\lambda_C-3\lambda_O=0\\ \dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{Na}^{(g)}}-\lambda_{Na}=0\\ \dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{CO_2}^{(g)}}-\lambda_C-2\lambda_O=0\\ \dfrac{\partial G\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)}{\partial n_{O_2}^{(g)}}-2\lambda_O=0\end{array}\right\} \tag{101}$$

Using the definition of the chemical potential, given by equation (81), gives:

$$\left\{\begin{array}{l}\mu_{Na_2CO_3}^{(l)}\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)-2\lambda_{Na}-\lambda_C-3\lambda_O=0\\ \mu_{Na}^{(g)}\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)-\lambda_{Na}=0\\ \mu_{CO_2}^{(g)}\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)-\lambda_C-2\lambda_O=0\\ \mu_{O_2}^{(g)}\left(T,P,n_{Na_2CO_3}^{(l)},n_{Na}^{(g)},n_{CO_2}^{(g)},n_{O_2}^{(g)}\right)-2\lambda_O=0\end{array}\right\} \tag{102}$$

Application of equation (90) to (102) yields the following:

$$\left\{\begin{array}{l}G_{Na_2CO_3}^{o(l)}\left(T\right)+RT\ln\left(\dfrac{\hat{f}_{Na_2CO_3}^{(l)}}{f_{Na_2CO_3}^{o(l)}}\right)-2\lambda_{Na}-\lambda_C-3\lambda_O=0\\ G_{Na}^{o(g)}\left(T\right)+RT\ln\left(\dfrac{\hat{f}_{Na}^{(g)}}{f_{Na}^{o(g)}}\right)-\lambda_{Na}=0\\ G_{CO_2}^{o(g)}\left(T\right)+RT\ln\left(\dfrac{\hat{f}_{CO_2}^{(g)}}{f_{CO_2}^{o(g)}}\right)-\lambda_C-2\lambda_O=0\\ G_{O_2}^{o(g)}\left(T\right)+RT\ln\left(\dfrac{\hat{f}_{O_2}^{(g)}}{f_{O_2}^{o(g)}}\right)-2\lambda_O=0\end{array}\right\} \tag{103}$$

Using the same simplifications for the fugacity ratios and the Gibbs energy as shown in equations (92) to (94) gives:

$$\left\{\begin{array}{l}\Delta G^{o(l)}_{f_{Na_2CO_3}}(T)+RT\ln\left(x_{Na_2CO_3}\right)-2\lambda_{Na}-\lambda_C-3\lambda_O=0\\ \Delta G^{o(g)}_{f_{Na}}(T)+RT\ln\left(P_{Na}\right)-\lambda_{Na}=0\\ \Delta G^{o(g)}_{f_{CO_2}}(T)+RT\ln\left(P_{CO_2}\right)-\lambda_C-2\lambda_O=0\\ \Delta G^{o(g)}_{f_{O_2}}(T)+RT\ln\left(P_{O_2}\right)-2\lambda_O=0\end{array}\right\} \tag{104}$$

Since sodium carbonate is the only species in the liquid phase, this reduces to:

$$\left\{\begin{array}{l}\Delta G^{o(l)}_{f_{Na_2CO_3}}(T)-2\lambda_{Na}-\lambda_C-3\lambda_O=0\\ \Delta G^{o(g)}_{f_{Na}}(T)+RT\ln\left(P_{Na}\right)-\lambda_{Na}=0\\ \Delta G^{o(g)}_{f_{CO_2}}(T)+RT\ln\left(P_{CO_2}\right)-\lambda_C-2\lambda_O=0\\ \Delta G^{o(g)}_{f_{O_2}}(T)+RT\ln\left(P_{O_2}\right)-2\lambda_O=0\end{array}\right\} \tag{105}$$

The equilibrium constant for the decomposition of sodium carbonate into sodium, carbon dioxide, and water is defined as:

$$K \triangleq \exp\left[\frac{-\Delta G^{o}_{rxn}(T)}{RT}\right]=\exp\left[\frac{-\left(4\Delta G^{o(l)}_{f_{Na}}(T)+2\Delta G^{o(g)}_{f_{CO_2}}(T)+\Delta G^{o(g)}_{f_{O_2}}(T)-2\Delta G^{o(g)}_{f_{Na_2CO_3}}(T)\right)}{RT}\right] \tag{106}$$

Solving for the Gibbs energy of formation of each species in (105) and substituting into the expression for the equilibrium constant gives:

$$\left\{\begin{array}{l}K=\exp\left[\frac{-\Delta G^{o}_{rxn}(T)}{RT}\right]=\\ =\exp\left[\frac{-\left(4\Delta G^{o(l)}_{f_{Na}}(T)+2\Delta G^{o(g)}_{f_{CO_2}}(T)+\Delta G^{o(g)}_{f_{O_2}}(T)-2\Delta G^{o(g)}_{f_{Na_2CO_3}}(T)\right)}{RT}\right]=\\ =\exp\left[\frac{\left[\begin{array}{l}4RT\ln\left(P_{Na}\right)-4\lambda_{Na}+2RT\ln\left(P_{CO_2}\right)-2\lambda_C+\\ -4\lambda_O+RT\ln\left(P_{O_2}\right)-2\lambda_O+4\lambda_{Na}+2\lambda_C+6\lambda_O\end{array}\right]}{RT}\right]=\\ \exp\left[4\ln\left(P_{Na}\right)+2\ln\left(P_{CO_2}\right)+\ln\left(P_{O_2}\right)\right]=P^4_{Na}P^2_{CO_2}P_{O_2}\end{array}\right\} \tag{107}$$

This result demonstrates that the Gibbs minimization problem and solution using equilibrium constants will give the same solution.

For the species present in reactor 2, this minimization problem is given by:

$$\left\{\begin{array}{ll} \nu \triangleq \min\limits_{n_{Na}^{(l)},n_{H_2O}^{(g)},n_{NaOH}^{(l)},n_{H_2}^{(g)}} & n_{Na}^{(l)}\Delta G_{f_{Na}}^{o(l)}\left(T\right)+n_{NaOH}^{(l)}\Delta G_{f_{NaOH}}^{o(l)}\left(T\right)+ \\ & +n_{H_2}^{(g)}\Delta G_{f_{H_2}}^{o(g)}\left(T\right)+n_{H_2O}^{(g)}\Delta G_{f_{H_2O}}^{o(g)}\left(T\right)+ \\ & +RT\left(\begin{array}{l} n_{Na}^{(l)}\ln\left(\dfrac{n_{Na}^{(l)}}{n_{Na}^{(l)}+n_{NaOH}^{(l)}}\right)+n_{NaOH}^{(l)}\ln\left(\dfrac{n_{NaOH}^{(l)}}{n_{Na}^{(l)}+n_{NaOH}^{(l)}}\right)+ \\ +n_{H_2}^{(g)}\ln\left(\dfrac{n_{H_2}^{(g)}}{n_{H_2}^{(g)}+n_{H_2O}^{(g)}}P\right)+n_{H_2O}^{(g)}\ln\left(\dfrac{n_{H_2O}^{(g)}}{n_{H_2}^{(g)}+n_{H_2O}^{(g)}}P\right) \end{array}\right) \\ s.t. & a_{Na}-\left(n_{Na}^{(l)}+n_{NaOH}^{(l)}\right)=0 \\ & a_H-\left(n_{NaOH}^{(l)}+2n_{H_2}^{(g)}+2n_{H_2O}^{(g)}\right)=0 \\ & a_O-\left(n_{NaOH}^{(l)}+n_{H_2O}^{(g)}\right)=0 \\ & n_{Na}^{(l)}\geq 0 \\ & n_{NaOH}^{(l)}\geq 0 \\ & n_{H_2}^{(g)}\geq 0 \\ & n_{H_2O}^{(g)}\geq 0 \end{array}\right\} \quad (108)$$

For the species present in reactor 3, this minimization problem is given by:

$$\left\{\begin{array}{ll}
\nu \triangleq \min\limits_{n^{(l)}_{Na_2CO_3}, n^{(l)}_{NaOH}, n^{(g)}_{CO_2}, n^{(g)}_{H_2O}} & n^{(l)}_{Na_2CO_3}\Delta G^{o(l)}_{f_{Na_2CO_3}}(T) + n^{(l)}_{NaOH}\Delta G^{o(l)}_{f_{NaOH}}(T) + \\
& +n^{(g)}_{CO_2}\Delta G^{o(g)}_{f_{CO_2}}(T) + n^{(g)}_{H_2O}\Delta G^{o(g)}_{f_{H_2O}}(T) + \\
& +RT\left(\begin{array}{l} n^{(l)}_{Na_2CO_3}\ln\left(\dfrac{n^{(l)}_{Na_2CO_3}}{n^{(l)}_{Na_2CO_3}+n^{(l)}_{NaOH}}\right) + n^{(l)}_{NaOH}\ln\left(\dfrac{n^{(l)}_{NaOH}}{n^{(l)}_{Na_2CO_3}+n^{(l)}_{NaOH}}\right) + \\ +n^{(g)}_{CO_2}\ln\left(\dfrac{n^{(g)}_{CO_2}}{n^{(g)}_{CO_2}+n^{(g)}_{H_2O}+n^{(g)}_{Ar}}P\right) + n^{(g)}_{H_2O}\ln\left(\dfrac{n^{(g)}_{H_2O}}{n^{(g)}_{CO_2}+n^{(g)}_{H_2O}+n^{(g)}_{Ar}}P\right)\end{array}\right) \\
s.t. & a_{Na} - \left(2n^{(l)}_{Na_2CO_3} + n^{(l)}_{NaOH}\right) = 0 \\
& a_C - \left(n^{(l)}_{Na_2CO_3} + n^{(g)}_{CO_2}\right) = 0 \\
& a_H - \left(n^{(l)}_{NaOH} + 2n^{(g)}_{H_2O}\right) = 0 \\
& a_O - \left(3n^{(l)}_{Na_2CO_3} + n^{(l)}_{NaOH} + 2n^{(g)}_{CO_2} + n^{(g)}_{H_2O}\right) = 0 \\
& a_{Ar} - \left(n^{(g)}_{Ar}\right) = 0 \\
& n^{(l)}_{Na_2CO_3} \geq 0 \\
& n^{(l)}_{NaOH} \geq 0 \\
& n^{(g)}_{CO_2} \geq 0 \\
& n^{(g)}_{H_2O} \geq 0 \\
& n^{(g)}_{Ar} \geq 0
\end{array}\right\} \quad (109)$$

For each reaction, the minimization is carried out using Microsoft Excel's solver function by minimizing the objective function subject to the given constraints.

2.7. WSTC Flash Separation Process Calculation Inside Separator 1

For the flash calculation, the vapor pressure of sodium as a function of temperature was compared between [64], given by equation(110), and [65], given by equation (111). Both curves were nearly identical and [64] was used for the calculations. Equations (110) and (111) are given by [64] and [65] respectively where P_{Na} is in bar and T is in Kelvin.

$$\log P_{Na} = 4.51961 - \frac{5202.12}{T} \tag{110}$$

$$\log P_{Na} = 4.521 - \frac{5220}{T} \tag{111}$$

Consider a liquid-vapor phase equilibrium process. For such an operation the following equations must hold, [66] – p. 147:

$$\left[\begin{array}{l}
\left\{\begin{array}{ll} y_j V + x_j L = z_j F & \forall j = 1, NC \\ \mu_j^{(g)} = \mu_j^{(l)} & \forall j = 1, NC \\ \sum_{j=1}^{NC} y_j = 1 & \\ \sum_{j=1}^{NC} x_j = 1 & \\ \sum_{j=1}^{NC} z_j = 1 & \end{array}\right\} \underset{ideal\ liquid}{\overset{ideal\ vapor}{\Rightarrow}} \left\{\begin{array}{ll} y_j V + x_j L = z_j F & \forall j = 1, NC \\ y_j P = x_j P_j^{sat}(T) & \forall j = 1, NC \\ \sum_{j=1}^{NC} y_j = 1 & \\ \sum_{j=1}^{NC} x_j = 1 & \\ \sum_{j=1}^{NC} z_j = 1 & \end{array}\right\} \overset{K_j \triangleq \frac{P_j^{sat}(T)}{P}\ \forall j=1,NC}{\Rightarrow} \\
\left\{\begin{array}{ll} y_j V + x_j L = z_j F & \forall j = 1, NC \\ y_j = K_j x_j & \forall j = 1, NC \\ \sum_{j=1}^{NC} y_j = 1 & \\ \sum_{j=1}^{NC} x_j = 1 & \\ \sum_{j=1}^{NC} z_j = 1 & \end{array}\right\} \Rightarrow \left\{\begin{array}{ll} V + L = F & \\ x_j \left(K_j V + L\right) = z_j F & \forall j = 1, NC \\ y_j = K_j x_j & \forall j = 1, NC \\ \sum_{j=1}^{NC} y_j - \sum_{j=1}^{NC} x_j = 0 & \\ \sum_{j=1}^{NC} x_j = 1 & \\ \sum_{j=1}^{NC} z_j = 1 & \end{array}\right\}
\end{array}\right] \tag{112}$$

Further combination of the equation yields:

$$\left\{\begin{array}{l}
\dfrac{L}{F}=1-\dfrac{V}{F} \\
x_j=\dfrac{1}{1+\left(K_j-1\right)\dfrac{V}{F}}z_j \ \ \forall j=1,NC \\
y_j=\dfrac{K_j}{1+\left(K_j-1\right)\dfrac{V}{F}}z_j \ \ \forall j=1,NC \\
\displaystyle\sum_{j=1}^{NC}\dfrac{\left(K_j-1\right)}{1+\left(K_j-1\right)\dfrac{V}{F}}z_j=0 \\
\displaystyle\sum_{j=1}^{NC}x_j=1 \\
\displaystyle\sum_{j=1}^{NC}z_j=1
\end{array}\right\} \tag{113}$$

Normally, the equation $\displaystyle\sum_{j=1}^{NC}\dfrac{\left(K_j-1\right)}{1+\left(K_j-1\right)\dfrac{V}{F}}z_j=0$ is solved numerically for its unique root $\dfrac{V}{F}\in\left[0,1\right]$. However, the equations describing the behavior of the equilibrium flash considered in this work can be analytically solved as shown next.

$$\left\{\begin{array}{l}
y_{CO_2}V=z_{CO_2}F \\
y_{O_2}V=z_{O_2}F \\
y_{Na}V+x_{Na}L=z_{Na}F \\
y_{Ar}V+x_{Ar}L=z_{Ar}F \\
y_{Na}=K_{Na}x_{Na} \\
K_{Na}=\dfrac{P_{Na}^{sat}\left(T\right)}{P} \\
x_{CO_2}=0, x_{O_2}=0,\ x_{Ar}=0,\ x_{Na}=1 \\
x_{CO_2}+x_{O_2}+x_{Na}+x_{Ar}=1 \\
y_{CO_2}+y_{O_2}+y_{Na}+y_{Ar}=1 \\
z_{CO_2}+z_{O_2}+z_{Na}+z_{Ar}=1
\end{array}\right\} \Rightarrow \left\{\begin{array}{l}
y_{CO_2}V=z_{CO_2}F \\
y_{O_2}V=z_{O_2}F \\
y_{Na}V+F-V=z_{Na}F \\
y_{Ar}V=z_{Ar}F \\
y_{Na}=K_{Na} \\
K_{Na}=\dfrac{P_{Na}^{sat}\left(T\right)}{P} \\
x_{CO_2}=0, x_{O_2}=0,\ x_{Ar}=0,\ x_{Na}=1 \\
x_{CO_2}+x_{O_2}+x_{Na}+x_{Ar}=1 \\
y_{CO_2}+y_{O_2}+y_{Na}+y_{Ar}=1 \\
z_{CO_2}+z_{O_2}+z_{Na}+z_{Ar}=1
\end{array}\right\} \tag{114}$$

Further rearrangement of (114) yields:

$$\left\{\begin{array}{l} \dfrac{V}{F} = \dfrac{\left(1 - z_{Na}\right)}{\left(1 - K_{Na}\right)} \\ y_{CO_2} = z_{CO_2} \dfrac{\left(1 - K_{Na}\right)}{\left(1 - z_{Na}\right)} \\ y_{O_2} = z_{O_2} \dfrac{\left(1 - K_{Na}\right)}{\left(1 - z_{Na}\right)} \\ y_{Ar} = z_{Ar} \dfrac{\left(1 - K_{Na}\right)}{\left(1 - z_{Na}\right)} \\ y_{Na} = K_{Na} = \dfrac{P_{Na}^{sat}\left(T\right)}{P} \\ x_{CO_2} = 0, x_{O_2} = 0,\ x_{Ar} = 0,\ x_{Na} = 1 \\ z_{CO_2} + z_{O_2} + z_{Na} + z_{Ar} = 1 \end{array}\right\} \tag{115}$$

The equations shown in (115) are used to calculate the level of separation between the sodium, argon, oxygen, and carbon dioxide stream being output by Reactor 1; the flash separation takes places in Separator 1 in Figure 1. The objective of the flash separation is to condensed sodium vapor into sodium liquid in order to process this liquid metal in Reactor 2 while the stream of remaining gases is process further in Reactor 3.

3. Results and Discussion

The results from the equilibrium constant calculations for reactions(R1), (R2), (R3), and (R5) are provided below along with the results from the Gibbs free energy minimization. Results generated using equilibrium constants are presented as lines and results generated using Gibbs minimization are presented as points. Interpretations of the data shown in the following figures are also provided.

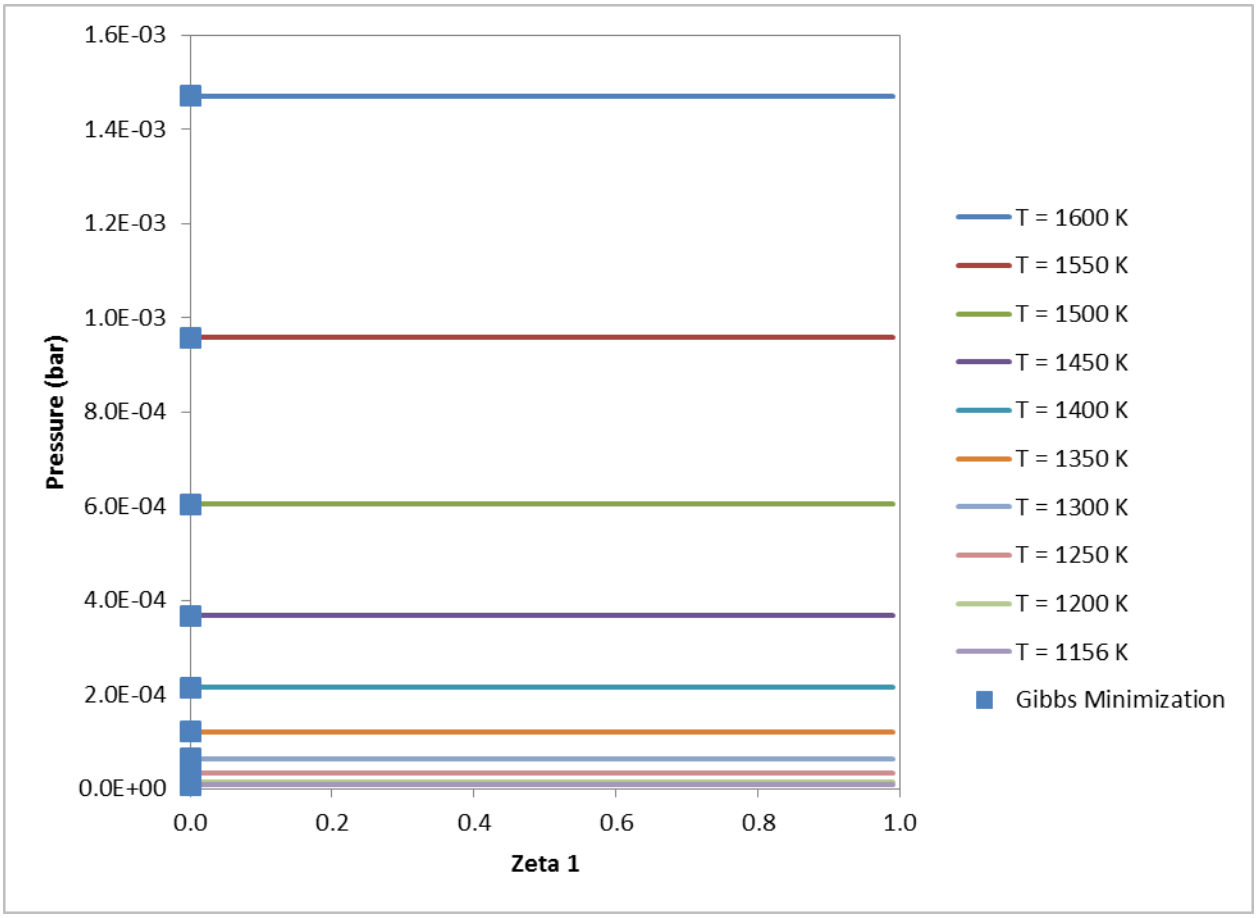

Figure 2 - Reaction (R1) pressure as a function of zeta 1 (conversion) for selected isotherms at alpha = 0 (moles of inert over moles of initial sodium carbonate).

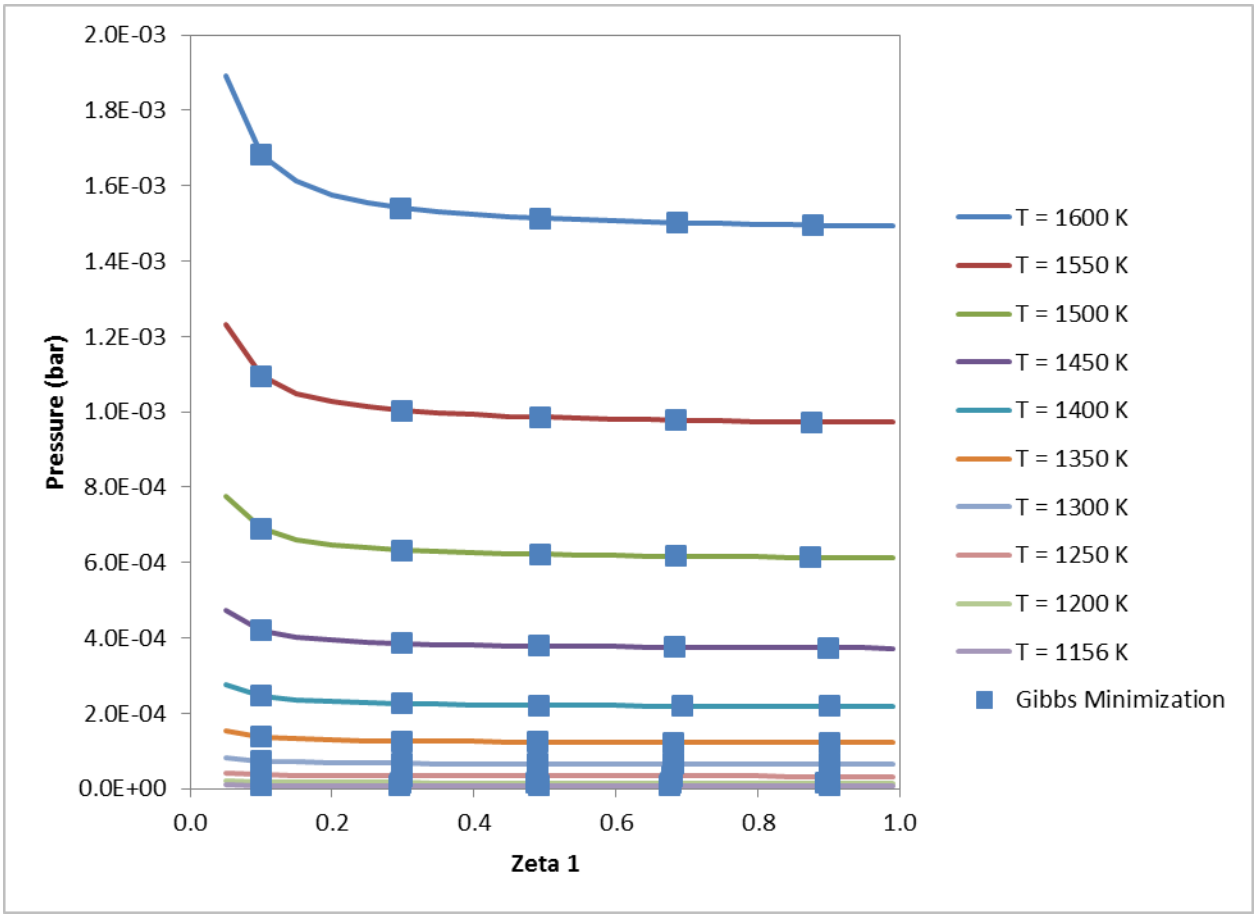

Figure 3 - Reaction (R1) pressure as a function of zeta 1 (conversion for selected isotherms at alpha = 0.05 (moles of inert over moles of initial sodium carbonate)

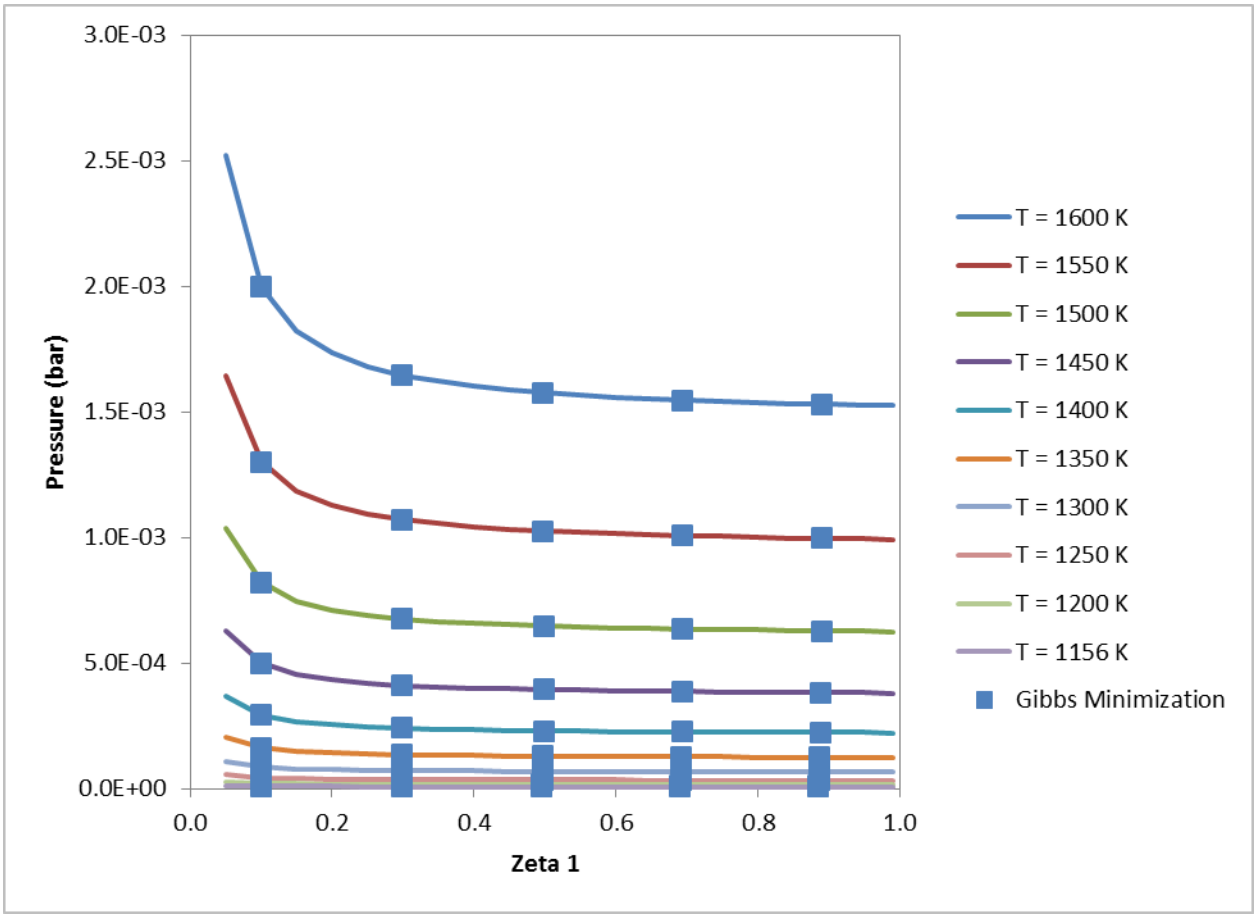

Figure 4 - Reaction (R1) pressure as a function of zeta 1 (conversion) for selected isotherms at alpha = 0.125 (moles of inert over moles of initial sodium carbonate)

As seen in Figure 2, any conversion can be achieved for a given isotherm with a constant equilibrium pressure when there is no inert present in the reaction, i.e. alpha = 0; however, these pressures are in the range of 10^{-4} to 10^{-3} bar, and according to Le Chatelier's principle the pressure needs to be less than or equal to the equilibrium pressure in order for the reaction to favor the gaseous products, that is the decomposition of the carbonate. This also applies to Figures 4 and 5 when there is an inert sweep gas present in the reaction, but the pressure has a decreasing trajectory from lower conversions to higher conversions. In addition, there is a clear increase in decomposition pressure as the ratio of moles of inert is increased as seen in the

maximum pressures displayed in Figure 2 to Figure 4. As the temperature increases the pressure increases too. Also, is it evident that both the equilibrium constant and the Gibbs free energy minimization methods yield the same result.

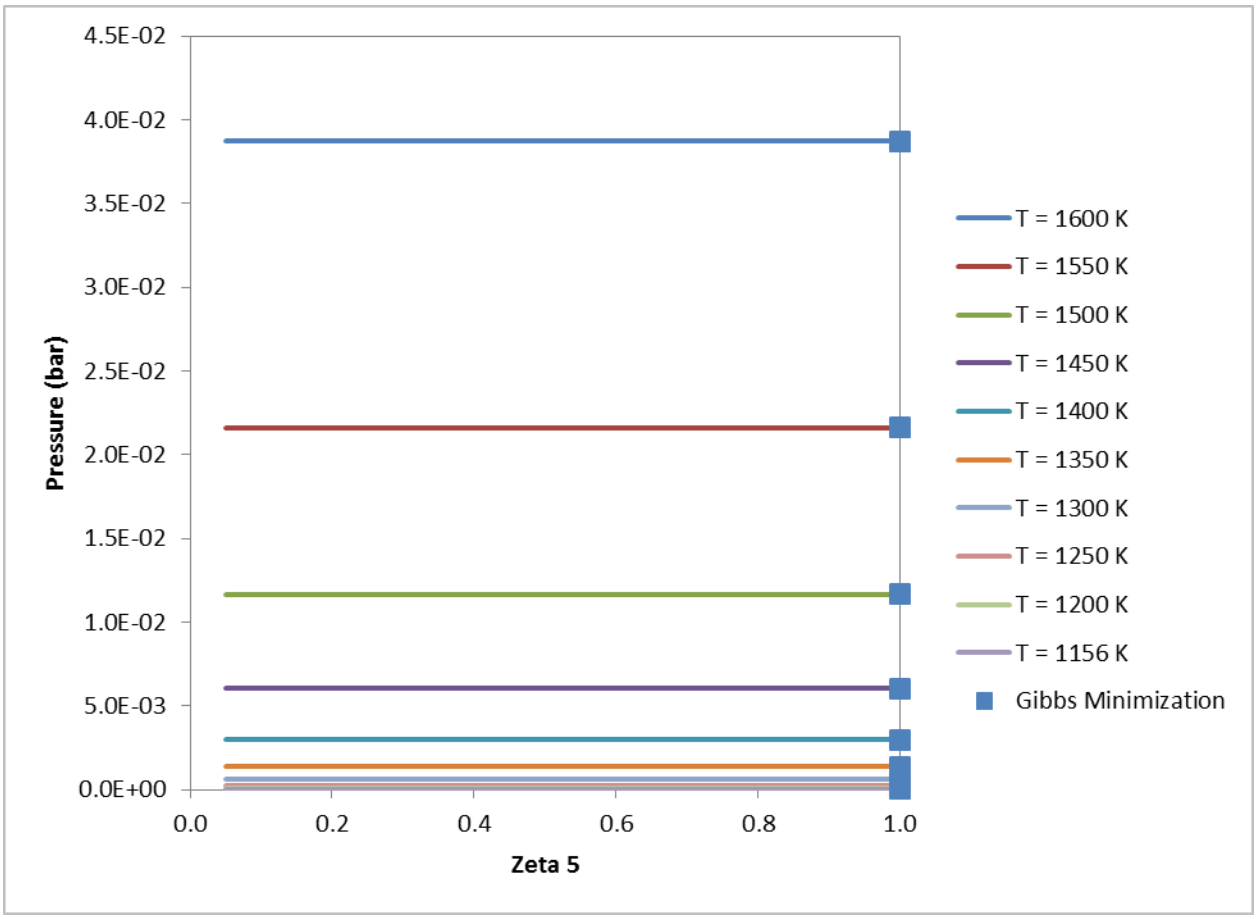

Figure 5 - Reaction (R5) pressure as a function of zeta 5 (conversion) for selected isotherms at alpha = 0 (moles of inert over moles of initial sodium oxide)

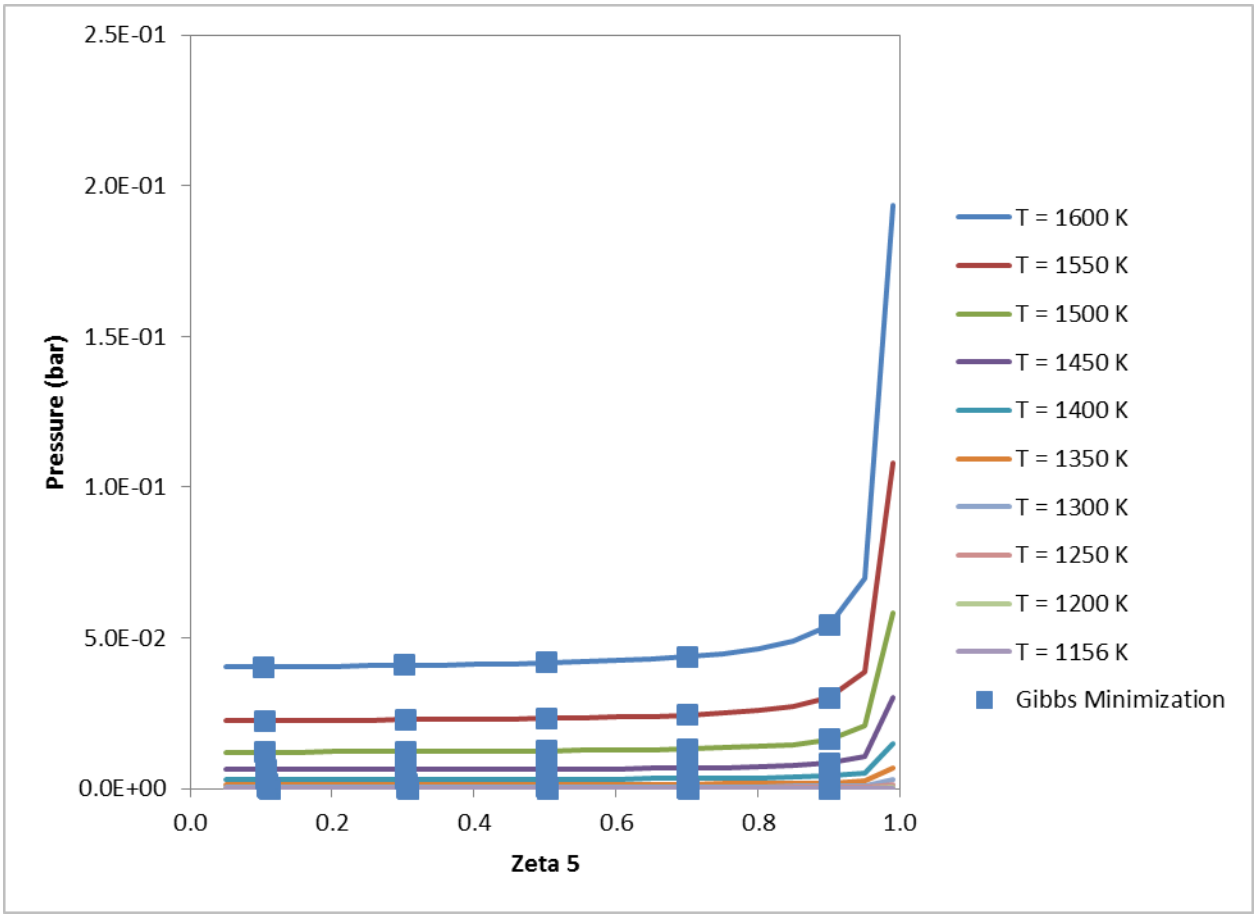

Figure 6 - Reaction (R5) pressure as a function of zeta 5 (conversion) for selected isotherms at alpha = 0.05 (moles of inert over moles of initial sodium oxide)

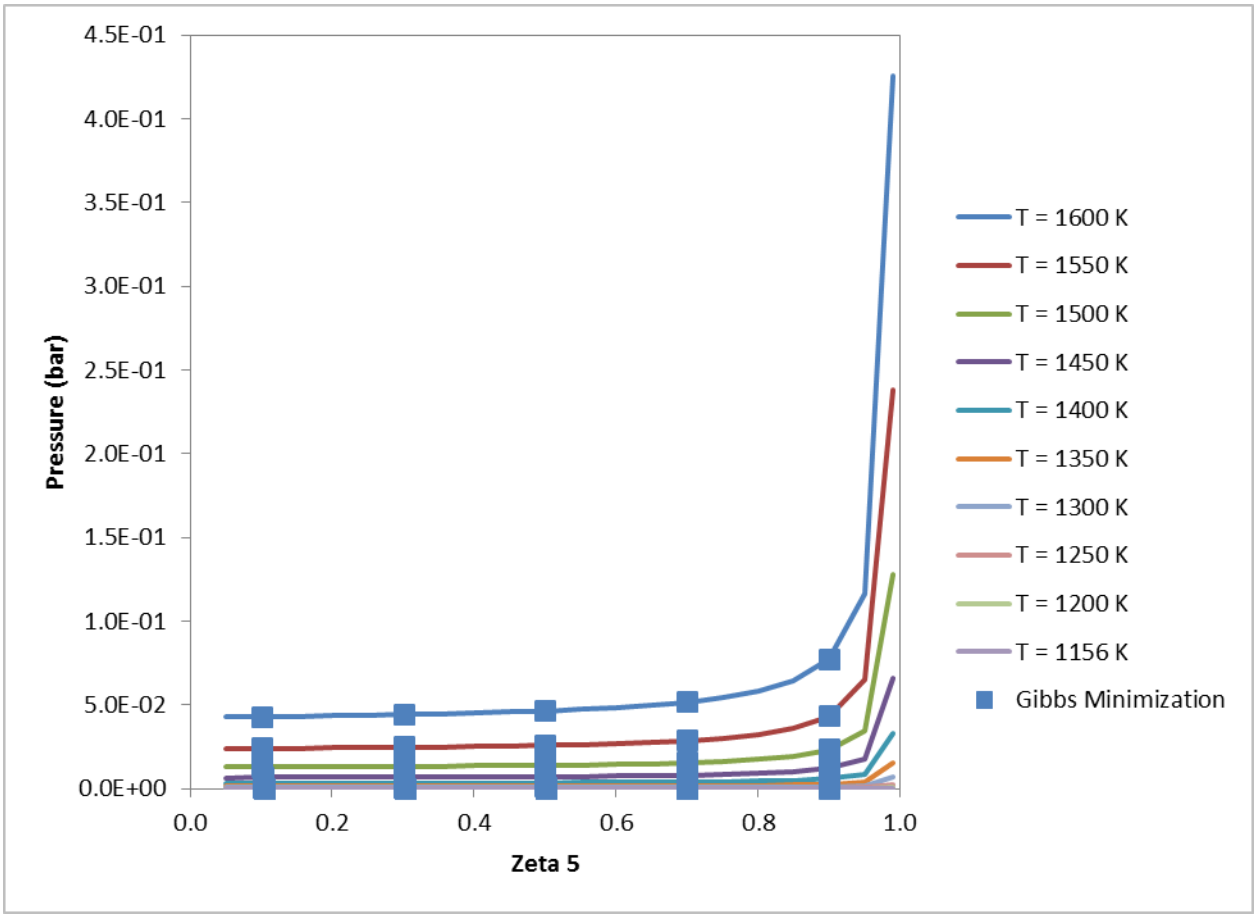

Figure 7 - Reaction (R5) pressure as a function of zeta 5 (conversion) for selected isotherms at alpha = 0.125 (moles of inert over moles of initial sodium oxide)

As seen in Figure 5, any conversion can be achieved for a given isotherm with a constant equilibrium pressure when there is no inert present in the reaction, i.e. alpha = 0; however, these pressure are in the range of 10^{-3} to 10^{-2}, and according to Le Chatelier's principle the pressure needs to be less than or equal to the equilibrium pressure in order for the reaction to favor the gaseous reactants, that is no formation of sodium oxide. This also applies to Figure 6 and Figure 7 when there is an inert sweep gas present in the reaction, but the pressure has an increasing trajectory from lower conversions to higher conversions. In addition, there is a clear increase in equilibrium pressure as the ratio of moles of inert is increased as seen in the maximum pressures

displayed in Figure 5 to Figure 7. As the temperature increases the pressure increases too. Also, is it evident that both the equilibrium constant method and the Gibbs free energy minimization method yield the same result.

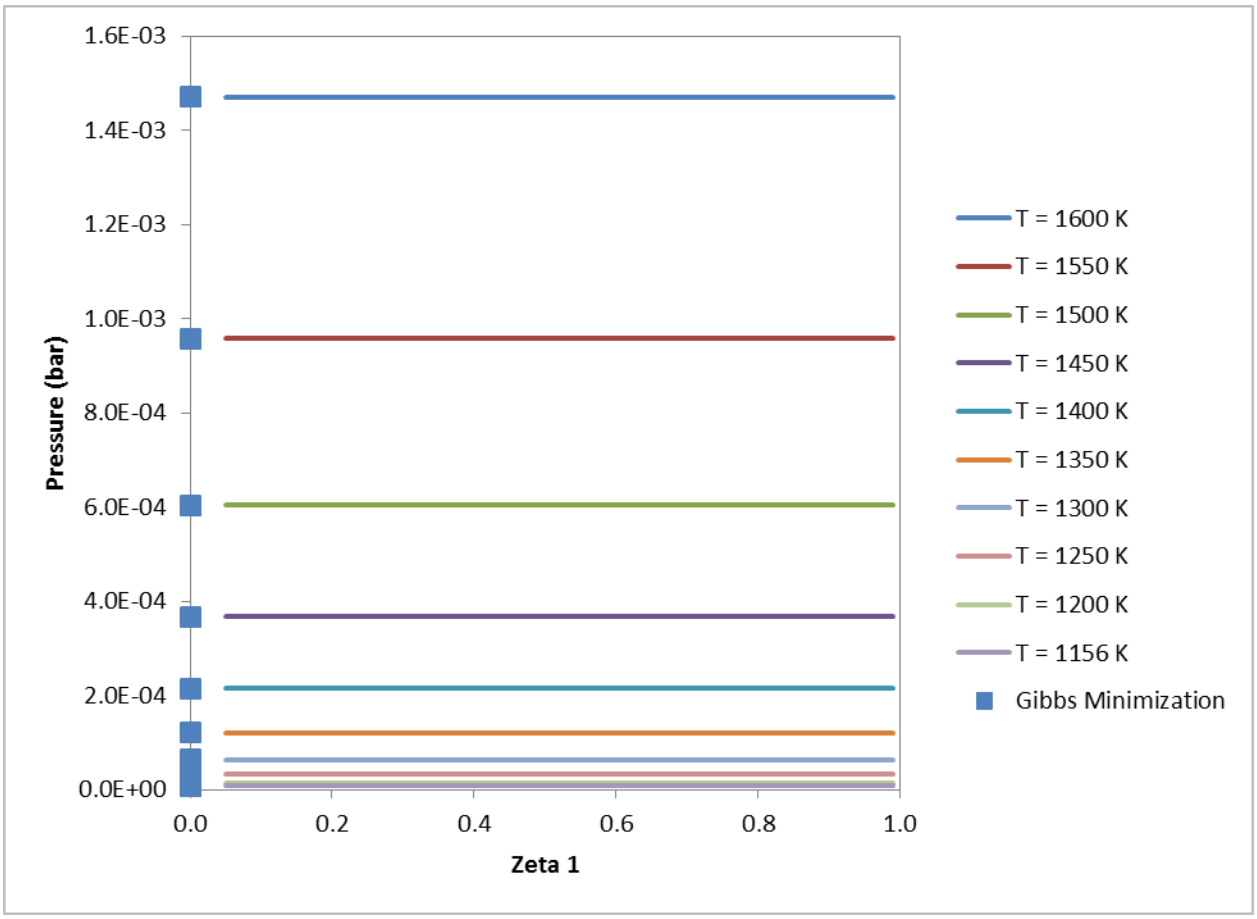

Figure 8 - Reactions (R1) and (R5) pressure as a function of zeta 1 (conversion) for selected isotherms at alpha = 0 (moles of inert over moles of initial sodium carbonate)

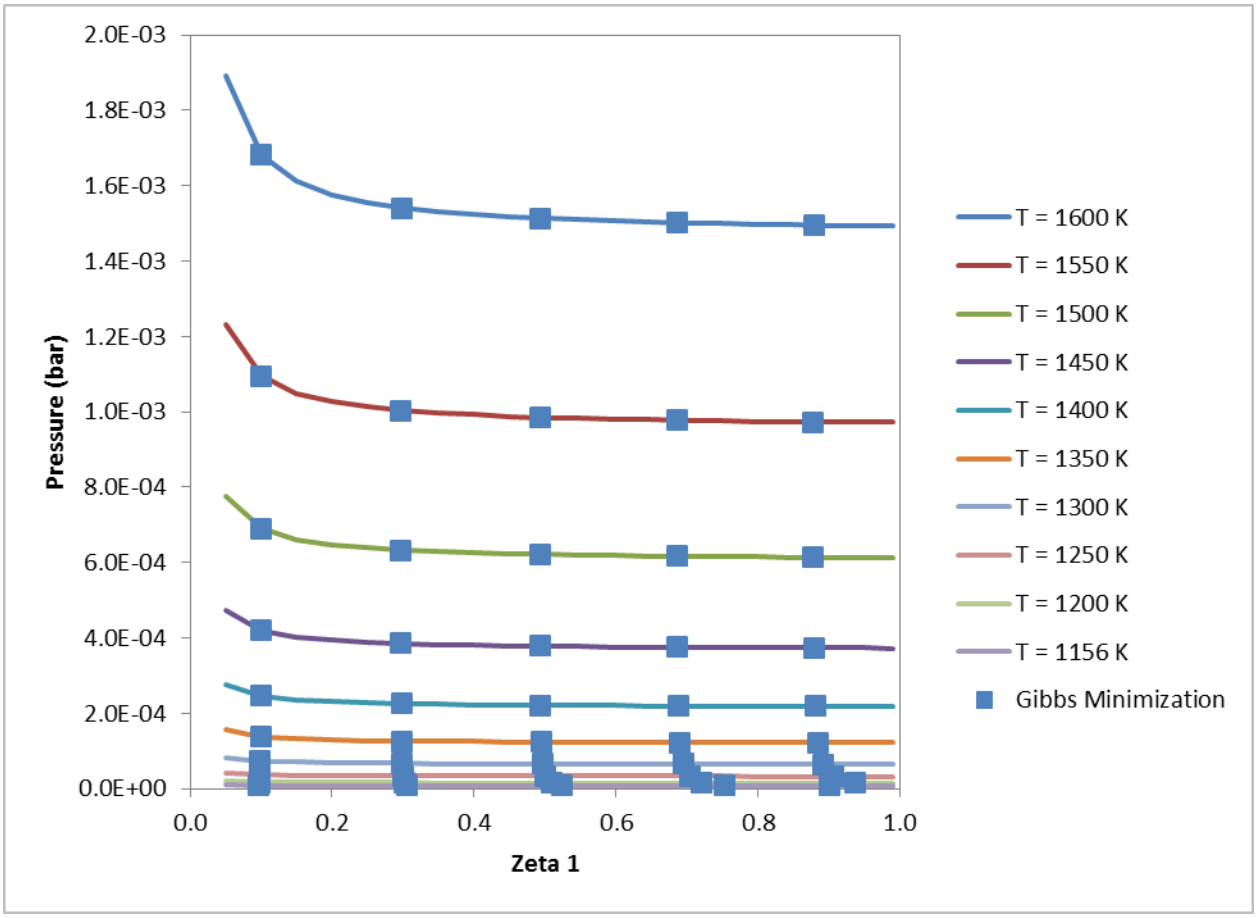

Figure 9 - Reactions (R1) and (R5) pressure as a function of zeta 1 (conversion) for selected isotherms at alpha = 0.05 (moles of inert over moles of initial sodium carbonate)

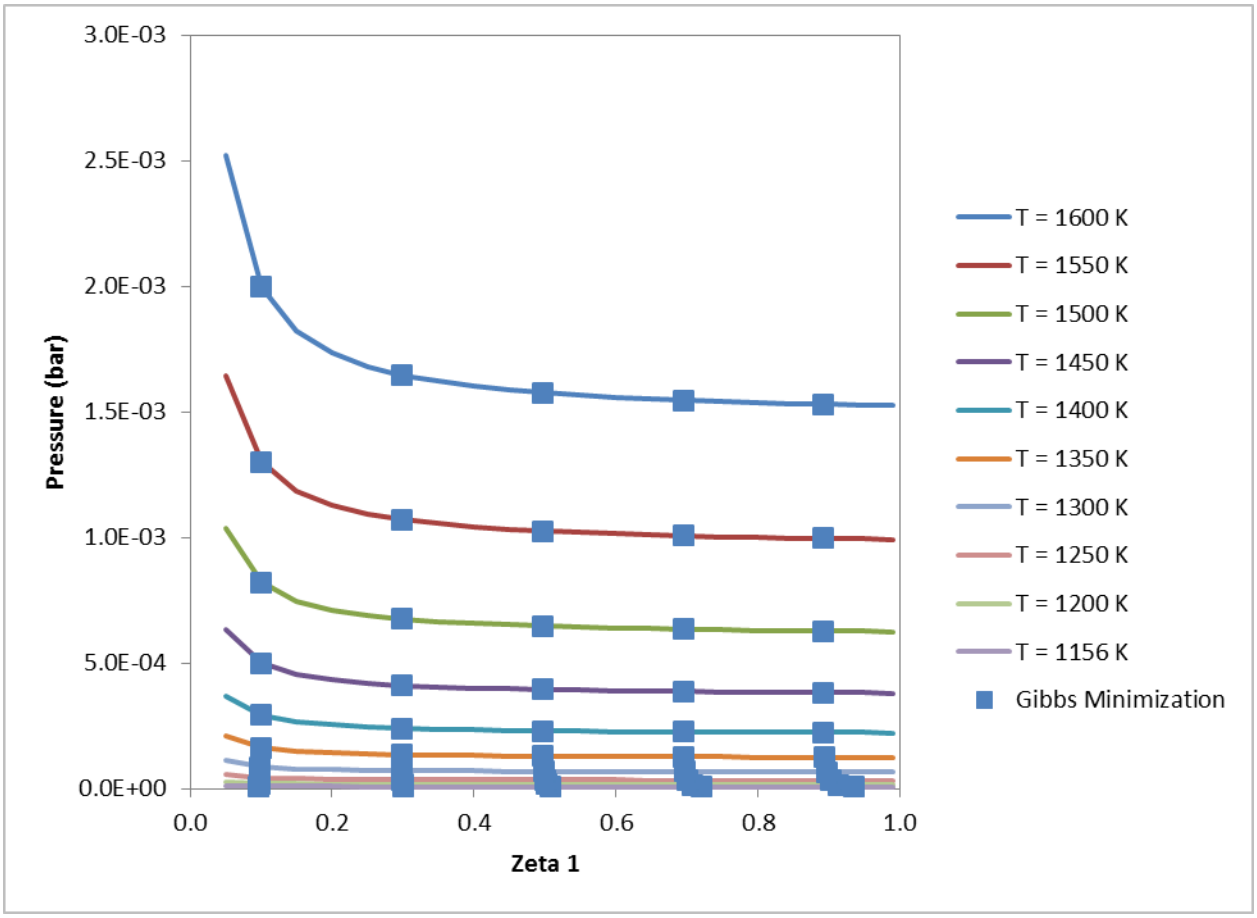

Figure 10 - Reactions (R1) and (R5) pressure as a function of zeta 1 (conversion) for selected isotherms at alpha = 0.125 (moles of inert over moles of initial sodium carbonate)

As seen in Figure 8, any conversion can be achieved for a given isotherm with a constant equilibrium pressure when there is no inert present in the reaction, i.e. alpha = 0; however, these pressure are in the range of 10^{-4} to 10^{-3} bar, and according to Le Chatelier's principle the pressure needs to be less than or equal to the equilibrium pressure in order for the reaction to favor the gaseous products, that is the decomposition of the carbonate. This also applies to Figure 9 and Figure 10 when there is an inert sweep gas present in the reaction, but the pressure has a decreasing trajectory from lower conversions to higher conversions. In addition, there is a clear increase in decomposition pressure as the ratio of moles of inert is increased as seen in the

maximum pressures displayed in Figure 8 to Figure 10. As the temperature increases the pressure increases too. Furthermore, the conversion of gaseous sodium and oxygen into sodium oxide, for all figures/cases, is below 0.7 % conversion at 1156 K while it is 0.01% conversion at 1600 K, demonstrating that the amount of sodium oxide produced from the reaction of gaseous sodium and oxygen is negligible. Also, is it evident that both the equilibrium constant method and the Gibbs free energy minimization method yield the same result.

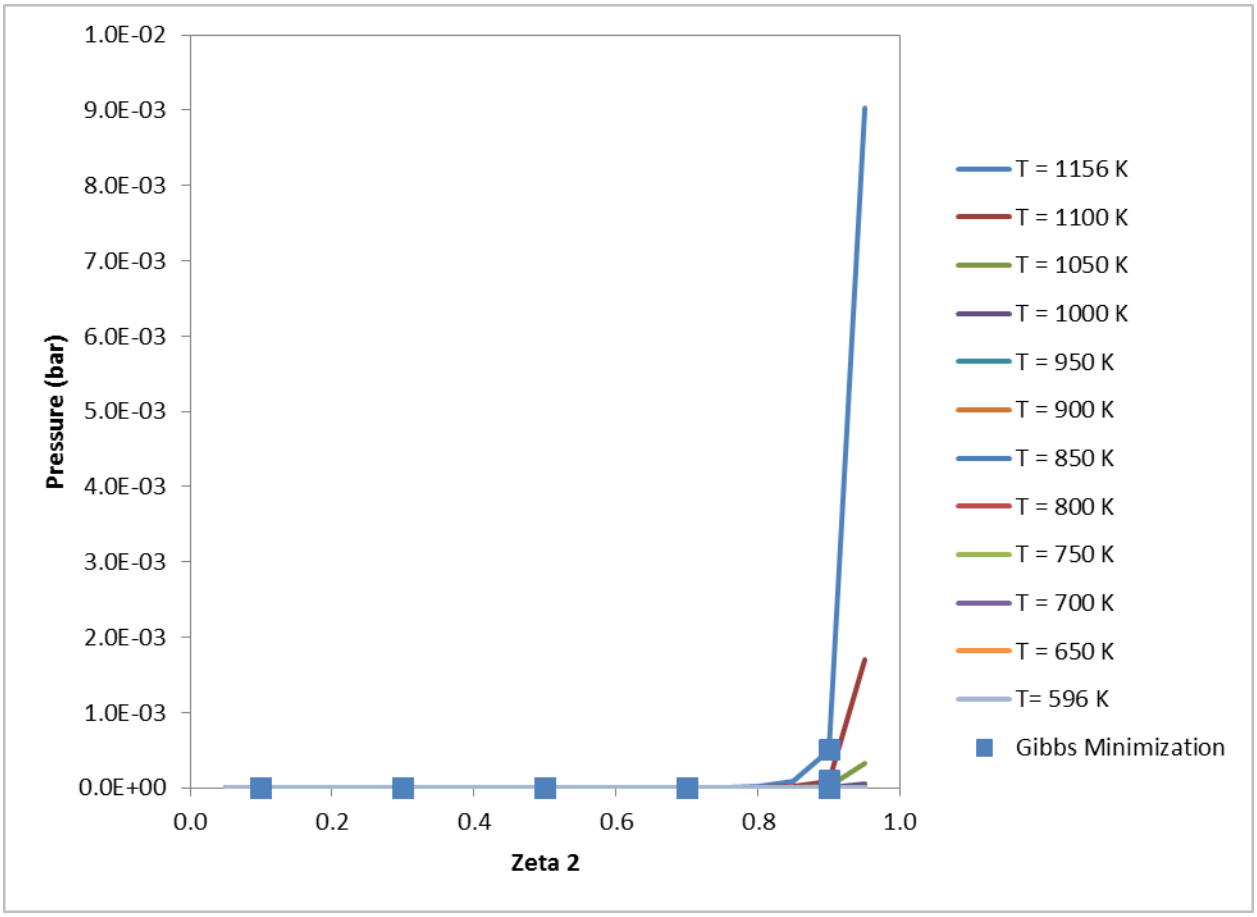

Figure 11 - Reaction (R2) pressure as a function of zeta 2 (conversion) for selected isotherms with beta = 1 (moles of water over moles of sodium)

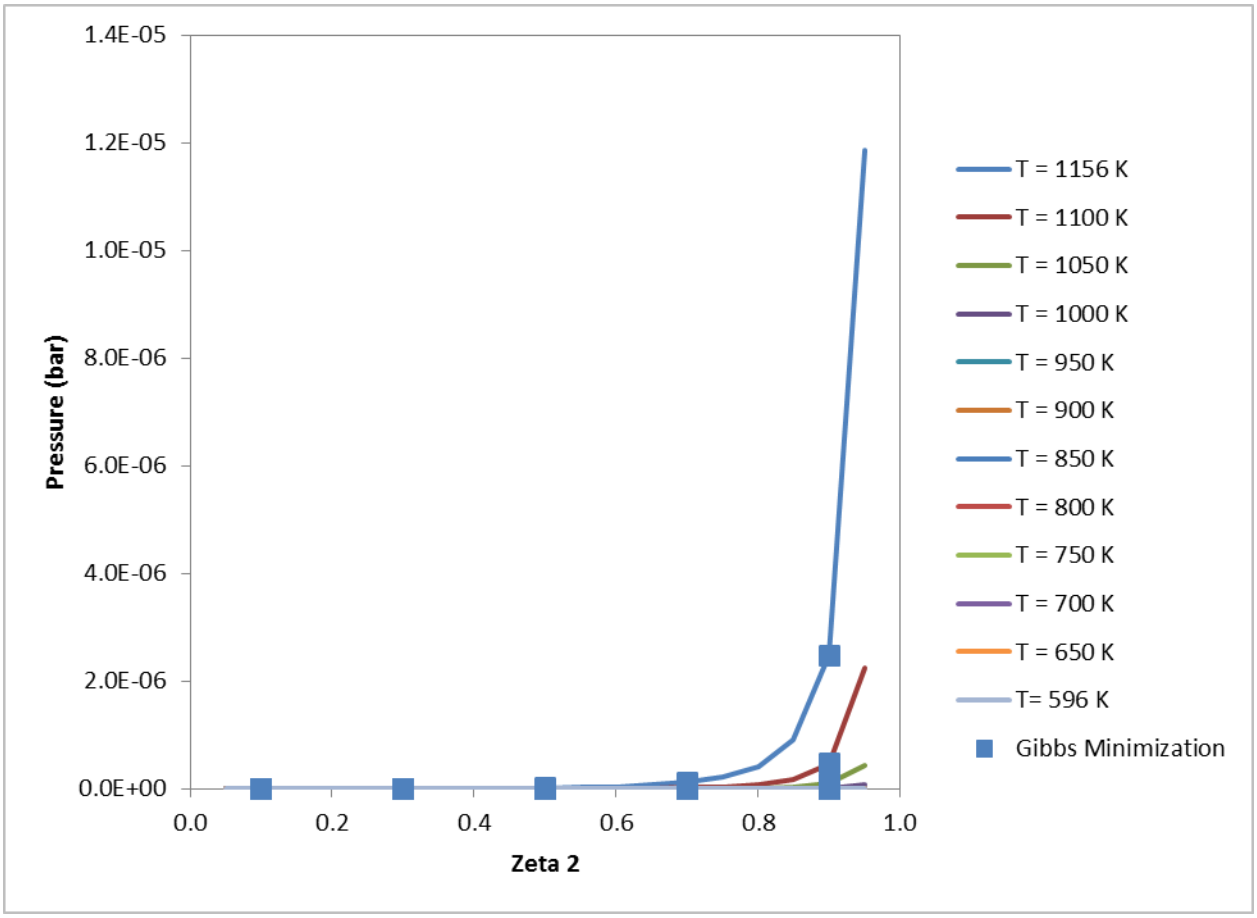

Figure 12 - Reaction (R2) pressure as a function of zeta 2 (conversion) for selected isotherms with beta = 5 (moles of water over moles of sodium)

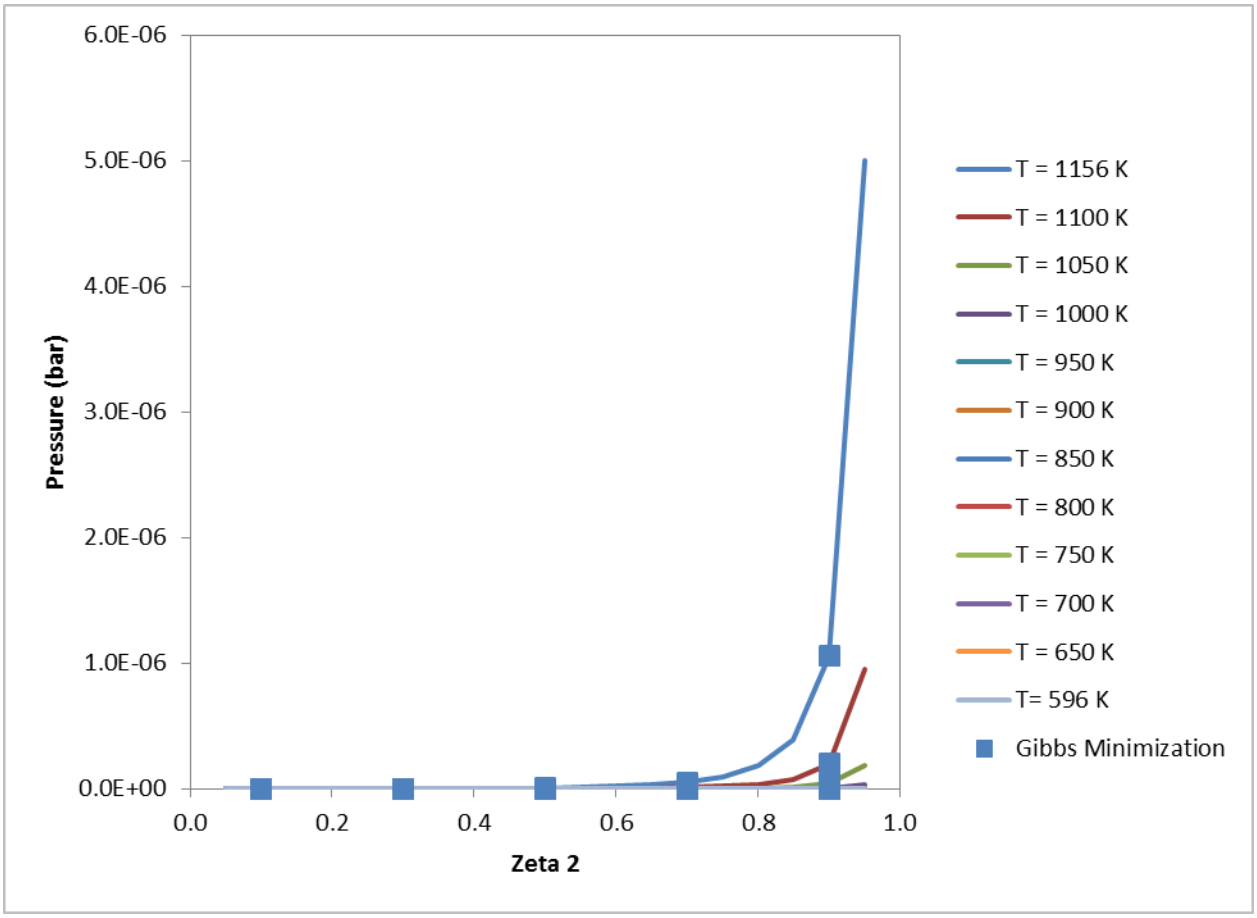

Figure 13 - Reaction (R2) pressure as a function of zeta 2 (conversion) for selected isotherms with beta = 10 (moles of water over moles of sodium)

As seen in Figure 11, Figure 12, and Figure 13, reaction (R2) yields 0.05% to 99% conversion with a corresponding pressure/temperature pair. For a given isotherm, the pressure increases monotonically with increasing conversion. According to Figure 11, 99% conversion when beta = 1 can be achieved when the pressure is greater than or equal to 6 bar at 1156 K, the sodium boiling point; however, for both beta = 5 and 10, Figure 12 and Figure 13 show that the equilibrium pressure is ~10^{-4} bar, so as long as those pressures are achieved at a minimum, the reaction will take place with 99% conversion. Since reaction (R2) has the same number of gaseous molecules on each side of the reaction equation, a change of pressure will not move the

position of the equilibrium. Also, is it evident that both the equilibrium constant method and the Gibbs free energy minimization method yield the same result.

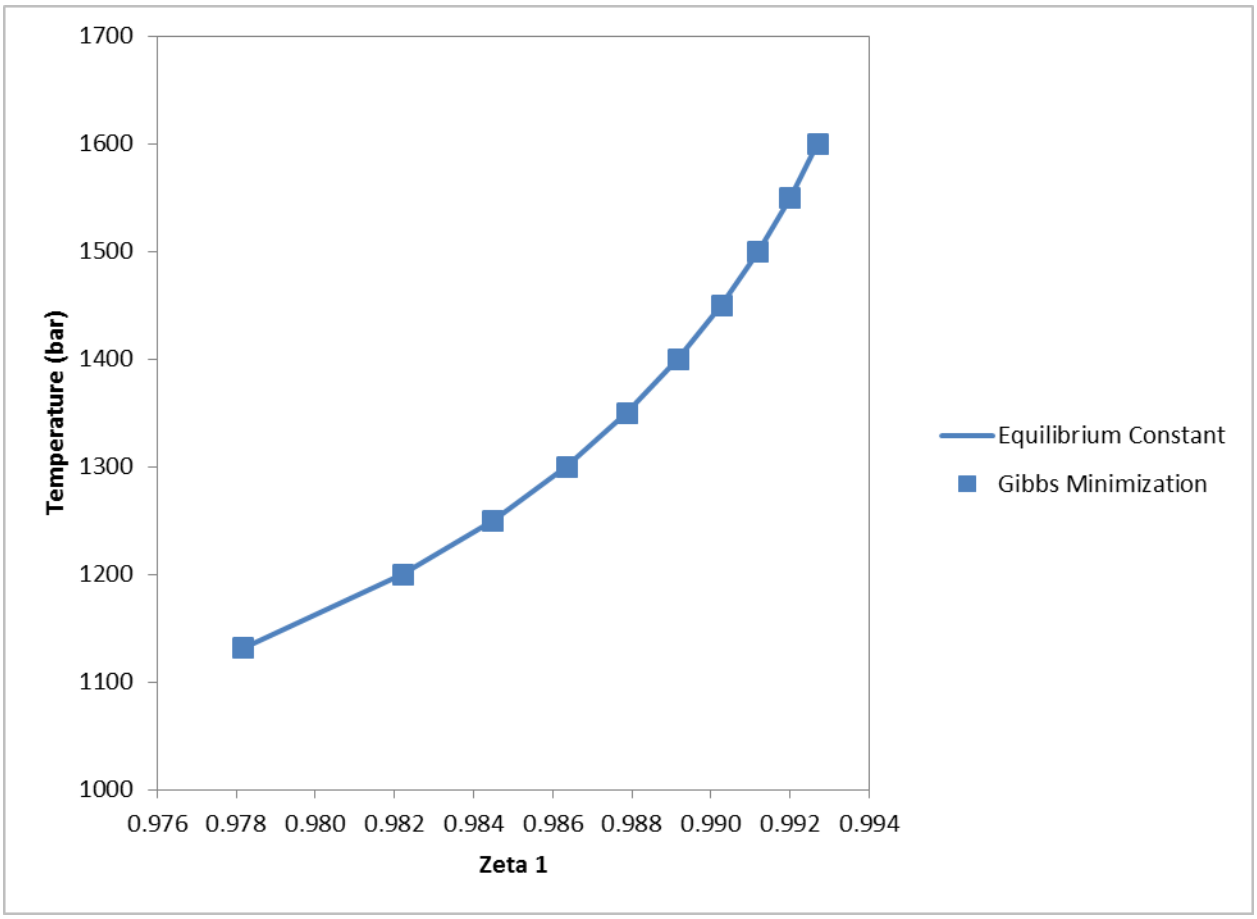

Figure 14 - Reaction (R3) temperature as a function of zeta 3 (conversion)

As seen in Figure 14, reaction (R3) yields 97% to 99% conversion in the temperature range of 1131.25 K to 1600 K. The conversion increases monotonically as temperature increases. The concentration of the inert gas, Ar, does not affect the conversion as seen in the equilibrium constant derivation for this reaction since it is independent of pressure; however, the Ar does change the equilibrium mole fractions since it modifies the total gaseous moles in the system.

Also, is it evident that both the equilibrium constant method and the Gibbs free energy minimization method yield the same result.

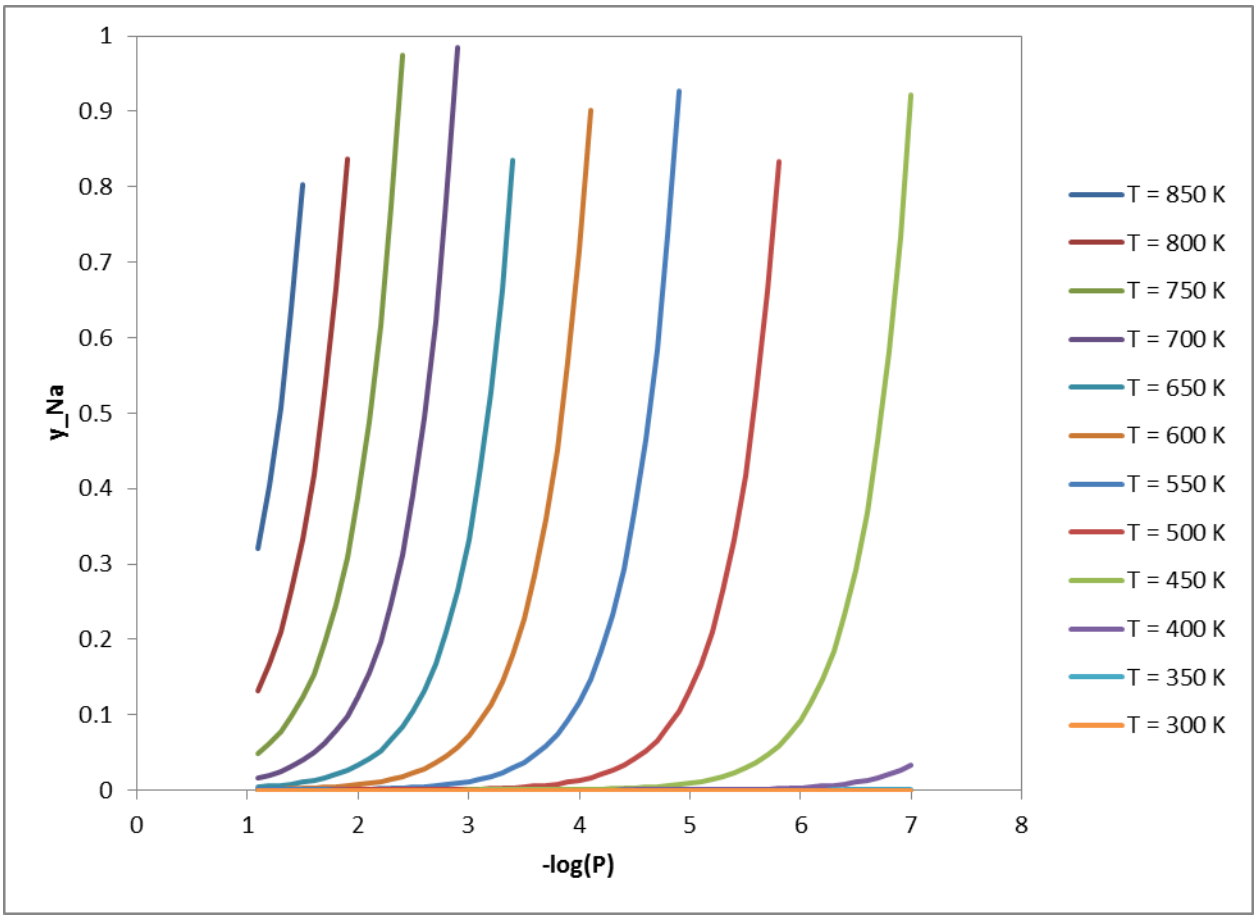

Figure 15 - Separator 1 sodium vapor concentration as a function of negative log of pressure

As shown by Figure 15, the separation achieved in Separator 1 is heavily influenced by both temperature and pressure. Reducing the pressure allows for greater separation as does reducing the temperature. As temperature and pressure increase, the vapor fraction of sodium goes to one, at which point the calculated vapor pressure has equaled or exceeded the system pressure.

4. Conclusions

In this paper, the thermodynamics of a thermochemical cycle using sodium carbonate as a catalyst to split water was examined. The feasibility of the three reactions involved in the cycle as well as one undesirable potential side reaction were examined at a variety of potential feed conditions as well as temperatures and pressures. The flash separation required by this process was also examined at a variety of temperatures and pressures. Further research must be conducted using the data provided in this work to determine appropriate operating conditions and to optimize operation of the cycle.

5. Appendix A

Table 2 - Thermodynamic constant-pressure heat capacity data for species involved in the sodium carbonate based WSTC

CO_2 (g)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	23.50610	3.80656E-02	7.40233E-05	-2.22713E-07	2.34375E-10	-1.14648E-13	2.16815E-17	0	150-1500
Kelley (1960)	44.22488	0.0087864	0	0	0	0	0	-861904	298-2500
Green (2008)	43.26256	0.01146416	0	0	0	0	0	-817972	237-1200

O_2 (g)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	29.79024	-9.48854E-03	2.85799E-05	9.87286E-09	-5.66511E-11	4.30016E-14	-1.02189E-17	0	150-1500
Kelley (1960)	28.57672	0.0037656	0	0	0	0	0	-50208	298-3000
Green (2008)	27.196	0.004184	0	0	0	0	0	0	300-3000

Na (g)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	20.786	0	0	0	0	0	0	0	150-1500
Kelley (1960)	20.79448	0	0	0	0	0	0	0	1178-2000
Green (2008)	20.79448	0	0	0	0	0	0	0	All

Na (l)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	37.04225	-1.75153E-02	9.02758E-06	2.44514E-10	0	0	0	0	371.01-2000
Kelley (1960)	28.57672	0	0	0	0	0	0	4.51872E-05	371-1178
Green (2008)	31.38	0	0	0	0	0	0	0	371-451

Na (s)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	-2.53430	0.798827	-0.0108331	7.81020E-05	-3.00440E-07	5.83138E-10	-4.47274E-13	0	100-371.01
Kelley (1960)	16.81968	0.03782336	0	0	0	0	0	0	298-371
Green (2008)	20.96184	0.02242624	0	0	0	0	0	0	273-371

Na_2CO_3 (l)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	140.01	0.048571	-1.6402E-06	0	0	0	0	0	1127-1210
Kelley (1960)	188.28	0	0	0	0	0	0	0	1124-1500
Green (2008)	-	-	-	-	-	-	-	-	-

Na_2CO_3 (s)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	132.43845	-1.89299	1.70893E-02	-6.36359E-05	1.18977E-07	-1.09244E-10	3.93361E-14	0	100-723.15
Kelley (1960)	113.51192	0.06535408	0	0	0	0	0	-1999952	298-1124
Green (2008)	120.9176	0	0	0	0	0	0	0	288-371

Na_2O (g)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	33.88794	0.15340	-4.11668E-04	5.76107E-07	-4.38413E-10	1.72843E-13	-2.76825E-17	0	150-1500
Kelley (1960)	-	-	-	-	-	-	-	-	-
Green (2008)	-	-	-	-	-	-	-	-	-

Na_2O (l)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	104.6	0	0	0	0	0	0	0	1405.2-3000
Kelley (1960)	-	-	-	-	-	-	-	-	-
Green (2008)	-	-	-	-	-	-	-	-	-

Na_2O (s)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	-14.30944	0.64003	-2.03278E-03	3.75793E-06	-3.92969E-09	2.15662E-12	-4.82882E-16	0	100-1023.15
Kelley (1960)	65.6888	0.0225936	0	0	0	0	0	0	298-1100
Green (2008)	-	-	-	-	-	-	-	-	-

NaOH (l)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	88.60908	-3.12265E-03	-2.48285E-06	7.27700E-10	0	0	0	0	600-2820
Kelley (1960)	89.5376	-0.00577392	0	0	0	0	0	0	592.3-1000
Green (2008)	-	-	-	-	-	-	-	-	-

NaOH (s)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	-52.83730	1.99743	-2.01130E-02	1.08128E-04	-3.00364E-07	4.09238E-10	-2.15960E-13	0	100-572
Kelley (1960)	1.00416	0.13564528	0	0	0	0	0	1619208	298-566
Green (2008)	-	-	-	-	-	-	-	-	-

H_2 (g)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	19.67100	6.96815E-02	-2.00098E-04	2.89493E-07	-2.22475E-10	8.81466E-14	-1.42043E-17	0	150-1500
Kelley (1960)	27.27968	0.00326352	0	0	0	0	0	50208	298-3000
Green (2008)	27.69808	0.00338904	0	0	0	0	0	0	273-2500

H_2O (g)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	33.17438	-3.24633E-03	1.74365E-05	-5.97958E-09	0	0	0	0	150-1500
Kelley (1960)	30.5432	0.01029264	0	0	0	0	0	0	298-2750
Green (2008)	34.39248	0.0006276	5.60656E-06	0	0	0	0	0	300-2500

H_2O (l)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	-22.41702	0.876972	-2.57039E-03	2.48383E-06	0	0	0	0	273.15-585
Kelley (1960)	75.47936	0	0	0	0	0	0	0	298-373
Green (2008)	276.37	-2.0901	8.125E-03	1.4116E-05	9.3701E-09	0	0	0	273.16-533.15

C (s)	A (J/(mol K))	B (J/(mol K^2))	C (J/(mol K^3))	D (J/(mol K^4))	E (J/(mol K^5))	F (J/(mol K^6))	G (J/(mol K^7))	H (J K/mol)	Range (K)
Yaws (2012)	10.89	0	0	0	0	0	0	0	298.15-303.15
Kelley (1960)	16.86152	0.00476976	0	0	0	0	0	-853536	298-2500
Green (2008)	11.183832	0.010949528	0	0	0	0	0	-489109.6	273-1373

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