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# Equilibrium conversion in Cu–Cl cycle multiphase processes of hydrogen production

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ABSTRACT

This paper performs a thermodynamic equilibrium analysis of individual steps within the copper–chlorine (Cu–Cl) thermochemical cycle of hydrogen production. The cycle has a maximum temperature of 550 °C and it involves four reaction steps – producing hydrogen, copper, hydrogen chloride and oxygen – and a cupric chloride drying step. In this paper, the chemical reaction steps of the cycle are analyzed to determine the effects of process variables on chemical equilibrium conversion. It is found that the hydrogen production reaction can occur as a two-phase gas–solid system, rather than three phases. The optimal conditions for hydrogen production occur at a temperature below 400 °C, at atmospheric pressure. The study also found that the ideal condition to minimize excess steam, and completely consume any chlorine formed during the reaction, is a temperature of 400 °C, at atmospheric pressure. The operating conditions for complete consumption of chlorine were identified by the equilibrium partial pressure of chlorine formed, during decomposition of cupric chloride solid ($CuCl_2$), and the equilibrium partial pressure of chlorine from the reverse chlorine consumption reaction. Furthermore, the ideal condition for the copper oxychloride decomposition reaction is a temperature around 500 °C, atmospheric pressure, which minimizes cuprous chloride (CuCl) vaporization.

## 1. Introduction

Hydrogen is a promising sustainable energy carrier to supply future energy needs. With current technologies, it can be generated from electricity, hydrocarbons or water splitting processes. Direct thermal decomposition of water into hydrogen and oxygen requires very high temperatures above 2000 °C, so thermochemical cycles are being developed to reduce this maximum temperature via intermediate compounds that progressively decompose the water molecules. Thermochemical cycles consist of a series of reactions for splitting water into hydrogen and oxygen. Many thermochemical cycles have been proposed and studied [1–4], but only a few have been shown to be economically viable and technically feasible [2,4]. Apart from the most well-known sulfur–iodine (S–I) cycle, Lewis and Taylor [5] identified the following other cycles as promising: cerium–chlorine (Ce–Cl), iron–chlorine (Fe–Cl), magnesium–iodine (Mg–I), vanadium–chlorine (V–Cl), copper–chlorine (Cu–Cl), copper–sulfate (Cu–$SO_4$) and hybrid chlorine. The copper–chlorine (Cu–Cl) cycle is particularly promising because of its lower temperature requirements (below 550 °C), as compared with the other above cycles.

The Argonne National Laboratory [6] demonstrated the individual steps in a Cu–Cl cycle. Lewis et al. [2,7,8] conducted systematic evaluations of the Cu–Cl thermochemical cycle. Naterer et al. [9] presented recent Canadian advances in nuclear hydrogen production, by electrolysis and the Cu–Cl cycle. Individual processes, reactor developments and other related aspects of the Cu–Cl cycle were presented. Orhan et al. [10–13] performed energy and exergy analyses for the Cu–Cl cycle. Wang et al. [14] discussed scale-up issues in the processes. The sequence of steps in the five-step Cu–Cl cycle is shown in Table 1. Fig. 1 illustrates the conceptual layout of the Cu–Cl cycle.

The Cu–Cl cycle involves four chemical reaction steps – hydrogen production (step 1), hydrogen chloride production (step 4), oxygen production (step 5) and an electrochemical step (step 2) to produce copper – as well as a drying step (step 3) for preparation of cupric chloride solid for hydrogen chloride production (step 4). Water is supplied externally, in the form of steam into the hydrogen chloride reactor (step 4), and reacted with cupric chloride solid ($CuCl_2$) to produce copper oxychloride solid ($CuOCuCl_2$) and hydrogen chloride gas (HCl). The hydrogen chloride reaction occurs between 350 and 400 °C. One of the reaction products (HCl gas) is heated and transferred to the hydrogen production step (step 1) to react with copper (Cu) between 430 and 475 °C and produce hydrogen gas

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## Nomenclature

| | |
|---|---|
| $\hat{f}_i$ | fugacity of the reacting species |
| $f_o$ | fugacity at the reference state (1 bar) |
| $\Delta G^{\circ}_{rxn}$ | Gibbs free energy of a reaction (kJ/mol) |
| $\Delta h^{\circ}_{rxn}$ | heat of reaction (kJ/mol) |
| $K_{1-5}$ | chemical equilibrium constants |
| $P$ | total pressure (bar) |
| $p$ | partial pressure (bar) |
| $R$ | gas constant (J/mol K) |
| $T$ | temperature (K) |
| $y$ | mole fraction |

*Greek letters*

| | |
|---|---|
| $\eta$ | number of moles |
| $\xi$ | extent of reaction |
| $\upsilon$ | stoichiometric coefficient |

*Subscripts*

| | |
|---|---|
| g | gas |
| $i$ | reacting species |
| l | liquid |
| s | solid |

**Table 1**
Five-step Cu–Cl thermochemical cycle.

| Step | Reaction | Temperature range (°C) |
|---|---|---|
| 1 | $2Cu(s) + 2HCl(g) \rightarrow 2CuCl(l) + H_2(g)$ | 430–475 |
| 2 | $2CuCl(s) \rightarrow 2CuCl\,(aq) \rightarrow CuCl_2(aq) + Cu(s)$ | Ambient (electrolysis) |
| 3 | $CuCl_2(aq) \rightarrow CuCl_2(s)$ | <100 |
| 4 | $2CuCl_2(s) + H_2O(g) \rightarrow CuOCuCl_2(s) + 2HCl(g)$ | 350–400 |
| 5 | $CuOCuCl_2(s) \rightarrow 2CuCl(l) + (1/2)O_2(g)$ | 530 |

and molten cuprous chloride (CuCl). The other product, copper oxychloride solid ($CuOCuCl_2$), is heated and transferred to the oxygen production step (step 5) for decomposition, at temperatures below 530 °C, to produce oxygen gas and molten cuprous chloride (CuCl). The molten cuprous chloride formed from step 1 and step 5 is transferred to the electrochemical step (step 2) to produce copper (Cu) solid and aqueous cupric chloride ($CuCl_2$). The electrochemical step is conducted at ambient conditions. The copper solid moves to the hydrogen reactor to produce hydrogen, and the other product (aqueous cupric chloride solution) is transferred to the drying process to produce cupric chloride solid ($CuCl_2$) for the hydrogen chloride production step (step 4). The cycle continues producing hydrogen and oxygen, recycling the inner products within the cycle, and only consuming water, heat and electricity from externally. This paper will examine this five-step copper–chlorine cycle, with a thermodynamic equilibrium analysis to identify suitable operating conditions to maximize equilibrium conversion.

In Table 1, the hydrogen (step 1), hydrogen chloride (step 4) and oxygen production (step 5) steps of the Cu–Cl cycle are thermal reactions, while step 2 is an electrochemical reaction. Step 3 is a drying step. The thermal reaction steps in the Cu–Cl cycle will be examined in this paper with a thermodynamic equilibrium analysis. The first thermal reaction is a hydrogen production reaction. This reaction is exothermic and reducing the temperatures will favor higher conversions. It is a two-phase reaction and becomes three-phase if the temperatures climb above 423 °C, because of melting of cuprous chloride (CuCl) at 412 °C. In the second thermal reaction, the hydrogen chloride reaction (step 4) is an endothermic reaction. It is a challenging process because of potential decomposition of cupric chloride ($CuCl_2$), and a requirement for excess steam to complete the reaction. The decomposition of $CuCl_2$ during the hydrolysis reaction is important because of its chlorine formation. The chlorine formed during the reaction must be completely consumed or minimized. The formation of CuCl is not problematic because of its presence in the subsequent reaction. Minimizing or completely consuming the chlorine formed during the reaction can be achieved by selecting suitable operating conditions for

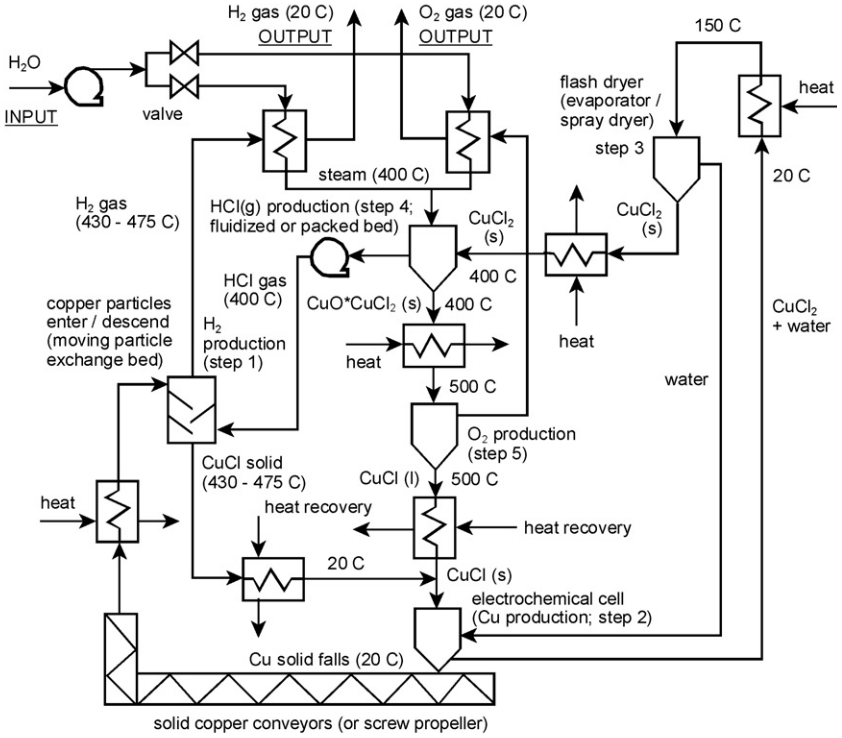

**Fig. 1.** Conceptual layout of the Cu–Cl cycle.

**Table 2**
Enthalpy and free energy formation data.

| Compound | enthalpy, kJ/mol | free energy, kJ/mol | Reference |
|---|---|---|---|
| $CuCl_2$(s) | −217.4 | −173.6 | [7] |
| CuO(s) | −155.8 | −128.4 | [7] |
| CuCl(s) | −137 | −120 | [7] |
| $CuOCuCl_2$(s) | −381.0 | −310.45 | [7] |
| HCl(g) | −92.312 | −95.29 | [25] |
| $H_2O$(g) | −241.82 | −228.57 | [25] |

the reactor. In this paper, a goal of the analysis will be complete consumption or minimization of chlorine, and suitable operating conditions to achieve this in the hydrogen chloride reaction step. For the third thermal reaction, copper oxychloride is decomposed to produce oxygen (step 5). This is an endothermic three-phase reaction with gas–liquid–solid phases. This paper will also address a challenge in this reaction step, involving the loss of cuprous chloride into the gas phase at temperatures above 500 °C.

The overall objective of this paper is to analyze the effects of varying operating conditions (such as temperature, pressure and excess reactant) on the production of hydrogen, hydrogen chloride and oxygen reaction steps of the five-step copper–chlorine thermochemical cycle, using a chemical equilibrium analysis. Also, criteria will be developed to identify the operating conditions in the hydrogen chloride reaction for complete consumption of chlorine during the reaction.

## 2. Chemical equilibrium constant of the hydrogen reaction

The equilibrium constant, $K_i$, for the hydrogen reaction will be determined from the total Gibbs free energy, which reaches a minimum at equilibrium. The values of the enthalpy of formation and the free energy of formation at 298.15 K are given in Table 2. Lewis et al. [7] observed a discrepancy in the thermodynamic data for copper–chlorine compounds reported by NIST [15] and HSC [16], and later gave corrected values. The heat capacities in the present study are given in Table 3. The chemical equilibrium constant at different temperatures will be equated with the concentration of reacting species in an individual reaction step.

The relationship between the chemical equilibrium constant, $K$, and the concentration of reacting species may be written as

$$\ln \prod \left(\frac{\hat{f}_i}{f_i^o}\right)^{\upsilon_i} = -\frac{\Delta G^\circ{}_{rxn}}{RT} = K \tag{1}$$

where $\hat{f}_i$ is fugacity of reacting species at a given condition and $f_i^o$ is the fugacity of the species at the reference state (1 bar). Also, $\Delta G^\circ{}_{rxn}$ is the Gibbs free energy of a reaction. The Gibbs energy term in the right side of the equation depends on temperature, while the left side of the equation is a function of fugacity and can be related to process variables, such as pressure and composition of the reactants, in terms of the extent of the reaction. Pressure is primarily affected by the term $\upsilon_i$, the sum of stoichiometric coefficients in the reaction. The temperature dependence of $K$ may be related to the enthalpy of reaction as follows:

$$\frac{d\ln K}{dT} = \frac{\Delta h^\circ{}_{rxn}}{RT^2} \tag{2}$$

where $\Delta h^\circ{}_{rxn} = \Delta h^\circ{}_{rxn}(T)$. The enthalpy of reaction dependence on temperature may be determined using the heat capacity, $Cp_i$, of each of the $i$ reacting species. The enthalpy of reaction at any temperature $T$ is written as

$$\Delta h^\circ{}_{rxn,T} = \Delta h^\circ{}_{rxn,298} + R\sum_i \upsilon_i \times \left(\int_{298}^{T_1} \left(C_{pi}/R\right) dT + \left(\Delta h_{pti}/R\right) + \int_{T_1}^{T} \left(C_{pi}/R\right) dT\right) \tag{3}$$

where $A$, $B$, $C$, $D$ and $E$ are the specific heat coefficients reported in Table 3 for all of the reacting species. Also, $\Delta h_{pt}$ is the phase transition enthalpy at temperature $T_1$. The hydrogen generation reaction is an exothermic non-catalytic reaction. The equilibrium constant, $K_1$, in terms of fugacity is

$$K_1 = \left(\frac{\hat{f}_{CuCl}}{f^o_{CuCl}}\right)^2 \left(\frac{\hat{f}_{H_2}}{1\,\text{bar}}\right) \left(\frac{\hat{f}_{Cu}}{f^o_{Cu}}\right)^{-2} \left(\frac{\hat{f}_{HCl}}{1\,\text{bar}}\right)^{-2} \tag{4}$$

Each of the three phases must be treated separately. For low and moderate pressures, the terms corresponding to solids and liquids become 1.

Assuming that the pressure is low enough for ideal gas conditions at equilibrium, the equilibrium constant can be re-written as

$$K_1 = \left(\frac{y_{HCl}\cdot P}{1\,\text{bar}}\right)^{-2} \left(\frac{y_{H_2}\cdot P}{1\,\text{bar}}\right) = \frac{1}{P}\frac{y_{H_2}}{y^2_{HCl}}. \tag{5}$$

where $y_{HCl}$ and $y_{H_2}$ are the mole fractions of HCl and hydrogen in the gas phase.

The mole fraction of gaseous components can be expressed in terms of the extent of reaction, $\xi_1$. The equilibrium constant, $K_1$, should be as low as possible to achieve a higher equilibrium conversion. This can be achieved by increasing the mole fraction of hydrogen chloride and total pressure of the system. The initial moles of reactants can be written as $\eta^o_{Cu} = 2$, $\eta^o_{HCl} = N_1$. The number of moles of the species in terms of the extent of the reaction, $\xi_1$, is written as $\eta_{Cu} = 2 - 2\xi_1$, $\eta_{HCl} = N_1 - \xi_1$, $\eta_{CuCl} = 2\xi_1$ and $\eta_{H_2} = \xi_1$. The total

**Table 3**
Heat capacity of species in the Cu–Cl cycle: $(Cp/R) = A_i + B_iT + C_iT^2 + D_iT^{-2} + E_iT^3$, $T$ in K.

| Compound | $A$ | $B \times 10^3$ | $C \times 10^5$ | $D \times 10^{-5}$ | $E \times 10^9$ | $T_{min}$, K | $T_{max}$, K | Reference |
|---|---|---|---|---|---|---|---|---|
| $H_2$(g) | 3.249 | 0.422 | 0 | 0.083 | 0 | 298 | 3000 | [25] |
| HCl(g) | 3.156 | 0.623 | 0 | 0.151 | 0 | 298 | 2000 | [25] |
| $Cl_2$(g) | 4.442 | 0.089 | 0 | −0.344 | 0 | 298 | 3000 | [25] |
| $H_2O$(g) | 3.47 | 1.45 | 0 | 0.121 | 0 | 298 | 2000 | [25] |
| $O_2$(g) | 3.639 | 0.506 | 0 | −0.227 | 0 | 298 | 2000 | [25] |
| Cu(s) | 2.723 | 0 | 0 | 0 | 0 | 298 | 1357 | [25] |
| $CuOCuCl_2$ | 6.461 | 40.2 | −6.28 | 0 | 0.3608 | 298 | 675 | [7,26] |
| $CuCl_2$ | 8.646 | 0 | 0 | 0 | 0 | 300 | 675 | [27] |
|  | 9.923 | 0 | 0 | 0 | 0 | 675 | 871 |  |
|  | 12.028 | 0 | 0 | 0 | 0 | 871 | 1320 |  |
| CuCl | 6.145 | 2.124 | 0 | 0.32234 | 0 | 298 | 683 | [27] |
|  | 7.549 | 0 |  | 0 | 0 | 683 | 709 |  |
|  | 7.750 | 0 | 0 | 0 | 0 | 709 | 1482 |  |

number of moles in the gas phase is $N_1 - \xi_1$ and the equilibrium constant in terms of the extent of the reaction is

$$K_1 = \frac{1}{P}\frac{\xi_1/(N_1 - \xi_1)}{((N_1 - 2\xi_1)/(N_1 - \xi_1))^2} \tag{6}$$

Rearranging this equation leads to

$$-(1 + 4K_1P)\xi_1^2 + (N_1 + 4N_1K_1P)\xi_1 - K_1PN_1^2 = 0 \tag{7}$$

The binary equation gives a direct solution for $\xi_1$, with two roots. The positive root, less than 1, will be used for predicting the extent of the reaction.

## 3. Hydrogen chloride production reaction

The hydrogen chloride production reaction in step 4 (see Table 1) is a non-catalytic gas–solid reaction. It may be divided into three parallel reaction steps as follows:

(i) copper oxychloride formation or hydrolysis reaction;

$$2CuCl_2(s) + H_2O(g) \rightarrow CuOCuCl_2(s) + 2HCl(g) \tag{8}$$

(ii) decomposition of cupric chloride;

$$2CuCl_2(s) \rightarrow 2CuCl(s) + Cl_2(g) \tag{9}$$

(iii) consumption of chlorine;

$$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + (1/2)O_2(g) \tag{10}$$

The competing reaction (Eq. (9)) along with the hydrolysis step (Eq. (8)) is a thermal decomposition of cupric chloride ($CuCl_2$) into cuprous chloride (CuCl) and chlorine ($Cl_2$). The cuprous chloride formation is not problematic because of its presence in the subsequent reaction of the thermochemical cycle, provided chlorine formation during the reaction (Eq. (9)) is completely consumed or minimized. The total consumption or minimization of chlorine is critically important in this reaction step. It may be achieved by selecting suitable operating conditions. The hydrolysis reaction (Eq. (8)) requires excess steam for complete conversion. This excess steam may also react with chlorine that is formed by decomposition of cupric chloride (Eq. (9)). A criterion is developed as follows to identify the operating conditions for complete consumption of chlorine. The equilibrium partial pressure of chlorine formed due to decomposition of cupric chloride (Eq. (9)) should be less than the equilibrium partial pressure of chlorine from the reversible chlorine consumption reaction (Eq. (10)). Eqs. (8)–(10) will be analyzed with respect to the extent of reaction and preferable operating conditions.

For the copper oxychloride formation reaction (Eq. (8)), the equilibrium constant, $K_2$, in terms of partial pressures is written as

$$K_2 = \left(\frac{y_{HCl}P}{1\ \mathrm{bar}}\right)^2 \left(\frac{y_{H_2O}P}{1\ \mathrm{bar}}\right)^{-1} = \frac{y_{HCl}^2}{y_{H_2O}}P \tag{11}$$

The mole fraction of gaseous components can be expressed in terms of the extent of the reaction, $\xi_2$. The equilibrium constant, $K_2$, should be as low as possible to permit higher equilibrium conversion. This may be achieved by increasing the mole fraction of steam and decreasing the total pressure of the system. The initial moles of reactants can be written as $\eta^o_{CuCl_2} = 2$, $\eta^o_{H_2O} = N_2$. The number of moles of the species in terms of the extent of reaction, $\xi_2$, are $\eta_{CuCl_2} = 2 - 2\xi_2$, $\eta_{H_2O} = N_2 - \xi_2$, $\eta_{Cu_2OCl_2} = \xi_2$ and $\eta_{HCl} = 2\xi_2$. The total number of moles in the gas phase is $N_2 + \xi_2$ and the equilibrium constant in terms of the extent of reaction becomes

$$K_2 = P\frac{(2\xi_2/(N_2 + \xi_2))^2}{((N_2 - \xi_2)/(N_2 + \xi_2))} \tag{12}$$

Rearranging this equation leads to

$$\xi_2 = \left(\frac{K_2N_2^2}{4P + K_2}\right)^{0.5} \tag{13}$$

This equation yields positive and negative roots. The positive value of the extent of reaction is used to determine the formation of copper oxychloride ($CuOCuCl_2$).

The chemical equilibrium constant, $K_3$, for the $CuCl_2$ decomposition reaction can be written in terms of partial pressures as

$$K_3 = (y_{Cl_2}P) = p_{Cl_2} \tag{14}$$

$$\frac{p_{Cl_2}}{P} = K_3 \tag{15}$$

The equilibrium constant, $K_3$, equals the partial pressure of $Cl_2$. The cupric chloride dissociates until the partial pressure of $Cl_2$ reaches the equilibrium constant, $K_3$, at a given temperature. The cupric chloride decomposition rate increases with temperature.

Chlorine consumption (Eq. (10)) is analyzed for both forward and backward reaction steps to determine the consumption of chlorine. The chemical equilibrium analysis determines the effect of excess steam, temperature and pressure on consumption of chlorine, whereas the reverse reaction will establish the maximum allowable equilibrium partial pressure for stable operation.

- Chlorine forward reaction (consumption reaction):

$$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + (1/2)O_2(g) \tag{16a}$$

- Chlorine reverse reaction (formation reaction):

$$2HCl(g) + (1/2)O_2(g) \rightarrow Cl_2(g) + H_2O(g) \tag{16b}$$

For the chlorine consumption reaction (Eq. (10)), the chemical equilibrium constant is written in terms of mole fractions as follows:

$$K_4 = \frac{y_{O_2}^{0.5}y_{HCl}^2}{y_{Cl_2}y_{H_2O}}P^{0.5} \tag{17}$$

The mole fraction of gaseous components can be expressed in terms of the extent of the reaction, $\xi_3$. The equilibrium constant, $K_4$, should be as low as possible to have a higher equilibrium conversion. This can be achieved by increasing the mole fraction of steam and decreasing the total pressure of the system. The initial moles of reactants can be written as $\eta^o_{Cl_2} = 1$, $\eta^o_{H_2O} = N_3$ and the number of moles of the species in terms of the extent of reaction, $\xi_3$, are $\eta_{Cl_2} = 1 - \xi_3$, $\eta_{H_2O} = N_3 - \xi_3$, $\eta_{O_2} = 0.5\xi_3$ and $\eta_{HCl} = 2\xi_3$. The total number of moles in the gas phase is $N_3 + 1 + 0.5\xi_3$. The equilibrium constant in terms of extent of reaction becomes

$$K_4 = \left(\frac{0.5\xi_3}{N_3 + 1 + 0.5\xi_3}\right)^{0.5} \left(\frac{4\xi_3^2}{(1 - \xi_3)(N_3 - \xi_3)}\right) P^{0.5}. \tag{18}$$

For the chlorine reverse reaction (Eq. (16)), the chemical equilibrium constant is written in terms of partial pressures as

$$K_5 = \frac{p_{Cl_2}p_{H_2O}}{p_{O_2}^{0.5}p_{HCl}^2} = \frac{(y_{Cl_2} \cdot P)(y_{H_2O} \cdot P)}{(y_{O_2}P)^{0.5}(y_{HCl}P)^2} \tag{19}$$

The initial moles of reactants can be written as $\eta^o_{HCl} = 2$, $\eta^o_{O_2} = N_4$ and the numbers of moles of the species in terms of the extent of reaction, $\xi_4$, are $\eta_{O_2} = N_4 - 0.5\xi_4$, $\eta_{HCl} = 2 - 2\xi_4$, $\eta_{Cl_2} = \xi_4$ and $\eta_{H_2O} = \xi_4$. The total number of moles in the gas phase is $2 + N_4 - 0.5\xi_4$ and the equilibrium constant in terms of the extent of reaction becomes

$$K_5 = \left(\frac{N_4 + 2 - 0.5\xi_4}{N_4 - 0.5\xi_4}\right)^{0.5} \frac{\xi_4^2}{(2 - 2\xi_4)^2P^{0.5}}. \tag{20}$$

where the partial pressure of chlorine may be written as

$$p_{\mathrm{Cl}_2} = (y_{\mathrm{Cl}_2} \cdot P) = \frac{\xi_4}{2 + N_4 - 0.5\xi_4} P \tag{21}$$

## 4. Oxygen production reaction

The chemical equilibrium constant, $K_5$, for the copper oxychloride ($CuOCuCl_2$) decomposition reaction step 5 (see Table 1) can be written in terms of the partial pressures as

$$K_5 = (y_{\mathrm{O}_2} P)^{0.5} = p_{\mathrm{O}_2}^{0.5} \tag{22}$$

Rearranging the equation for the equilibrium partial pressure,

$$\frac{p_{\mathrm{O}_2}}{P} = K_5^2 \tag{23}$$

The copper oxychloride dissociates until the partial pressure of $O_2$ reaches the square of the equilibrium constant, $K_5$, at a given temperature. The $CuOCuCl_2$ decomposition rate increases with temperature. In the following section, predicted results will be presented based on the previous formulations.

## 5. Results and discussion

In this section, numerical results will be presented for the effect of operating variables on the extent of the individual chemical reaction steps of hydrogen production, hydrogen chloride and oxygen generation reactions in the Cu–Cl thermochemical cycle. Fig. 2 illustrates the effects of operating pressure, temperature and excess reactant on the extent of the reaction for the hydrogen production reaction. The equilibrium conversion values have been evaluated with Eq. (7). For the exothermic reaction, an increase in temperature reduces the equilibrium conversion. The increase in the operating pressure and excess reactant hydrogen chloride raises the equilibrium conversion values. At the operating pressure of 1 bar, the equilibrium conversion values are above 90%, with 40% excess reactant (hydrogen chloride) and 55% excess reactant for complete conversion of the copper solid. The gas–solid reaction may be conducted either by increasing the operating pressure or excess reactant below 400 °C. Above 423 °C, the reaction system becomes three-phase, with gas–liquid–solid phases, because of the melting point of cuprous chloride, at about 412 °C [7].

Figs. 3–7 show the effects of varying operating parameters on the hydrogen chloride reaction. Fig. 3 depicts the variation of equilibrium conversion with operating variables for the hydrolysis reaction (Eq. (8)). The equilibrium conversion values have been calculated with Eq. (13). The predicted values are compared against experimental data [17] for the hydrolysis of $CuCl_2$ at 375 °C. The equilibrium conversion of cupric chloride increases with higher temperatures and excess steam quantities. The excess steam requirement for complete conversion of cupric chloride solid decreases at higher temperatures, from 38.5 to 26.5 mol of excess steam, for a temperature change from 375 to 400 °C. A decrease in the operating pressure also reduces the excess steam requirement.

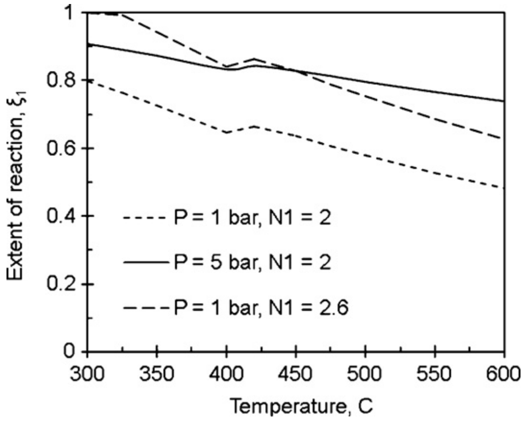

**Fig. 2.** Variation of the extent of reaction with operating variables for the hydrogen reaction.

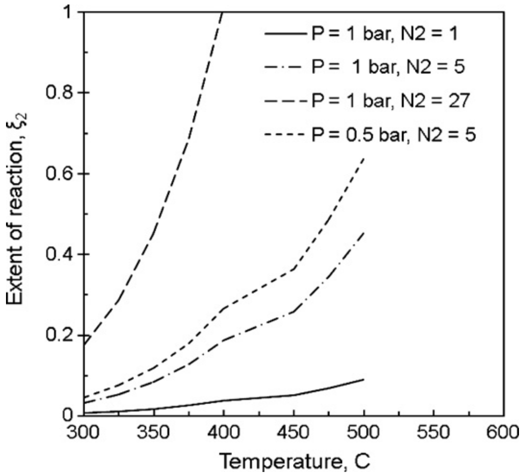

**Fig. 3.** Variation of the extent of reaction with operating variables for the hydrolysis reaction.

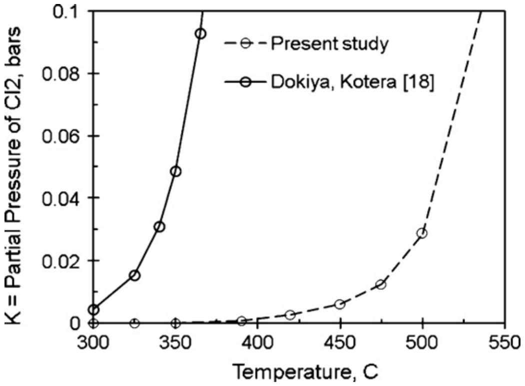

**Fig. 4.** Variation of equilibrium constant with temperature for decomposition of cupric chloride solid.

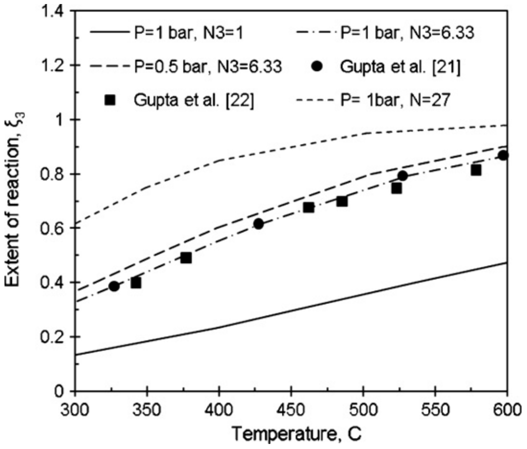

**Fig. 5.** Variation of extent of reaction with operating variables for the chlorine consumption reaction.

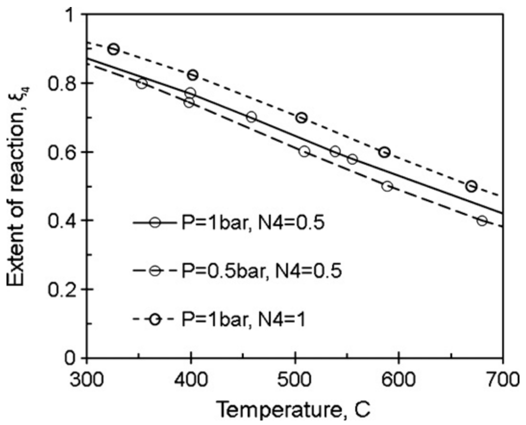

**Fig. 6.** Variation of extent of reaction with the operating variables for chlorine reverse reaction.

Fig. 4 illustrates the variation of the equilibrium constant with temperature for the cupric chloride decomposition reaction (Eq. (9)). The equilibrium constant is equal to the equilibrium partial pressure of chlorine released, due to decomposition of $CuCl_2$. The partial pressure values have been evaluated using Eq. (15) from the equilibrium constant $K_3$. The equilibrium constants from data of Dokiya and Kotera [18] give a higher partial pressure for chlorine. The partial pressure values determined based on a corrected thermodynamic data source (see Tables 2 and 3) are found to be consistent with data of Serbon et al. [19] and Barbooti and Al-ani [20], regarding the decomposition of cupric chloride solid with a thermo gravimetric analysis. Serban et al. [19] observed the decomposition temperature for cupric chloride ($CuCl_2$) solid between 390 and 450 °C. Barbooti and Al-ani [21] observed the decomposition, beginning at a temperature of 345 °C with chlorine formation, reaching a maximum at 447 °C and terminating at 521 °C. Contrary to the above observations, the partial pressure values for chlorine start below 300 °C and they reach a maximum at 400 °C (Dokia and Kotera; [18]).

Figs. 5 and 6 depict the effects of operating variables on the chlorine reaction. Fig. 5 shows the effects of equilibrium conversion with varying operating parameters, such as temperature, pressure and excess steam, on the extent of the reaction for chlorine consumption (Eq. (10)). The forward reaction (Eq. (10)) is an endothermic reaction and the backward reaction (Eq. (16)) is an exothermic reaction. All of the reactants and products are in the gas phase. The equilibrium conversion values have been calculated using Eq. (18) for the forward reaction (chlorine consumption reaction) and Eq. (20) for the chlorine reverse reaction. A higher temperature increases the equilibrium conversion of the forward reaction and decreases for the backward reaction. An increase in pressure favors the forward reaction, whereas a decrease in pressure favors the reverse reaction. Excess steam influences the forward reaction. The equilibrium conversion of chlorine in the forward reaction rises from 23.5% for a stoichiometric steam requirement (1 mol) to 55% at 6.33 mol steam, and 85% at 27 mol steam at a temperature of 400 °C, atmospheric pressure. The predicted values are compared against experimental data reported previously for the forward reaction [21,22]. Nanda and Ulrichson [23] reported the kinetics of the chlorine consumption reaction and found that the reaction rate depends on the hydrogen chloride concentration. A higher concentration of product (hydrogen chloride) lowers the rate of consumption of chlorine. The chlorine reverse reaction (Eq. (16)) favors higher pressures, lower temperatures and excess oxygen for a higher equilibrium conversion.

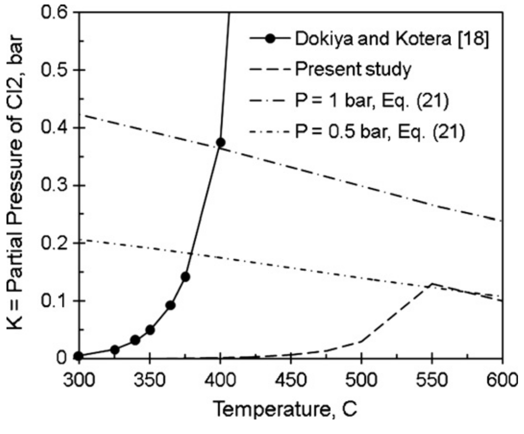

**Fig. 7.** Partial pressure of chlorine from reverse chlorine consumption reaction with cupric chloride decomposition reaction.

Fig. 7 shows the variation of equilibrium partial pressure of chlorine with temperature. The equilibrium partial pressure of chlorine for cupric chloride decomposition was evaluated using Eq. (15), and for the chlorine reverse reaction using Eq. (21). The criteria used to identify the operating conditions for complete consumption of chlorine is that the equilibrium partial pressure of chlorine in the decomposition reaction (Eq. (15)) should be lower than the equilibrium partial pressure of the chlorine reverse reaction (Eq. (21)) for stable operation. Podworny et al. [24] used similar criteria to identify the stable operating range using thermodynamic analysis for an $MgO–MgR_2O_4$ (R: Al, Cr, Fe) spinels–$SO_2$–$O_2$ system, based on the dissociation pressure of sulfates (IV). Fig. 7 shows that the pressure of chlorine formed due to decomposition of solid is lower than the equilibrium partial pressure of chlorine from the reverse chlorine reaction, for temperatures below 400 °C [18]. It remains much lower with the present study for the entire temperature range. The operating range increases at higher pressures.

Overall, in the hydrogen chloride production step, the hydrolysis reaction (Eq. (8)) favors higher temperatures, excess steam and lower pressures for maximizing the yield, copper oxychloride ($CuOCuCl_2$). This will also increase the decomposition of cupric chloride solid (Eq. (9)) and formation of chlorine. The equilibrium conversion of chlorine (Eq. (10)) also increases with more excess steam, higher temperatures and lower pressures. The excess steam available from the hydrolysis reaction will consume the chlorine formed, due to decomposition of $CuCl_2$. For complete consumption of chlorine, the partial pressure of chlorine formed, due to decomposition of solid (Eq. (9)), should be less than the equilibrium partial pressure of chlorine from the chlorine reverse reaction (Eq. (16)). At temperatures higher than 423 °C, the two-phase gas–solid reaction system becomes a three-phase (gas–solid–liquid) system with the melting of cuprous chloride solid at 412 °C. Temperatures above 500 °C increase the loss of cuprous chloride into the gas phase. Based on the above observations, the operating temperature for the hydrogen chloride production reaction should be kept at a temperature around 400 °C, atmospheric pressure, for most effective operation.

Fig. 8 illustrates the effect of temperature on the decomposition of copper oxychloride ($CuOCuCl_2$). The equilibrium partial pressure of oxygen has been evaluated using Eq. (23). The decomposition rate increases at higher temperatures. The partial pressure of oxygen is very low, below 420 °C, and it rapidly increases with a change in temperature from 0.04 bar at 475 °C to 0.14 bar at 500 °C. Serban et al. [19] observed oxygen production from the copper oxychloride ($CuO{\cdot}CuCl_2$) decomposition between 380 and 500 °C using TGA, and also the associated presence of CuCl vapors in the vapor phase for temperatures above 500 °C. Based on these observations, the

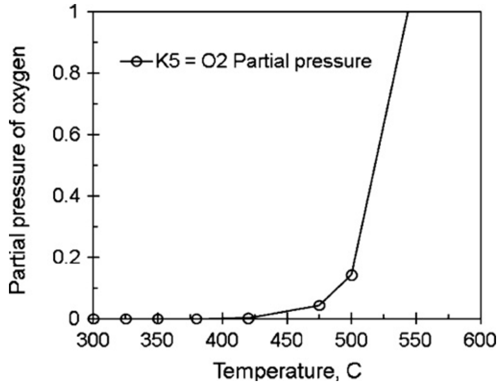

**Fig. 8.** Variation of partial pressure of oxygen with temperature for the copper oxychloride decomposition reaction.

operating temperature should be kept around 500 °C, atmospheric pressure, for the effective decomposition of copper oxychloride and minimizing the loss of CuCl into the vapor phase. These results provide useful trends and valuable data for the engineering equipment development in the copper–chlorine thermochemical cycle of hydrogen production.

## 6. Conclusions

A thermodynamic equilibrium analysis has been performed in this paper for the chemical reaction steps of the Cu–Cl thermochemical cycle of hydrogen production. The equilibrium conversion for the hydrogen production reaction favors lower temperatures, higher pressures and excess hydrogen chloride. The study revealed that higher conversion is possible at higher pressure with stoichiometric quantities of reactant, hydrogen chloride at around 400 °C, or at atmospheric pressure and 55% excess hydrogen chloride. It becomes two-phase (gas–solid reaction) for temperatures around 400 °C. The hydrogen chloride production step favors higher temperatures, excess steam and lower pressures. The study also revealed that the best operating conditions for complete consumption of chlorine during the hydrolysis reaction and minimization of excess steam is at a temperature of about 400 °C. The criterion used for complete consumption of chlorine is that the equilibrium partial pressure of chlorine formed during copper decomposition should be lower than the partial pressure of chlorine in the chlorine reverse reaction. Finally, the oxygen production reaction favors higher temperatures. The results indicate that the best operating conditions for maximizing the decomposition rate of copper oxychloride and minimizing the loss of cuprous chloride is at a temperature of about 500 °C. The results in this paper provide useful insight and new data of valuable utility for selecting proper operating conditions for the thermal reaction steps of the Cu–Cl thermochemical cycle of nuclear-based hydrogen production.

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