Experimental and analytical study of solubility of carbon dioxide in aqueous solutions of potassium carbonate

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In this study, the solubility of CO2 in aqueous solutions of potassium carbonate was measured using pressure-decay method at temperatures of 313.15 K, 323.15 K, and 333.15 K and solution concentrations of 15 wt%, 20 wt% and 30 wt%. Results showed that decreasing temperature and increasing solution concentration enhanced the solubility of CO2 in the solvent. Another important observation which was not studied to date was that the solubility of CO2 increased with increasing pressure until a specific pressure after which it started decreasing. This phenomenon was explained by detail using Henderson–Hasselbalch equation for the bicarbonate formation reaction. Finally, the solubility data was correlated using nonlinear regression. The mean deviation between the experimental solubility and the predicted values by the correlation was less than 3.7%.

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1. Introduction

The climate of the earth is increasing continuously due to various factors such as increasing greenhouse gases concentration. The greenhouse effect is the phenomenon where water vapor, carbon dioxide (CO2), nitrous oxide (N2O), and methane (CH4) absorb outgoing infrared radiation and consequently, increase the earth’s temperature (global warming). Several sources contribute to the emission of several greenhouse gases into the atmosphere such as burning of fossil fuel and industrial processes (Višković et al., 2014). Among these greenhouse gases, CO2 is the major contributor for global warming and it has the greatest adverse impact which accounts approximately 55% of the observed global warming (Mondal et al., 2012).

A number of methods are available for the capture of CO2 from gas streams and flue gases of power plants. Some of the more commonly used methods are chemical solvents, physical solvents and membranes. Ethanolamines (MEA, DEA, MDEA, etc.) and potassium carbonate are chemical solvents which rely on chemical reaction to remove acid gas constituents from sour gas streams. In general, the economics of CO2 recovery is strongly influenced by the partial pressure of CO2 in the feed gas. At low partial pressure, chemical solvents might be a better choice than physical solvents (Newman, 1985).

Bum et al. (1997) provided the solubility of CO2 in the aqueous potassium carbonate solutions and potassium carbonate–polyethylene glycol (PEG) at temperatures of 298.2 K and 323.2 K with a CO2 partial pressure range of 0.005–2 MPa for different concentrations of K2CO3 and PEG. Based on their results, the addition of PEG to 5 wt% K2CO3 solution has slightly lowered the solubility of CO2 at a constant temperature and pressure.

Kim et al. (2012) experimentally verified the CO2 solubility in aqueous solution of potassium carbonate with 2-methylpiperazine and piperazine at temperatures between 313 K and 333 K, and pressure up to 0.7 MPa and various solution concentrations. Their results showed that the CO2 loading capacities of K2CO3 15 wt%–2-MPZ and PZ 10 wt% solutions were higher than MEA 30 wt% or AMP 30 wt% at the specific pressure of CO2. Additionally, the CO2 loading capacity of K2CO3/2-MPZ was similar to K2CO3/PZ.

Majchrowicz and Brilman (2012) presented experimental data on the solubility of CO2 in aqueous potassium l-proline solutions at temperatures of 285 K and 323 K, and pressures up to 0.7 MPa, and amino acid concentrations of 0.5 M, 1 M, 2 M and 3 M. Their results showed that the amino acid was a good absorbent alternative and the presence of l-proline in the solution can improve the CO2 absorption capacity of the system. Also, precipitation was observed in the system when absorbing CO2 in 3 M potassium l-proline solution at 285 K.
Moreover, the solubility of CO2 has been measured at different pressures and temperatures in various systems such as: CO2 in aqueous potassium carbonate + piperazine (Tim and Rochelle, 2005), CO2 in aqueous potassium carbonate promoted by piperazine (Tim and Rochelle, 2004a), CO2 in aqueous carbonate promoted by arginine (Shufeng et al., 2013a), CO2 in aqueous potassium carbonate with 2-methylpiperazine and piperazine (Boumedine et al., 2004), CO2 and H2S in aqueous solutions of N-methyl-dietanolamine (Huttenhuis et al., 2007), and CO2 in potassium carbonate solutions promoted with various amino acids (Thee et al., 2014).

The hot potassium carbonate process, also known as the Benfilled process, has been used commercially for treating acid gas streams for many years. When CO2 dissolved in aqueous solution of potassium carbonate, the following equilibrium reactions occur in the solution (Ahmadi et al., 2008; Gianni et al., 1981; Rahimpour and Kashkooli, 2004):

- Hydrolysis of K2CO3:
  \[ \text{K}_2\text{CO}_3(s) + \text{H}_2\text{O}(l) \rightleftharpoons 2\text{K}^+ + \text{HCO}_3^- + \text{OH}^- \]  

- Ionization of water:
  \[ 2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]  

- Bicarbonate formation:
  \[ \text{OH}^- + \text{CO}_2(\text{aq}) \rightleftharpoons \text{HCO}_3^- \]  

- Carbonate formation:
  \[ \text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O} \]  

Since the reaction of the carbonate formation is instantaneous, the overall reaction between the aqueous potassium carbonate and CO2 can be represented as follows:

\[ \text{K}_2\text{CO}_3(l) + \text{H}_2\text{O}(l) + \text{CO}_2(\text{aq}) \rightleftharpoons 2\text{KHC}O_3 \]  

In comparison to the benchmark amine-based solvents such as monoethanolamine (MEA), potassium carbonate has a number of advantages such as low heat of absorption, low cost, lower toxicity, lower solvents losses, no thermal and oxidative degradation, and no formation of heat-stable salts (Shufeng et al., 2013b). Although there were several reports on the equilibrium study of the absorption of acidic gases in the K2CO3 solutions (Bum et al., 1997; Kim et al., 2012; Majchrowicz and Brilman, 2012; Tim and Rochelle, 2004a, 2005; Shufeng et al., 2013a; Boumedine et al., 2004; Huttenhuis et al., 2007; Thee et al., 2014), but they were mainly focused on the low concentrations of K2CO3 in a mixture with other solvents. Therefore, study on the high concentrations of K2CO3 is totally lacking. Due to this reason, in this study, the experimental data on the solubility of CO2 in aqueous solutions of potassium carbonate was reported. The equilibrium data was measured at temperatures of 313, 315, 323, 315 K, and 333, 315 K, and pressures of 0.03–1.1 MPa, and potassium carbonate solution concentrations of 15, 20 and 30 wt%. The ranges of the operating parameters are selected according to the commercial applications of this solvent in CO2 capture processes. The Benfiled process as an example of a commercial process uses K2CO3 20–30 wt% solution. Furthermore, the absorber typically operates at high pressures (>1 MPa) and high temperature (>100 °C). The ranges of concentration and pressure in this study are close to commercial processes but because of some limitations in the experimental setup, the range of temperature is slightly lower than the real conditions. Also, it must be emphasized that a new phenomenon about the pressure increase and its effect on the solubility was observed in this study which was not published previously.

2. Experimental

2.1. Materials

Potassium carbonate (K2CO3) with the purity higher than 99.5 wt% was purchased from Merck Company whilst carbon dioxide with the purity of 99.9 mol% was purchased from Balon Gas Co., Iran. All the chemicals were utilized without future purification and their purities were obtained from suppliers.

2.2. Experimental apparatus and procedure

The equipments and procedure used for the solubility measurements are similar to our prior work (Bohloul et al., 2014). This type of batch absorption cell was extensively utilized in the previous investigations as well (e.g. Bermejo et al., 2005; Taib and Murugesan, 2012). Fig. 1 shows a schematic representation of the experimental setup. The operating conditions were similar to CO2 capture in the PFBC (pressurized fluidized bed combustion) power plant (Tim and Rochelle, 2004b). The apparatus consisted of gas reservoir, regulator, middle cell, absorption cell, vacuum pump, pressure and temperature measuring instruments, pH meter, and data acquisition system. The middle cell and absorption cell were made of 316-stainless steel with internal volume of approximately 500 cm3 and 320 cm3, respectively. The middle cell was employed to set the gas temperature for the gas absorption process. Two Pt–100 Ω thermo-resistances were used to indicate the temperature of the CO2 gas in the middle cell and the temperature of the solution in the absorption cell. The pressure of the gas in the middle cell and the absorption cell was constantly measured using a pressure sensor (Sensys, Model: PSCH0025BCL). The middle cell and the absorption cell were heated using a water bath, and the temperature of the water bath was sustained the steady temperature with a precision of ±0.2 K. The pH of solution was measured by a pH meter (Mettler-Toledo-MP225) at the beginning and the end (equilibrium state) of the absorption process. The calibration of the pH meter was performed by using buffer solutions with pH 4.01, 7.00, and 10.10. A magnetic stirrer was also used in the absorption cell to attain the equilibrium condition faster. The rate of absorption depends strongly on the experimental conditions such as speed and size of stirrer, the purpose of which was to increase the mass transfer rate and reduce the time needed to achieve equilibrium.
In all of the experiments, stirring was performed continuously in the absorption cell at a speed of 300 rpm, maintaining a smooth interfacial area.

In this study, experimental data on the solubility of CO₂ in aqueous solutions of potassium carbonate was presented at temperatures of 313.15 K, 323.15 K, and 333.15 K, and solution concentrations of 15, 20 and 30 wt%. The pressure of the gas from CO₂ reservoir was controlled using a regulator. Subsequently, the gas was sent into the middle cell to adjust the temperature; ultimately, it enters the absorption cell and the gas absorption process begins. It is important to mention that the inlet CO₂ is heated prior to entering the middle cell in order to prevent the gas freezing due to sudden pressure drop in the regulator. Moreover, 100 ml of solution is kept in the absorption cell. Before starting the experiment, residual gas in the middle cell, piping and absorption cell are evacuated by a vacuum pump (JB Industries DV-200N, USA). The pressure change of CO₂ during absorption was measured and recorded, and the solubility of CO₂ is evaluated by measuring the difference between initial and final pressure (equilibrium point) in the absorption cell. The major feature of this experimental procedure is that no analysis of the liquid phase is necessary since the variation of CO₂ partial pressure during the course of absorption can be used to calculate the amount of CO₂ absorbed. The real gas law is applied to determine the number of absorbed moles of CO₂:

$$n_{CO_2} = \frac{P_1 V_1 R T}{Z_1} - \frac{P_1 V_f R T}{Z_f} = \frac{V_G (P_1 - P_f)}{R T}$$

(6)

where $n_{CO_2}$ represents the number of moles of CO₂ in the solvent, $P_1$ and $P_f$ are initial and final pressure of CO₂, $V_1$ and $V_f$ are initial and final volumes of the gas, and $Z_1$ and $Z_f$ are compressibility factors of CO₂ at initial and final stage of the absorption process. Compressibility factors were calculated using PR-EOS (Ziaabaksh-Ganj and Kooi, 2012). Before and after each experiment, the volume of solvent is measured. The results showed that volume of solvent has not changed, thus, $V_f$ is equal to $V_1$ in Eq. (6).

### 2.3. Uncertainty analysis

In this work, solution loading was measured using the following equation:

$$\alpha = \frac{n_{CO_2}}{n_{CO_2} + n_{K_2CO_3} + n_{water}} = \frac{(P_1 - P_f) V_G}{(P_1 - P_f) V_G + m_{K_2CO_3} \frac{\delta m_{K_2CO_3}}{m_{K_2CO_3}} + V_{water} \frac{\delta \rho_{water}}{\rho_{water}}}$$

(7)

where $\alpha$ is the solution loading, $P_0$ and $P_f$ are initial and equilibrium pressures of CO₂, $V_G$ is gas volume, $V_{water}$ is initial volume of water without salt, $\rho_{water}$ is density of water, $Z$ is CO₂ compressibility factor, $T$ is operating temperature, $m$ is mass of potassium carbonate salt, and $M_w$ is molecular weight.

Uncertainty analysis was carried out by calculating the error of the measurements, based on the procedure described by Moffat (1988). The uncertainty of the solution loading comes from the errors in the measurement of gas volume, initial volume of water, initial and equilibrium pressures, operating temperature and weight of potassium carbonate as follows:

$$\left(\frac{\delta \alpha}{\alpha}\right)^2 = \left(\frac{\partial \alpha}{\partial (P_1 - P_f)} \frac{\delta (P_1 - P_f)}{P_1 - P_f}\right)^2 + \left(\frac{\partial \alpha}{\partial V_G} \frac{\delta V_G}{V_G}\right)^2 + \left(\frac{\partial \alpha}{\partial m_{K_2CO_3}} \frac{\delta m_{K_2CO_3}}{m_{K_2CO_3}}\right)^2 + \left(\frac{\partial \alpha}{\partial V_{water}} \frac{\delta V_{water}}{V_{water}}\right)^2$$

(8)

The derivatives in Eq. (8) have been explained in detail in Appendix A. The measurement error of the solution loading was ±1%. The contributions of the main parameters involving in the evaluation of solution loading according to Eq. (8) are summarized in Table 1. The analysis showed that pressure measurement had the greatest effect on the uncertainty of the solution loading. Furthermore, to check the reproducibility of the experiments, some runs were repeated. The repetition of the experiments showed that the results were reproducible with maximum 1.5% deviation which is in the range of uncertainty of the measurements.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Accuracy of the measurement device</th>
<th>Contribution in the uncertainty of $x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(P_1 - P_f)$</td>
<td>±0.01 bar</td>
<td>43.21%</td>
</tr>
<tr>
<td>$V_G$</td>
<td>±1 ml</td>
<td>16.80%</td>
</tr>
<tr>
<td>$m$</td>
<td>±0.1 g</td>
<td>10.53%</td>
</tr>
<tr>
<td>$T$</td>
<td>±0.2 °C</td>
<td>19.23%</td>
</tr>
<tr>
<td>$V_{water}$</td>
<td>±1 ml</td>
<td>10.23%</td>
</tr>
</tbody>
</table>

(171)
3. Results and discussion

3.1. Kinetic analysis

Pressure decay during absorption of CO₂ in aqueous solutions of potassium carbonate at three different concentrations and at the constant temperature of 313.15 K is presented in Figs. 2–4. It was previously shown that the pressure reduction in the absorption cell presents the amount of gas absorption. The pressure reduction would continue until the solvent becomes saturated with gas, and equilibrium is established between the two phases.

The time needed to reach the equilibrium was different for each concentration of the solvent. Equilibrium time for concentration of 15 wt% was about 100 min, 20 wt% about 130 min, and 30 wt% about 180 min. The reason for different equilibrium times is the concentration of aqueous solution of potassium carbonate. As the concentration of potassium carbonate increases, the CO₂ absorption capacity of the solution increases, as well. This increases the time required to reach the equilibrium state. In this study, the equilibrium point was considered a time in which the pressure did not change for about 20 min.

The equilibrium data for CO₂–aqueous potassium carbonate solutions is shown in Figs. 5–7. In these figures, equilibrium data of the present work were compared with the equilibrium data of the same system published by Kim et al. (2012). Although the range of operating pressures was different, very good agreement can be observed. The results at all solvent concentrations revealed that at constant pressure, the solution loading was decreased with increasing temperature. The increase in the mass fraction of K₂CO₃ decreased the solution loading, but according to Figs. 9–11, the absolute amount of CO₂ absorbed in the solution increased. At constant temperature, initially the solution loading increased as the pressure increased; however, after a specific pressure it started decreasing. This phenomenon can be explained by measuring the pH of the solution (it will be discussed later). Furthermore, at a constant concentration and different temperatures, the maximum solubility occurs at the same pressure.

The number of absorbed moles of CO₂ in pure water and aqueous solution of 15 wt% potassium carbonate (minimum salt
concentration) are shown in Table 2. According to these results, the number of absorbed moles of CO\textsubscript{2} in the aqueous solution of potassium carbonate was an order of magnitude greater than that in pure water. It means that the effect of chemical reaction dominated the physical mass transfer inside the liquid film in the absorption of CO\textsubscript{2} in aqueous potassium carbonate solution. Thus, the presence of physical absorption can be neglected.

### Table 2

<table>
<thead>
<tr>
<th>CO\textsubscript{2} in pure water</th>
<th>CO\textsubscript{2} in K\textsubscript{2}CO\textsubscript{3} 15 wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_{eq}) (MPa)</td>
<td>Number of absorbed moles of CO\textsubscript{2}</td>
</tr>
<tr>
<td>1.231</td>
<td>0.019</td>
</tr>
<tr>
<td>1.096</td>
<td>0.013</td>
</tr>
<tr>
<td>0.901</td>
<td>0.011</td>
</tr>
</tbody>
</table>

### 3.2. Effect of \(pH\)

The final \(pH\) values of the equilibrium solution were recorded and presented in Fig. 8. From this figure, it is observed that the measured solution loading is strongly affected by the variation of \(pH\). In all the experiments, the initial \(pH\) of the solution was approximately 13 and during the absorption period the \(pH\) of the solutions was decreased. Also, by measuring the \(pH\) of the solution, one can estimate the amount of CO\textsubscript{2} chemically absorbed by the solvent using Henderson–Hasselbalch equation (Henry and Senozan, 2001). The derivation of Henderson–Hasselbalch equation for carbonate formation reaction is (Eq. (4)) as follows:

\[
K = \frac{[H_2O][CO_2]}{[HCO_3][H_2O]} \tag{9}
\]

\[
K[H_2O] = \frac{[H_2O][CO_2]}{[HCO_3]} \tag{10}
\]


![Graph](image)

Fig. 10. Number of absorbed moles of CO₂ into different concentrations of aqueous K₂CO₃ solutions at 323.15 K.

\[
pK_a = -\log([\text{H}_2\text{O}]) \quad \text{(11)}
\]

\[
\text{pH} = -\log([\text{H}_3\text{O}^+]) \quad \text{(12)}
\]

\[
\text{pH} = pK_a + \log \left( \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \right) \quad \text{(13)}
\]

where \( K \) is equilibrium constant, \( pK_a \) is a dissociation constant of the weak acid. The second \( pK_a \) of carbonic acid is 6.37. (Greenwood and Earnshaw, 1984). From Eq. (13), it can be seen that as CO₂ is chemically absorbed via the formation of bicarbonate, the pH of the solution decreases. The carbonate→bicarbonate has another \( pK_a \) at 6.37 however, associated with the conversion of bicarbonate to carbonic acid (\( \text{H}_2\text{CO}_3 \)). As the pH is decreased beyond the point halfway between the two \( pK_a \)'s (approximately pH = 8.3 as can be seen from Fig. 8), this reaction becomes the dominant reaction in the system. As \( \text{H}_2\text{CO}_3 \) has a very low solubility in water, the solution is further acidified by the physical absorption of CO₂; the resultant decrease in pH begins to convert bicarbonate into carbonic acid, effectively decreasing the amount of CO₂ chemically absorbed in the solution, and thus the loading observed.

3.3. Effect of solution concentration

The number of absorbed moles of CO₂ into the aqueous potassium carbonate 15, 20 and 30 wt% at temperatures of 313.15 K, 323.15 K, and 333.15 K are shown in Figs. 9–11. These figures show that at a given temperature and pressure, the number of absorbed moles of CO₂ increased with increasing the concentration of potassium carbonate in the solution. Furthermore, at given concentration and temperature, the solubility did not monotonically increase with increasing the equilibrium pressure. As can be seen in Figs. 9–11, these curves have maximum points and the locations of these maximum points have inverse proportionality with pressure. This pressure for concentration of 15 wt% is about 0.9 MPa, 20 wt% is about 0.8 MPa and 30 wt% is about 0.65 MPa.

3.4. Correlation of experimental data

As shown, the solution loading is a function of pressure and temperature for each salt concentration. The solution loading results were fitted to the following equations using nonlinear regression analysis. The following equation satisfactorily fits the experimental data:

\[
\alpha = \alpha_1 (P [\text{MPa}])^2 + \alpha_2 (P [\text{MPa}]) + \frac{\alpha_3}{[\text{K}]} + \frac{\alpha_4}{[\text{C} [\text{mol}\text{l}^{-1}]]} + \alpha_5 \quad \text{(14)}
\]

where \( \alpha \) is the potassium carbonate concentration, \( P \) is the equilibrium pressure, and \( T \) is temperature. Correlation results for the 89 data points at pressures up to 1.1 MPa, potassium carbonate concentration 15 wt%, 20 wt% and 30 wt%, and temperatures of 313.15 K, 323.15 K, and 333.15 K are shown in Table 3. The mean deviation between the experimental solubility and the predicted values by the correlation was calculated to be less than 3.7%. The predicted values by the correlation are shown in Fig. 12.

![Graph](image)

Fig. 11. Number of absorbed moles of CO₂ into different concentrations of aqueous K₂CO₃ solutions at 333.15 K.

![Graph](image)

Fig. 12. All the experimental data points obtained in this study against the prediction of the proposed correlation.

Table 3

<table>
<thead>
<tr>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
<th>( \alpha_3 )</th>
<th>( \alpha_4 )</th>
<th>( \alpha_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.022</td>
<td>0.032</td>
<td>21.879</td>
<td>0.079</td>
<td>0.041</td>
</tr>
</tbody>
</table>
4. Conclusion

The solubility of CO₂ in aqueous potassium carbonate solution was examined at different temperatures, pressures and solution concentrations. The experimental solution loading data showed that at a similar pressure, the solution loading decreased with increasing temperature. Indeed, at a constant temperature, the solution loading increased as the pressure increased but after a specific pressure it started decreasing. This effect was attributed to the pH of solution. When the pH of solution decreases and solution becomes acidic, the carbonate is converted to bicarbonate and finally the excess bicarbonate instead converts to CO₂, and CO₂ is evolved from liquid phase. Finally, a new correlation was proposed for the prediction of the solution loading data using nonlinear regression analysis. The mean deviation between the experimental data and the predicted values by correlation was determined to be less than 3.7%.

Appendix A.

The derivatives in Eq. (8) for calculating the uncertainty analysis are presented here as follows:

\[ \frac{\partial \alpha}{\partial (P_1 - P_f)} = \frac{V_g}{ZRT \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]} \]
\[ - \frac{(P_1 - P_f) V_g^2}{2 Z^2 R^2 T^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]^2} \]  \hspace{1cm} (A.1)

\[ \frac{\partial \alpha}{\partial T} = - \frac{ZRT^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]}{\frac{(P_1 - P_f) V_g^2}{2 Z^2 R^2 T^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]^2}} \]
\[ + \frac{(P_1 - P_f)^2 V_g^2}{2 Z^2 R^2 T^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]^2} \]  \hspace{1cm} (A.2)

\[ \frac{\partial \alpha}{\partial V_g} = - \frac{ZRT \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]}{\frac{(P_1 - P_f) V_g^2}{2 Z^2 R^2 T^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]^2}} \]
\[ - \frac{(P_1 - P_f)^2 V_g^2}{2 Z^2 R^2 T^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]^2} \]  \hspace{1cm} (A.3)

\[ \frac{\partial \alpha}{\partial m_{k_2}CO_3} = - \frac{ZRT \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]}{\frac{(P_1 - P_f) V_g^2}{2 Z^2 R^2 T^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} \right]^2}} \]  \hspace{1cm} (A.4)

\[ \frac{\partial \alpha}{\partial V_{\text{water}}} = - \frac{ZRT \cdot M_{\text{water}} \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} + \frac{V_{\text{water}} \cdot \rho_{\text{water}}}{M_{\text{water}}} \right]}{\frac{(P_1 - P_f) V_g^2}{2 Z^2 R^2 T^2 \left[ \frac{(P_1 - P_f)V_g}{ZRT} + \frac{m_{k_2}CO_3}{M_{k_2}CO_3} + \frac{V_{\text{water}} \cdot \rho_{\text{water}}}{M_{\text{water}}} \right]^2}} \]  \hspace{1cm} (A.5)

References