The pH of CO₂-Saturated Water at Temperatures Between 308 K and 423 K at Pressures up to 15 MPa

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Abstract

We report pH measurements for CO₂-saturated water in the pressure range from (0.28 to 15.3) MPa and temperatures from (308.3 to 423.2) K. Commercially-available pH and Ag/AgCl electrodes were used together with a high pressure equilibrium vessel operating under conditions of precisely controlled temperature and pressure. The results of the study indicate that pH decreases along an isotherm in proportion to –log₁₀(x), where x is the mole fraction of dissolved CO₂ in H₂O. The expanded uncertainty of the pH measurements is 0.06 pH units with a coverage factor of 2. The reported results are in good agreement with the literature in pressure ranges up to 16 MPa at temperatures below 343 K. An empirical equation has been developed to represent the present results with an expanded uncertainty of 0.05 pH units. We also compare our results with a chemical equilibrium model and find agreement to within 0.1 pH unit.

Keywords: Carbon dioxide; high pressure; high temperature; pH; water
1. Introduction

Understanding of the impact of anthropogenic greenhouse gases (GHGs) on global warming has been greatly improved in recent years [1]. Four gases have been identified as the main GHGs: CH₄, N₂O, hydrofluorocarbons (HFCs) and CO₂. Although CO₂ has the lowest global warming potential (GWP) of this group, emission are by far the greatest making CO₂ the most important gas contributing to global warming [2].

It is generally agreed that a reduction of anthropogenic CO₂ emissions is required to stabilise the atmospheric concentration of CO₂ [3]. An effective long-term solution will be to transform the world from a fossil-fuel dominated society to one reliant solely on renewable energy sources. However, it is important to recognise that this transformation cannot be accomplished sufficiently rapidly to avoid dangerous climate change. Hence, to mitigate this problem in the near and medium term, carbon capture and storage (CCS) is proposed as a critically-important transitional technology, offering a near-term means of mitigating climate change consistent with continued extensive exploitation of fossil fuels [4]. CCS involves the capture of CO₂ at point sources, transportation, and subsequent injection into a suitable geological formations [5]. Potential geological sinks for CO₂ include active and depleted hydrocarbon reservoirs, coal seams and deep saline aquifers [6]. However, deep saline aquifers have, by far, the largest potential for CO₂ sequestration in terms of volume, duration, and economics with minimal environmental impacts [7]. Several complex mechanisms are involved in safely trapping CO₂ in a geological formation including: (1) structural and stratigraphic trapping; (2) capillary trapping; (3) solubility trapping and (4) mineral trapping [8]. Due to the great storage potential of deep saline aquifers, it is important to have a fundamental understanding of these principal trapping processes specifically in the context of such sinks. This includes studying the basic physical chemistry of CO₂-brine-mineral systems under typical reservoir conditions. One of the key properties is the pH of brines acidified by dissolved CO₂. Important issues concerning mineral stability and cap rock integrity are controlled by solution pH [9]. Also, pH affects the reaction rate and equilibrium state of reservoir rocks, resulting in changes in porosity and permeability of the formation and influencing mineralisation trapping processes that ultimately affect the total CO₂ storage capacity at a given site [10, 11].

A necessary first step is to gain a quantitative understanding of pH in the (CO₂ + H₂O) system under relevant conditions of temperature and pressure. There are primarily two methods that have been applied for measuring pH in aqueous solutions: electrometric and optical. The former employs an electrochemical cell, the e.m.f. of which is related to the pH of the sample solution it contains, while the latter involves relating changes in the optical absorption spectrum of an indicator dye to pH. The pros and cons for both methods have been evaluated in the literature [12, 13]. Electrometric methods have been extensively studied and used in practice for many decades. However, the existence of a liquid junction potentials is still a major source of uncertainty in quantifying the pH of aqueous solutions [13]. Some experimental methods have been developed to minimise liquid junction potentials, such as introducing salt bridges and using precise pH buffers for calibration. Optical methods, such as UV-Vis spectrophotometry developed in the late 1980s, have recently received a lot of attention due to their simple, rapid and precise measurement. For example, the pH of seawater has been measured with a precision on the order of ± 0.004 pH units [14-
However, this technique requires the introduction of an indicator to the system and has not yet been applied extensively to high-temperature high-pressure (HTHP) conditions where the indicators may be unstable.

An examination of the literature shows that previous experimental studies of $pH$ in the $(CO_2 + H_2O)$ system are very limited. Meyssami et al. [17] reported $pH$ measurements for CO$_2$-acidified citrus solutions for food and beverage applications. They used an electrometric method and covered a modest range of temperatures from (305 to 315) K at pressures up to 5.5 MPa. Toews et al. [18] and Parton et al. [19] both performed $pH$ measurements for $(CO_2 + H_2O)$ system using a UV-Vis spectrophotometry technique, allowing $pH$ measurement up to 20 MPa at temperatures up to 343 K. Their results indicated lower $pH$ values than found in earlier electrometric studies. A recent study performed by Rosenqvist et al. [3] used $pH$ probes to measure the $pH$ of CO$_2$ saturated H$_2$O containing mineral suspensions at $T = 294$ K and pressures up to 1 MPa. In summary, experimental $pH$ data for the $(CO_2 + H_2O)$ system are scattered and almost no experiments have been conducted at high pressures with temperatures above 343 K. Thus, we conclude that additional high-accuracy $pH$ measurements for the $(CO_2 + H_2O)$ system, especially at elevated temperatures and pressures, would be a valuable means of underpinning future studies on CO$_2$-saturated brines and their interaction with reservoir minerals.

The estimation of $pH$ for aqueous electrolyte solutions containing dissolved CO$_2$ has typically been achieved by means of calculation starting from the solubility of CO$_2$ in the aqueous phase and employing the known dissociation constant of CO$_2$(aq) and other relevant chemical equilibria at the corresponding temperature, pressure and electrolyte composition. Various methods have been applied to quantify the dissociation constants for the $(CO_2 + H_2O)$ system using electrometric, conductometric and spectrophotometric techniques. Harned et al. [20] determined the first dissociation constant of carbonic acid at temperatures from 273 K to 323 K using an e.m.f. cell. Patterson et al. [21] also applied a similar electrometric technique and determined the first and the second dissociation constants of CO$_2$ in both saturated water and NaCl solutions at temperatures from 323 K to 573 K. Read et al. [22] conducted extensive conductometric measurements and obtained both the first and the second dissociation constants at temperatures up to 523 K and at pressures up to 200 MPa. Several recent papers by Park et al. [23, 24] and Minami et al. [25] report the application of spectrophotometric techniques to measure the first and the second dissociation constants of CO$_2$(aq). Using different optical indicators, measurements were made at temperatures as high as 653 K that are particularly relevant to hydrothermal applications. By incorporating chemical equilibrium data in a geochemical simulator (such as PHREEQC, EQ3NR), $pH$ calculations could be extended to very high temperatures and pressures [26]. However, such calculations may be less reliable at high temperatures and pressures because of the uncertainties in the solubility of CO$_2$ [27]. In addition to large deviations from Henry’s law at high pressures, noticeable errors occur in the calculated activities of both hydrogen ions and dissolved CO$_2$ at higher pressures if the Poynting correction is not included [27]. Furthermore, very few experiments have been conducted to validate such simulation results for the $pH$ of CO$_2$ saturated H$_2$O and some discrepancies have been reported in the literature between simulations and experimental results [28].
The electrometric technique was chosen in this work since pH and reference electrodes have become available commercially that are suitable for pH measurement over wide ranges of temperature and pressure. Furthermore, primary buffer solutions for electrode calibration are well-studied in the literature and are obtainable with low uncertainty. Also, no additional substances need to be introduced in the solution under study as is the case with the optical indicator methods. The objective of this research was to investigate the dependence of pH on temperature, pressure, and CO₂ solubility in H₂O and to address some of the discrepancies in the literatures over the range of conditions applicable to CO₂ sequestration in deep reservoirs. In this paper, we described a new apparatus for carrying out the pH measurements for CO₂-saturated aqueous system using commercially available pH and reference probes and we present results for the (CO₂ + H₂O) system at temperatures up to 423 K and pressure up to 15 MPa.

2. Experiment

2.1. Materials
CP grade CO₂ was supplied in a liquid-withdrawal cylinder by BOC with a specific minimum mole-fraction 0.99995. Pure deionised water with electrical resistivity > 18 MΩ·cm at T = 298 K was produced with a reverse-osmosis apparatus (Millipore). Oxygen-free N₂ was supplied by BOC. Fluka standard pH 4 and pH 7 buffers, Hanna standard pH 4 and pH 7 buffers and 0.01 M HCl(aq) solution were purchased from Sigma Aldrich for pH electrode calibration. Hexane and propan-2-ol used in this work for cleaning purposes (Sigma Aldrich) were of purity 95% or higher.

2.2. High Pressure Apparatus
A new apparatus, shown in Figure 1, was constructed for pH measurements on both CO₂ acidified water and brine. Apart from the syringe pump, which was made from stainless steel, all the wetted metallic parts were made from either titanium or Hastelloy C276 both of which offer resistance to corrosion in concentrated brines at high temperature. The high pressure cell accommodating the pH electrodes and the aqueous sample solutions was made from commercially pure titanium (grade 2), and is shown in Figure 2. This cell was a vertically-oriented cylindrical vessel of 44 mm inner diameter and 60 mm internal depth with a nominal internal volume of 91 cm³. The lid of the vessel was sealed with a Viton O-ring. Three threaded fluid ports were machined in the body: one in the top for gas inlet; and two in the bottom, one plugged and other used for both liquid inlet and outlet. The maximum working temperature and pressure of the cell are 473 K and 24 MPa, respectively. A pressure relief valve was installed on the upstream tubing of the reactor. To enhance the mixing of CO₂ and sample fluids, an internal PTFE-coated magnetic stirrer bar of ellipsoidal shape (10 m long x 3 mm diameter) was placed inside the reactor and rotated by an external magnetic drive.

A Pt100 thermometer, placed in a blind vertical hole drilled in the vessel wall (1.6 mm diameter, 30 mm internal length), was used to measure the temperature. A close-fitting aluminium heater shell, insulated on the outside by a jacket of silicon-rubber foam with a thickness of 9 mm, was fitted around the cell. Four cartridge heaters and an additional Pt100
temperature sensor, fitted into vertical holes bored in the heater shell, were used with a PID process controller to regulate the temperature with a stability of better than ±0.05 K.

Liquid CO₂ was drawn into the system through a 0.5 µm pore size particulate filter. The CO₂ was pressurised by a syringe pump (Teledyne Isco, model 100DM) with a capacity of 100 cm³, a maximum operating pressure of 69 MPa and a resolution of 0.01 cm³. The pump cylinder was cooled by passing water at \( T = 283.15 \text{ K} \) from a circulating chiller through a cooling jacket thereby ensuring that the CO₂ remained in the liquid phase within the pump. A pressure transducer (OmegaDyne Model MMA) with a full scale range of 24.5 MPa was installed downstream of the pump. A three way ball valve (V7 in Figure 1) was installed between the pressure transducer and the syringe pump, allowing the connection of a N₂ purge line and also permitting the reactor cell to be evacuated for degassing the sample solution at the beginning of each measurement. The location of the pressure transducer was such that it gave a reading of the pressure in the cell during degassing, measurement and purging.

A glass \( \text{pH} \) electrode, a zirconia \( \text{pH} \) electrode and a Ag/AgCl reference electrode were purchased from Corr Instruments LLC. These electrodes have wetted metallic parts of Hastelloy C276 and their respective working temperature and pressure ranges are shown in Table 1. The e.m.f. developed between the chosen \( \text{pH} \) electrode (glass or zirconia) and the reference electrode was measured with a digital multimeter having an input impedance larger than \( 10^{12} \ \Omega \). The Ag/AgCl reference electrode is very vulnerable to sudden depressurisation due to the fact that CO₂ can diffuse into the inner compartment of the electrode. The CO₂ in the inner compartment does not change the electrode potential of the reference electrode, but it may cause mechanical damage during depressurisation. To avoid this, a programmable back pressure regulator (Jasco BP-2080, shown in Figure 1) was used to control the rate of depressurisation at < 0.4 MPa·hr⁻¹. Such slow depressurisation was also effective in limiting decompression damage to the Viton o-ring; nevertheless, this component was replaced frequently to avoid failure in service.

As implemented, the apparatus allowed the \( \text{pH} \) to be measured at temperatures up to 473 K with pressures up to 20 MPa. Leaks would be major concerns in this system since, as noted above; the reference electrode is very fragile and susceptible to damage when sudden reductions in pressure are experienced. The system was thoroughly tested over the whole working ranges with both N₂ and H₂O and exhibited a high level of integrity.

### 2.3. Operating Procedure

Prior to first use, the entire system was cleaned thoroughly with hexane, propan-2-ol, water, and CO₂ in sequence, repeated several times. To avoid electrode damage, each group of \( \text{pH} \) measurements was carried out at fixed pressure with rising temperatures. In order to investigate the entire temperature range of interest, both the glass electrode and the zirconia electrode were used in sequence. The entire system was cleaned according to the protocol described above whenever the measurement electrode was switched. Before every measurement, the previously evacuated cell was first flushed several times with water and then N₂. At the start of each experiment gas remaining in the headspace of the reactor cell
was removed by flushing with CO\(_2\)(g) for about 5 mins at \(T = 298\) K before the cell was sealed and pressurised. H\(_2\)O was degassed in an ultrasonic bath for 30 mins before injecting into the reactor cell. After sealing the system by shutting V1, V4, V5 and V6, the sample solution was further degassed using the vacuum pump for 1 hour with stirring, before pressuring with CO\(_2\). During the measurement, pressures and temperatures were constantly monitored and logged.

To ensure the sample solution was CO\(_2\)-saturated, the cell was initially filled with 80 cm\(^3\) of the sample solution through V5 and then CO\(_2\) was injected to reach the required pressure followed by stirring the system for at least 4 hours at a frequency of 0.8 s\(^{-1}\). The process of CO\(_2\) dissolution could be monitored by observing both the syringe pump volume and the e.m.f. across the electrodes. It was observed that the syringe-pump volume reading and the e.m.f. across the electrodes were constant within ±0.01 ml and ±1 mV, respectively, once the saturation state was reached. The time required to reach equilibrium varied with temperature and pressure and, at high pressures (>10 MPa), 24 hours of stirring was required to satisfy the criteria for equilibrium. The rotation frequency of the stirrer was maintained very low to reduce the formation of bubbles on the \(pH\) electrodes.

2.4. Calibration

The Pt100 thermometer inserted in the reactor cell body was calibrated in a constant-temperature bath over the range \(T = (273\) to 473) K by comparison with a standard platinum resistance thermometer having an expanded uncertainty of 2 mK. Taking sensor drift and fluctuations into account, we estimate that overall expanded uncertainty of the cell temperature measurements was 50 mK, with a coverage factor \(k = 2\).

The pressure transducer was calibrated by the manufacturers using instrumentation and standards that are traceable to the United States National Institute of Standards and Technology. All the calibration performance complied with MIL-STD 45662-A, ISO 10012-1, and ANSI/NCSL Z540-1-1994 requirements. The mean and maximum absolute deviations arising from nonlinearity and hysteresis given by the calibration certificate from the manufacturers were (22 and 33) kPa, respectively. Taking all factors into account, the expanded uncertainty of the pressure in the cell was estimated to be 65 kPa. \((k = 2)\)

The glass measurement electrode and Ag/AgCl reference electrode pair was calibrated with Hanna standard \(pH\) 4 and \(pH\) 7 buffers and with 0.01 M HCl solution for low temperature measurements \((T < 353\) K), while the zirconia measurement electrode and Ag/AgCl reference electrode pair was calibrated with Fluka standard \(pH\) 4 and \(pH\) 7 buffers and 0.01 M HCl solution for the higher temperature isotherms. Measurements were performed on all calibration solutions at pressures up to 16 MPa at ambient temperature, using N\(_2\) as the pressurising medium. Over these ranges, the changes in the e.m.f. with pressure alone were observed to be less than 2 mV, indicating that pressure did not significantly affect the calibration or the measured \(pH\) values. Therefore, calibration was subsequently performed at low pressure only for the glass measurement electrode. For calibrations at temperatures above 343K, a 1.5 MPa N\(_2\) blanket was applied to all the buffer solutions to avoid the formation of bubbles within the cell.
In theory, the electrode response should follow the Nernst equation [29],

\[ E = E^\circ - 2.3026 \left( \frac{RT}{F} \right) \Delta \mathrm{pH}, \]

where \( E \) is measured e.m.f. between the \( \mathrm{pH} \) and reference electrodes, \( E^\circ \) is a standard electrode potential, \( R \) is the gas constant, \( T \) is thermodynamic temperature and \( F \) is Faraday's constant. Calibrations were performed for every isotherm and fast, linear Nernstian response was observed in each case. Two typical calibration curves are shown in Figure 3. For both the glass and the zirconia electrodes, the measured e.m.f. exhibited high stability over long periods of time, with drift of less than 0.5 mV (equivalent to approximately 0.01 \( \mathrm{pH} \) units) over 24 hours. The theoretical slopes calculated at 308 K and 368 K from the Nernst equation are -61.1 mV and -83.85 mV, respectively. Both calibration curves showed an empirical sub-Nernstian slope close to the theoretical values. This sub-Nernstian response is consistent with other reported studies and the difference between theoretical and actual slope can be attributed to the variation in ionic mobility at the salt bridge, phase boundary equilibrium at the surface of the electrodes and the electromotive efficiency of the glass/zirconia membrane [30].

The overall relative standard uncertainty \( u_{\Delta \mathrm{pH}} \) was calculated from the relation

\[ u^2_{\Delta \mathrm{pH}} = \left[ \left( \frac{\partial \Delta \mathrm{pH}}{\partial T} u_T \right)^2 \right] + \left[ \left( \frac{\partial \Delta \mathrm{pH}}{\partial \rho} u_\rho \right)^2 \right] + \left[ \left( \frac{\partial \Delta \mathrm{pH}}{\partial \nu} u_\nu \right)^2 \right] \]

and was found to be 0.03 \( \mathrm{pH} \) units or less, leading to an expanded uncertainty at 95% confidence equal to 0.06 \( \mathrm{pH} \) units.

3. Results and Discussion

Five isotherms for the \((\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O})\) system were studied in the present work spanning the range (308.8 to 423.2) K at pressures up to 15.4 MPa. The experimental results are summarised in Table 2 and plotted in Figures 4 and 5. Some literature values obtained at similar conditions were also compared with the data from this study in Figures 6 and 7. The general trend observed is consistent with other reported studies. The \( \mathrm{pH} \) of \( \mathrm{CO}_2 \) saturated water decreased with an increase in pressure and decrease in temperature. This behaviour follows a similar trend found for \( \mathrm{CO}_2 \) solubility in \( \mathrm{H}_2\mathrm{O} \) [24, 31]. It was observed that the \( \mathrm{pH} \) of the \((\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O})\) system initially drops rapidly with increasing pressure but much more slowly at high pressure. Meyssami et al. [17] reported that \( \mathrm{pH} \) decreased from 5.68 to 3.55 in the first 0.7 MPa pressure increase while a 0.35 unit fall was observed from 2 MPa to 5 MPa at \( T = 305 \, \text{K} \). Similar effects were observed by Rosenqvist et al who found that pressurising the system to only 0.6 MPa resulted in a drop of \( \mathrm{pH} \) to 3.55 at \( T = 294 \, \text{K} \). In our experiment, at a \( \mathrm{CO}_2 \) pressure of 0.6 MPa, the \( \mathrm{pH} \) was 3.58 at \( T = 308.3 \, \text{K} \), consistent with the results obtained by Resenqvist et al and Meyssami et al. A much sharper drop was observed in our study and by Parton et al in which the \( \mathrm{pH} \) falls by 0.25 \( \mathrm{pH} \) units from around 1 MPa to around 2.5 MPa at 308.3 K and 295 K, respectively in contrast to Meyssami et al
who reported a moderate pH decrease of 0.12 units from 1.4 MPa to 2.76 MPa at 305 K. The other main difference is that Meyssami et al found that $d(pH)/dp$ dropped significantly after arriving at 5 MPa compared to the gradual decrease of $d(pH)/dp$ until the pressure reached 10 MPa observed in this study. Similar observations supporting this study were reported by Parton et al. Meyssami et al referenced their measurements by using two different pH probes at different pressure ranges but gave neither specific calibration details nor the time taken to reach equilibrium.

Toews et al and Parton et al reported pH results above 10 MPa for the (CO$_2$ + H$_2$O) system. Both sets of measurements used the UV-VIS spectrophotometry method by assessing the spectra of a pH sensitive dye and observed very limited pH changes with the increase of pressure above 8 MPa. Toews et al covered a temperature range up to 343 K as the CO$_2$ pressure increased from 7.1 to 20 MPa and reported a pH decrease from 2.83 to 2.80 as pressure increased while Parton et al concentrated on pH in the sub-critical regime at a temperature of 295.15 K as (0.95 to 8.0) MPa, which they reported as dropping from 2.78 to 2.74 as pressure increased from (8.0 to 10.3) MPa. The data from both studies (where they overlap) agreed to within 0.1 pH units. In our study at $T = (308, 323, 343)$ K, we reached a similar conclusion supporting both previous findings. It was observed that after reaching 10 MPa, further changes in pH were within the experiment uncertainty. The minimum pH obtained at $T = (308, 323, 343)$ K were 2.97, 3.04 and 3.12 respectively. These values agree with the calculation performed by Toews et al to within 0.05 pH units. They fall slightly higher than the results of Parton et al but this may be attributed to the higher temperatures and supercritical regime studied in this work. The minimum pH values obtained in this study at 308 K, 323 K and 343 K are systematically higher than the data measured by Toew et al at same temperatures by about 0.2 pH units.

No literature was found with which to compare our pH measurement at temperature above 368 K. The general trend of the high temperature data follows the same pattern as the low temperature isotherms. A rapid drop in pH was observed with increasing pressure at low pressures, while the pH gradually arrived at a plateau as the pressure was increased above 10 MPa. The main difference is that the final pH for each isotherm is significantly higher than the pH values obtained at lower temperatures. It was also observed that the minimum pH obtained on each isotherm increased with increase of temperature. This behaviour may be explained by the solubility of CO$_2$ in water and by the following dissociation reactions and corresponding equilibrium constants in aqueous solution [32]:

$$H_2O = H^+ + OH^- \quad K_w^\circ = \left(\frac{\alpha_{H^+} \alpha_{OH^-}}{m^\circ} \right)$$  \hspace{1cm} (3)

$$CO_2(aq) + H_2O = H^+ + HCO_3^- \quad K_1^\circ = \left(\frac{\alpha_{H^+} \alpha_{HCO_3^-}}{[CO_2(aq)] \alpha_{HCO_3^-}} \right)$$ \hspace{1cm} (4)

$$HCO_3^- = H^+ + CO_3^{2-} \quad K_2^\circ = \left(\frac{\alpha_{H^+} \alpha_{CO_3^{2-}}}{m^\circ \alpha_{HCO_3^-}} \right)$$ \hspace{1cm} (5)

Here, $K_w^\circ$ is the standard equilibrium constant for dissociation of water; $K_1^\circ$ and $K_2^\circ$ are the standard equilibrium constants of the first and second dissociation reactions of carbonic acid (CO$_2$(aq)/H$_2$O), $\alpha$ denotes activity, and $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ is the standard molality. Bandura and Lvov [25] have reported a semitheoretical approach to calculate the water ionisation
constant \((K_w^\circ)\) over wide ranges of density and temperature. Plummer and Busenberg [32] have reported empirical correlations for \(K_1^\circ\) and \(K_2^\circ\) as functions of temperature up to 523 K at atmosphere pressure as follows:

\[
\log_{10} K_1^\circ = -356.3094 - 0.06091964(T / K) + 21834.37(K / T) + 126.8339\log_{10}(T / K)
- 1684915(K / T)^2
\]

\[\text{(6)}\]

\[
\log_{10} K_2^\circ = -107.8871 - 0.03252849(T / K) + 5151.79(K / T) + 38.92561\log(T / K)
- 563713.9(K / T)^2
\]

\[\text{(7)}\]

These relations were used to calculate the values of the dissociation constants for each isotherm. As expected, the extent of reaction (5) was found to be negligible under the conditions of the present study. Furthermore, for the low temperature isotherms at \(T = (308, 323 \text{ and } 343)\) K, \(pK_1^\circ\) has rather similar values. However, above 343 K, \(pK_1^\circ\) begins to increase continuously with temperature. This is consistent with the trend observed in the minimum pH values found for the five isotherms in this study. No pH measurements were performed at pressures below 0.9 MPa for the isotherms at 398 K and 423 K due to concerns over liquid boiling within the reactor cell, with consequent unstable signals and possible damages to the reference electrodes.

For practical and modelling purposes, it is helpful to have an empirical equation to describe the dependence of pH upon temperature and pressure under CO2 saturation conditions. From Figure 8, it is clear that at each temperature the present results can be correlated as a linear function of the mole fraction of CO2 as follows:

\[pH = A(px) + B\]  \[\text{(8)}\]

Here, \(x\) is the mole fraction of CO2 in the aqueous phase and \(px = -\log_{10}(x)\). We computed \(x\) from the experimentally validated model proposed by Hou et al. [31] The parameters appearing in Eq. 8 for the five isotherms studied are given in Table 3. The expanded uncertainty of this correlation is within 0.04 pH units.

In order to obtain an empirical model for the whole ranges of temperature and pressure investigated, the parameters \(A\) and \(B\) in Eq. (8) were represented as function of temperature as follows:

\[A = a_0 + a_1(T / T_0) + a_2(T / T_0)^2 + a_3(T / T_0)^3\]  \[\text{(9)}\]

\[B = b_0 + b_1(T / T_0) + b_2(T / T_0)^2 + b_3(T / T_0)^3,\]  \[\text{(10)}\]

where \(T_0 = 300\) K. The parameters appearing in Eqs. 9 and 10 are given in Table 4, and relative deviations of the experimental data are shown in Figure 9. The standard error of this surface fit is 0.026 pH units. We do not recommend extrapolation of this empirical correlation to temperatures outside the range investigated in this work.
A predictive model was also developed based on the chemical equilibria of reactions (3) and (4). The individual ion activity coefficient for H⁺, HCO₃⁻ and OH⁻ were considered in the approximation of the Debye-Hückel limiting law [33],

\[-\log(\gamma_i) = Az_i^2 l^{1/2},\]  

where \(z_i\) is the ionic charge of solute \(i\), \(A\) is the temperature-dependent Debye-Hückel constant and \(l\) is the ionic strength of the solution given by

\[l = \frac{2}{Z} \sum_{j} (z_j^2 m_j).\]  

Since \(z^2\) is the same for H⁺, HCO₃⁻ and OH⁻, the activity coefficient of those three ions (\(\gamma_{\text{H}^+}\), \(\gamma_{\text{HCO}_3^-}\), \(\gamma_{\text{OH}^-}\)) can be considered to be the same. Hence, we have

\[\alpha_{\text{HCO}_3^-} = (a_{\text{H}^+} b_{\text{HCO}_3^-})/b_{\text{H}^+},\]  

\[\alpha_{\text{OH}^-} = (a_{\text{H}^+} b_{\text{OH}^-})/b_{\text{H}^+},\]  

where \(b\) is molality and \(\alpha\) denotes activity for the indicated species. Since we also have the condition for electro-neutrality,

\[b_{\text{H}^+} = b_{\text{OH}^-} + b_{\text{HCO}_3^-},\]  

the standard equilibrium constant of reaction (4) may be written as

\[K_{1\Theta}^\Theta = \frac{(a_{\text{H}^+})^2 b_{\text{HCO}_3^-}}{a_{\text{CO}_2(\text{aq})} m^\Theta b_{\text{H}^+}}.\]  

It follows that equilibrium constant \(K_{1\Theta}\) is given by

\[K_{1\Theta} = \frac{(a_{\text{H}^+})^2 (b_{\text{H}^+} - b_{\text{OH}^-})}{a_{\text{CO}_2(\text{aq})} m^\Theta b_{\text{H}^+}} = \frac{(a_{\text{H}^+}/m^\Theta)^2}{a_{\text{CO}_2(\text{aq})}/m^\Theta} - \frac{K_w^\Theta}{a_{\text{CO}_2(\text{aq})}/m^\Theta},\]  

where the water ionisation constant \(K_w^\Theta\) of reaction (3) is given by:

\[K_w^\Theta = \frac{(a_{\text{H}^+})^2 b_{\text{OH}^-}}{[m^\Theta] b_{\text{H}^+}}.\]  

It follows that the activity of H⁺, \(a_{\text{H}^+}\), is given by

\[a_{\text{H}^+}/m^\Theta = [(K_{1\Theta} a_{\text{CO}_2(\text{aq})}/m^\Theta) + K_w^\Theta]^{0.5}.\]  

The activity of CO₂ in aqueous solution may be expressed in the form

\[a_{\text{CO}_2(\text{aq})} = b_{\text{CO}_2(\text{aq})} Y_{\text{CO}_2(\text{aq})} F_P,\]
where $\gamma_{\text{CO}_2(\text{aq})}$ is the activity coefficient of CO$_2$ at the molality and temperature in question but at a reference pressure, and $F_p$ is a Poynting correction that expresses the dependence of activity upon pressure at constant temperature and composition. In term of these quantities, the pH is given by

$$\text{pH} = -\frac{1}{2}\log_{10}\left[K^\ominus_{1} b_{\text{CO}_2(\text{aq})} Y_{\text{CO}_2(\text{aq})} F_p / m^\ominus + K^\ominus_w\right].$$

(21)

In the present case, both the solubility of CO$_2$ in the aqueous phase, the activity coefficient of CO$_2$ (aq) and the Poynting correction were evaluated from the thermodynamic NRTL-based model of Hou et al [31]. Under the conditions investigated here, the water ionisation constant $K^\ominus_w$ is negligible compared with the term in Eq. (21) containing $K^\ominus_1$; however, inclusion of $K^\ominus_w$ ensures that the model behaves correctly also for under-saturated solutions.

The chemical equilibrium model established above was used to compute the pH of CO$_2$-saturated water system at every temperature and pressure measured in this work. The deviations of the experimental data from that model are shown in Figure 10 and were found to be within approximately ± 0.1 pH units.

An alternative analysis was also performed in which $pK^\ominus_1$ was obtained at each temperature and pressure directly from Eq. 21 using the measured pH values from this study. The average values of $pK^\ominus_1$ obtained at each temperature are compared with values from the literature [20, 21, 22, 23, 34] in Figure 11. It can be seen that the value derived from this study are generally in satisfactory agreement with various literature sources over the temperature range investigated.
4. Conclusions

$pH$ measurements have been reported for the CO$_2$-saturated water system on five isotherms at temperatures from 308.3 K to 423.2 K for pressures in the range up to 15.3 MPa. Consistent trends for each isotherm were observed with $pH$ decreasing with increase in pressure towards a plateau at high pressures. A generally good agreement with literature values was observed at low temperatures and pressure up to 16 MPa. The results have demonstrated a linear dependence of $pH$ on negative decimal logarithm of CO$_2$ mole fraction in H$_2$O over the whole range investigated. An empirical equation was proposed to correlate the data. The results were also shown to be consistent with a predictive chemical equilibrium model based on the known solubility and first dissociation constant of CO$_2$ in pure water. The same model may be applied to both saturated and under-saturated solutions.

5. Acknowledgments

This work was carried out as part of the activities of the Qatar Carbonates and Carbon Storage Research Centre (QCCSRC). We gratefully acknowledge the funding of QCCSRC provided jointly by Qatar Petroleum, Shell, and the Qatar Science and Technology Park, and their permission to publish this research.
### 6. Tables

**Table 1:** Operating ranges of the pH and reference electrodes

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>$T$ / K</th>
<th>$p$ / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass pH electrode</td>
<td>273 to 353</td>
<td>0 to 20</td>
</tr>
<tr>
<td>Zirconia pH electrode</td>
<td>363 to 578</td>
<td>0 to 34</td>
</tr>
<tr>
<td>Ag/AgCl reference electrode</td>
<td>273 to 473</td>
<td>0 to 34</td>
</tr>
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Table 2: pH of the (H₂O + CO₂) system at temperatures $T$ and pressures $p$.

<table>
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<tr>
<th>$T$ / K</th>
<th>$p$ / MPa</th>
<th>pH</th>
<th>$px$</th>
</tr>
</thead>
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<tr>
<td>308.3</td>
<td>0.38</td>
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<tr>
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<td>2.58</td>
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Table 3: Parameters in Eq. 8 for the pH as a function of $px$ in CO$_2$-saturated water.

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<td>423.2</td>
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Table 4: Parameters in Eqs 9 and 10 for the pH as a function of px and T in CO₂-saturated water.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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7. Figures

**Figure 1:** Schematic of the high-pressure pH measurement system for CO₂-saturated aqueous solutions: E1, E2, pH measurement and reference electrodes; V, digital voltmeter; SP, syringe pump; R1, R2, pressure relief valves (with relief pressure indicated); PT, pressure transducer; V1 to V6, needle valves; V7, V8, three way ball valves; V9, back-pressure regulator.
Figure 2: Illustration of the reactor cell showing the measurement electrode and reference electrode immersed in the sample solution: 1, pressure fitting for pH electrode; 2, pressure fitting for reference electrode; 3, bolted lid with Viton o-ring face seal; 4, cell body; $V$, digital voltmeter.
Figure 3: Measured e.m.f. $E$ for the glass and zirconia electrodes against the Ag/AgCl reference electrode during calibration at $\text{pH} = (2, 4 \text{ and } 7)$: ■, glass electrode at $T = 308 \text{ K}$; ●, zirconia electrode at $T = 368 \text{ K}$. The data for the zirconia electrode are lowered by 450 mV to keep them on scale.
Figure 4: pH of the (CO$_2$ + H$_2$O) system as a function of pressure $p$: ♦, $T = 308.3$ K; ■, $T = 323.0$ K; ▲, $T = 343.0$ K; ●, $T = 368.1$ K; ×, $T = 398.3$ K; ●, $T = 423.2$ K.
Figure 5: pH of the (CO₂ + H₂O) system as a function of temperature $T$: $\times$, $p = 0.38$ MPa; $\blacksquare$, $p = 0.61$ MPa; $\blacktriangle$, $p = 1.00$ MPa; $\blacklozenge$, $p = 2.43$ MPa; $\ast$, $p = 6.23$ MPa; $\bullet$, $p = 9.28$ MPa; $\oplus$, $p = 15.4$ MPa.
Figure 6: $p$H of the ($\text{CO}_2 + \text{H}_2\text{O}$) system as a function of pressure $p$ in log scale: ♦, this work $T = 308.3$ K; ■, this work $T = 323.0$ K; ○, Meyssamiet al. $T = 305.15$ K; ♣, Meyssami et al. $T = 310.15$ K; ✶, Meyssami et al. $T = 315.15$ K [17]; ×, Calculation performed by Toews et al. $T = 323.15$ K; △, Calculation performed by Toews et al. $T = 343.15$ K [18];
Figure 7: pH of the (CO$_2$ + H$_2$O) system as a function of pressure $p$ in log scale: ◈, this work $T = 308.3$ K; ■, this work $T = 323.0$ K; ▲, this work $T = 343.0$ K; ◇, Toews et al. $T = 313$ K; □, Toews et al. $T = 323.0$ K; △, Toews et al. $T = 343.0$ K [18]; ⋆, Rosenqvist et al. $T = 294$ K [3]. —, Parton et al. $T = 295.15$ K [19].
Figure 8: pH of the (CO₂ + H₂O) system as a function of $p_x = \log_{10}(x)$ where $x$ is the mole fraction of CO₂ in water: ♦; $T = 308.3$ K; ■; $T = 323.0$ K; ▲; $T = 343.0$ K; ---, $T = 368.1$ K; ×, $T = 398.3$ K; ●, $T = 423.2$ K. Lines are linear fit to the data.
Figure 9: Deviation $\Delta(pH)$ of the pH of (CO$_2$ + H$_2$O) system as a function of $px$ from the linear correlation model (Eqs. 9 and 10): $\bullet$, $T = 308.3$ K; $\blacksquare$, $T = 323.0$ K; $\blacktriangle$, $T = 343.0$ K; $\blacktriangleleft$, $T = 368.1$ K; $\times$, $T = 398.3$ K; $\bullet$, $T = 423.2$ K. Dashed lines are twice the standard deviation of this correlation.
Figure 10. Deviation $\Delta(pH)$ of the $pH$ of $(CO_2 + H_2O)$ system as a function of pressure from the chemical equilibrium model shown in Eq. 21: $\bullet$, $T = 308.3$ K; $\blacksquare$, $T = 323.0$ K; $\blacktriangle$, $T = 343.0$ K; $\blacktriangledown$, $T = 368.1$ K; $\times$, $T = 398.3$ K; $\bullet$, $T = 423.2$ K.
Figure 11: $pK_1^\Theta$ for the (CO$_2$ + H$_2$O) system as a function of system temperature ($T$): ○, this study (Eq. 21 with the experimental $pH$); ◊, Patterson et al. [21]; □, Read et al. [22]; △, Park et al. [23]; ×, Harned et al. [20]; +, Ryzhenko [34]. The line corresponds to the correlation proposed by Plummer et al. [32]. The error bars represent the expanded uncertainty of the $pK_1^\Theta$ values determined in this work.
References


[34] R. B.N, Determination of dissociation constants of carbonic acid and the degree of hydrolysis of the CO_3^{2-} and HCO_3^- ions in solutions of alkali carbonates and bicarbonates at elevated temperatures, Geochemistry, 2 (1963) 151-164.