# Improvements in Methodologies for Radiographic Measurement of Diffusion Properties in Low-permeability Rocks, and Development of Methods for pH Measurement in Brines

NWMO-TR-2016-16 June 2016

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## ABSTRACT

**Title:** **Improvements in Methodologies for Radiographic Measurement of Diffusion Properties in Low-permeability Rocks, and Development of Methods for pH Measurement in Brines**
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**Abstract**
The objectives of this research are to develop and improve methodologies for measurement of diffusion properties in low-permeability sedimentary and crystalline rocks, and to develop methods for measurement of pH in high-ionic-strength aqueous solutions. Four separate projects are described.

The first project involved improvement and further development of the radiography method by using a monochromatic Am-241 $\gamma$-ray source. The use of monochromatic $\gamma$-radiation ($\gamma$-RAD) eliminates beam hardening which is a limitation to the precision and accuracy of the X-ray radiography technique. With the elimination of beam hardening, the $\gamma$-RAD technique allows for reliable calibration that is essentially independent of background matrix.

In the second project, diffusion coefficients for iodide ($I^-$) tracer were measured simultaneously using $\gamma$-RAD and through-diffusion on granite. Although only one test was conducted, the results indicate that the $\gamma$-RAD method will be a viable alternative to through-diffusion for measurements on very-low-porosity crystalline rocks.

The third project focused on the investigation of the effect of partial gas saturation on diffusion coefficients. A method has been developed to generate partial gas saturation in a rock sample by equilibrating the porewater with nitrogen ($N_2$) gas at high pressure (up to 7000 kPa) and then rapidly lowering the $N_2$ pressure to atmospheric. The degree of partial saturation is determined by the $\gamma$-RAD method. The effective diffusion coefficient ($D_e$) for iodide tracer at 100% brine saturation was compared to that at different degrees of partial gas saturation. A preliminary result from Queenston Formation shale indicates a 53% decrease in $D_e$ as a result of 14.6% partial gas saturation. The results indicate good potential for evaluating the effect of partial saturation on diffusion in the low-permeability rocks that contain high salinity porewater.

The fourth project focussed on pH measurement in high-ionic-strength brine solutions. Buffers of varying composition and ionic strength were formulated and their pH values were determined by geochemical modelling using the Pitzer ion-interaction approach implemented in the geochemical program PHREEQC. These buffers were used to investigate two methods for pH measurement: potentiometric measurements with glass electrodes, and spectrophotometric measurements using the colorimetric indicator phenol red.

The pH electrode response is linear over a range from 1.4 to 9.1 and for ionic strengths up to 8.2 mol/kg. However, there is a systematic offset with increasing ionic strength such that an electrode calibrated with low-ionic-strength buffers will underestimate pH of a high-ionic-strength solution (8.2 mol/kg) by 0.6 to 0.7 pH units. For any given ionic strength, the potentiometric measurement is also sensitive to the ionic composition of the solution. Despite these effects, accurate potentiometric measurements are possible if the composition of the

calibration buffers is similar to the test solution. The results of spectrophotometric measurements indicate that the disassociation constant ($pK'_a$) of the phenol red indicator is virtually insensitive to the ionic composition of the solution. A maximum error of 0.2 units is possible for pH measured spectrophotometrically if the ionic strength of the buffers does not match the ionic strength of the test solution. However, the measurement range of phenol red is limited to a pH range from ~7 to 9; additional indicators can be used to increase the effective range for the spectrophotometric approach.

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| CT | Carbon Tan sandstone |
| $D_p$ | Pore diffusion coefficient: $D_p=(\delta/\tau)\cdot D_0$, where δ is constrictivity, $\tau$ is tortuosity, and $D_0$ is the free water diffusion coefficient |
| $D_e$ | Effective diffusion coefficient: $D_e=\phi D_p$. |
| DGR | Deep geological repository |
| ER | Edge Response |
| IUPAC | International Union of Pure and Applied Chemistry |
| L-SPW | DGR limestone synthetic porewater |
| MIN3P | Multicomponent reactive transport code |
| NIST | Nation Institute of Standards and Technology |
| NWMO | Nuclear Waste Management Organization |
| ODR | Optical Density Ratio |
| PHREEQC | A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations |
| $pK_a$ | Thermodynamic disassociation constant |
| $pK'_a$ | Conditional disassociation constant |
| RAD | Radiography |
| γ-RAD | Gamma-radiography |
| RSD | Relative Standard Deviation |
| SNR | Signal-to-noise ratio |
| SP | Spatial Resolution |
| S-SPW | DGR shale synthetic porewater |
| TD | Through-diffusion |
| Tris | Tris-[hydroxymethyl]aminomethane |
| TrisHCl | Tris-[hydroxymethyl]aminomethane hydrochloride |
| UNB | University of New Brunswick |
| URL | Underground research laboratory |
| $\phi_I$ | Iodide-accessible porosity |
| $\phi_w$ | Water-loss porosity |
| $\Delta\mu$ | Change in attenuation coefficient |
| $\mu_{brine}$ | Attenuation coefficient of brine–saturated rock |
| $\mu_{PS}$ | Attenuation coefficient for the partially brine-saturated sample |
| $\mu_{PS\text{-}tracer}$ | Attenuation coefficient for the partially tracer-saturated sample |
| $\mu_{tracer}$ | Attenuation coefficient of the tracer–saturated rock |

## 1. INTRODUCTION

This technical report documents activities and outcomes of research performed at the University of New Brunswick between March, 2012 and March, 2014 for the Nuclear Waste Management Organization. The research is intended to continue the development of new methodologies for laboratory measurements of diffusion properties in low permeability rocks and to gain a better understanding of the mechanisms controlling solute transport in diffusion-dominated sedimentary and crystalline rock systems. Such systems are under consideration in Canada as potential host and barrier rocks for a deep geological repository for the long-term management of radioactive waste.

The research is grouped into four projects that are presented separately in this report. The first involved improvement of the radiography method of tracer measurement in the estimation of diffusion properties in low permeability rocks by using a monochromatic $\gamma$-ray source ($\gamma$-RAD) instead of X-rays. One of the main advantages of the $\gamma$-RAD technique is to eliminate the beam hardening that occurs with a polychromatic X-ray source. A second advantage of the $\gamma$-RAD technique is that it allows for measurements on larger samples and provides greater flexibility in the experimental design. The second project involved development of methods for simultaneous measurement of diffusive tracer profiles in low permeability rocks using both $\gamma$-RAD and through-diffusion (TD) methods. This was tested for the first time using a granite sample. In the third project, a method was developed to create partial gas saturation conditions in porous sedimentary rock followed by the measurement of effective diffusion coefficient ($D_e$) values. The effect of partial gas saturation on diffusion coefficients was assessed by comparing the $D_e$ values measured at full brine saturation with those measured at different degrees of partial gas saturation. The fourth project involved development of improved methods for pH measurement in high salinity natural porewaters. Accurate and precise measurement of pH at high ionic strength is important for a range of research activities that seek to quantify water-rock reaction processes (e.g. ion exchange, speciation, surface complexation, and mineral precipitation and dissolution), most of which are sensitive to pH.

## 2. $\gamma$-RADIOGRAPHY METHOD

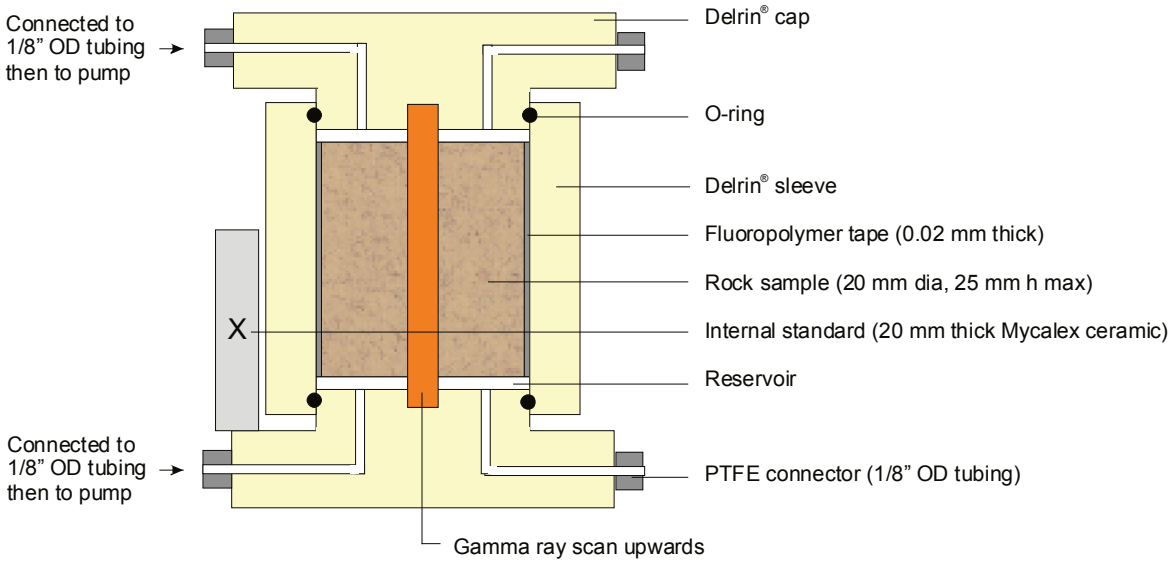
A $\gamma$-RAD technique was first developed by Subudhi (2009) and Subudhi et al. (2010) for measurement of porosity and diffusion coefficients of porous media. The method is similar in principle to the X-ray RAD technique (Al et al. 2010; Cavé et al. 2009, Cavé et al. 2010) except that it uses monochromatic gamma radiation from an Am-241 source. This has some advantages over the use of X-rays in that it minimizes or eliminates artefacts from beam hardening and X-ray-beam geometry and there are no restrictions on the sample size.

New sample cells were designed and constructed as shown in Figure 1. The cell shown in Figure 1a was used for simultaneous diffusion measurements with $\gamma$-RAD and TD methods, and the cell in Figure 1b was used for quantifying the degree of partial gas saturation and for measuring $D_e$ on rock samples with variable brine-gas saturation states.

The circumference of the cylindrical sample (nominal 20 mm diameter, 13-25 mm height) was wrapped with a thin Teflon® tape (0.02 mm thickness, Green Belting Industries). The seam was sealed with a thin bead of silicone. The sample was pressed into the Delrin® sleeve

(Figure 1) and then saturated with a background brine solution (Appendix A). After sample saturation, the diffusion cell was assembled by installing Delrin® caps at each end (Figure 1).

a)




b)

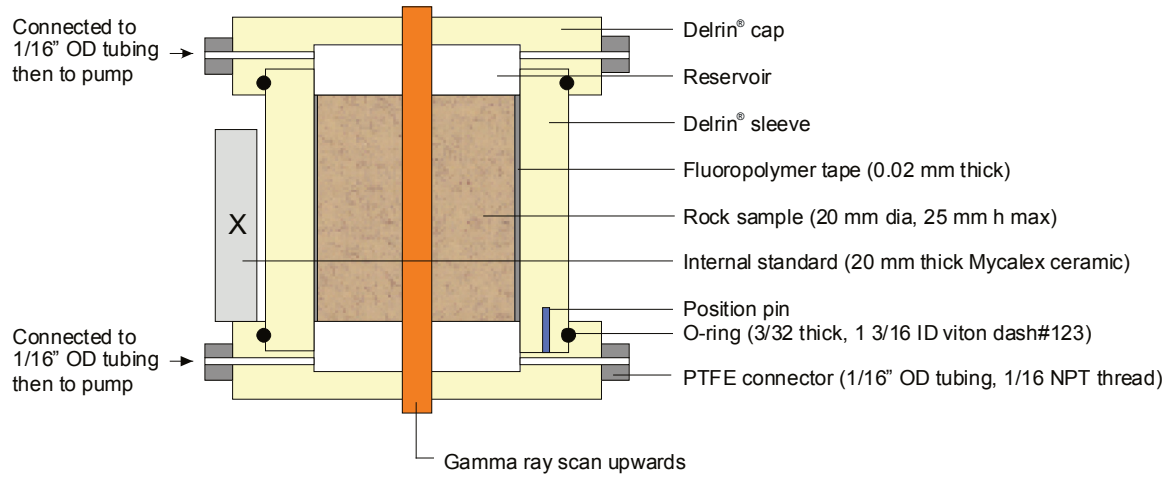



**Figure 1: Sample Cell Designs for γ-RAD Experiments: (a) Sample Cell for Simultaneous Measurements Using γ-RAD and TD Techniques, (b) Sample Cell Used for Partial Saturation Experiments**

Mycalex® ceramic was used for an internal standard because it has similar density and $\gamma$ attenuation to the experimental rock materials (Loomer et al. 2013a). The internal standard was fixed to the side of the cell. The radiation path along the rock sample is shown in Figure 1. The length of the radiation path is 20 mm for both the rock samples and for the ceramic standard. The diffusion cell was mounted on a stage controlled by an automated stepping motor (BiSlide® Velmex Inc.; Figure 2). Positioning pins were constructed on the stage so that the cell can be removed and replaced in the same position during the experiments.

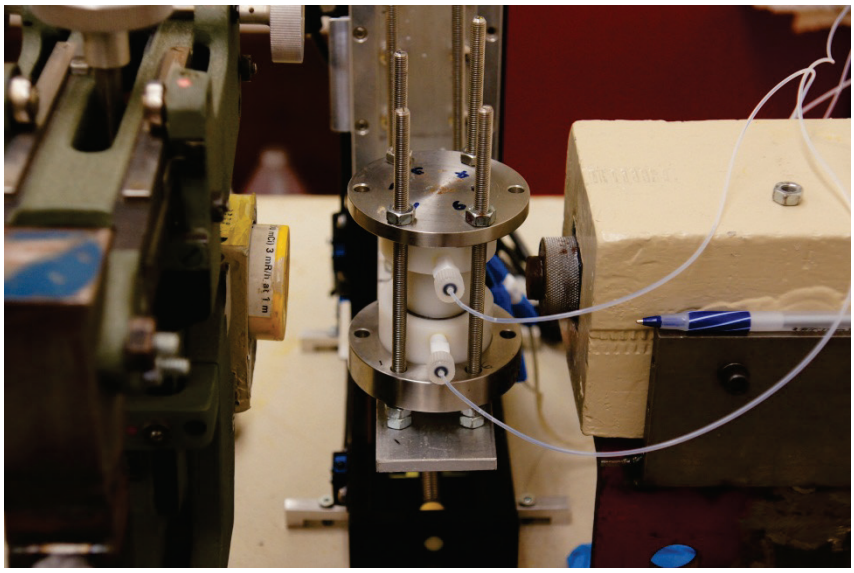


**Figure 2: Photograph of the $\gamma$-RAD System: The Am-241 $\gamma$-Ray Source is Visible at Left (Yellow), the Sample Cell is Mounted on a Computer-Controlled Stage in the Middle, and the Tl-NaI Detector is Encased in a Painted (Beige) Pb Brick at Right. Note that the Source Collimator was Removed for the Photo but the Detector Collimator is in Place**

The system employs an Am-241 sealed source (11.1 GBq), a Tl-NaI detector (Canberra model 802) powered by a Tennelec model TC950 detector bias supply, and a Tennelec model TC246 amplifier and single channel analyzer. The source and detector collimation, and the source-detector alignment are described by Subudhi et al. (2010). The operating parameters are presented in Table 1. The spatial resolution of the measurements (1.4 to 1.5 mm diameter) was determined using an Edge Response (ER) technique (Smith 2003; Hussein 2011). The ER measures how an instrument responds to a sharp discontinuity and involves collecting a line profile across the boundary of two sharply contrasting materials or media (such as the edge of a solid material and air). The spatial resolution is taken to be the distance required for the profile to rise from 10% to 90% of the difference in the values of the two contrasting materials or media. In this case the spatial resolution was determined by scanning (0.25 mm step size) across the sharp edge of a 3-mm-thick steel bar positioned on the sample stage (Figure 3).

**Table 1: Am-241 γ-RAD Operating Parameters**

| | |
|---|---|
| Collimator diameter | 3.0 mm |
| Sample thickness | 20 mm |
| Source-detector distance | 10 mm |
| Detector-sample distance | 4 mm |
| Source collimator length | 10.0 mm |
| Detector collimator length | 95 mm |
| Detector Output voltage | 1700 V |
| Coarse gain | 50 |
| Fine gain | 8 |
| Overall gain | 50 x 0.8 = 40 |
| Stage increments (X,Z) | 200 per 1.0 mm |
| Spatial resolution (diameter) | 1.4 - 1.5 mm |
| Measurement step size (mm) | 0.5 - 1.0 |
| Scan time/point (s) | 35 – 60 |

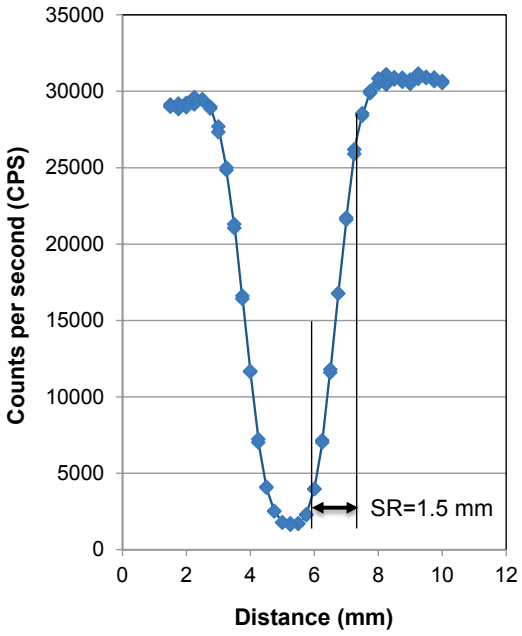



**Figure 3: Estimation of Spatial Resolution (SR) for γ-RAD Technique**

The radiography method for measuring diffusion coefficients uses a blank subtraction approach (Al et al. 2010; Cavé et al. 2009; Cavé et al. 2010) to remove the constant background attenuation effects of the porous matrix. Time-series radiographs (samples with tracer at t > 0) are subtracted from a reference radiograph (sample without tracer at t = 0) to determine the change in attenuation due to tracer mass in the pores, which we define as the parameter $\Delta\mu$:

$$\Delta\mu_x = \ln(I_{ref})_x - \ln(I_t)_x = (\mu_{p\ t=0} - \mu_{p\ t>0})_x \cdot \phi_x \quad (1)$$

where: t is time, $(I_{ref})_x$ is the transmitted $\gamma$-ray intensity at distance x on the t = 0 (reference) profile, $(I_t)_x$ is the transmitted $\gamma$-ray intensity at the same distance on one of the time-series profiles (t > 0), $\mu_{p\ t=0}$ and $\mu_{p\ t>0}$ are the attenuation coefficients of the pore fluids in the reference and time-series radiographs, respectively. The parameter $\Delta\mu$ is a function of the mass of tracer along the $\gamma$-ray path and is used to determine quantitative measurements of tracer concentration (Al et al. 2010; Cavé et al. 2009; Cavé et al. 2010).

There is significant ambiguity in the literature in terms of diffusion-related terms, so the following definitions are provided for clarity:

$$\text{Pore diffusion coefficient} = D_p = D_0 \cdot \tau_f \quad (2)$$

where: $D_0$ is the free-water diffusion coefficient and $\tau_f$ is the tortuosity factor,

$$\text{Effective diffusion coefficient} = D_e = D_p \cdot \emptyset \quad (3)$$

where: $\phi$ is porosity.

## 2.1 CALIBRATION

Calibration curves for $\Delta\mu$ as a function of $I^-$ concentration were generated by the method reported by Cavé et al. (2009) using the sample cell (Figure 1) filled with a series of brine/tracer standard solutions. The $\Delta\mu$ values were normalized to the diameter of the rock samples, which is slightly smaller than the inner diameter of the Delrin® sleeve. Results of the calibration in a 1.0 M $NaNO_3$ matrix and in a much more saline S-SPW matrix (shale synthetic porewater, see Table 4) are presented in Figure 4. This relationship is linear over a range of $\Delta\mu$ up to approximately 2 and the slope is almost independent of the background matrix. In contrast, calibration curves obtained with X-ray radiation are affected by beam hardening which results in non-linear relationships and matrix dependency.

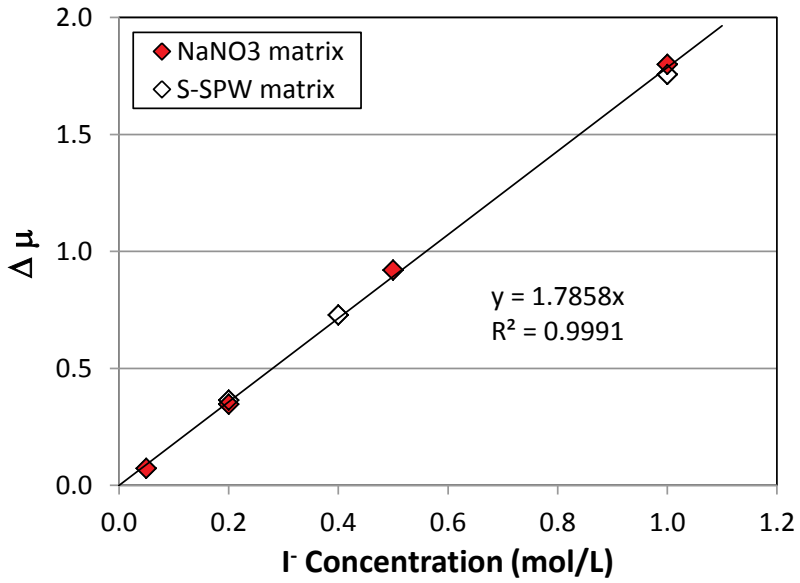



**Figure 4: Calibration between Δμ and $I^-$ Concentration Using the γ-RAD Technique**

## 2.2 SUMMARY

The use of monochromatic Am-241 γ radiation eliminates beam hardening, providing a precise calibration function. Results of calibration indicate a linear function over a large range in Δμ that is not sensitive to the background matrix. The method is appropriate for measurements of tracer concentration in cases where spatial resolution on the order of 1 mm or greater is satisfactory.

## 3. DIFFUSION MEASUREMENTS WITH GRANITE

### 3.1 METHODS

A test was conducted to determine the potential for using the γ-RAD method for measuring diffusion coefficients of crystalline rocks such as granite. The testing was conducted on archived granite sample from the Atomic Energy of Canada Limited Whiteshell Research Area, specifically a segment of borehole 209-069-PH3 (sample OPG-10 from Cavé and Al 2006). A subsample, 20 mm in diameter, was prepared by diamond coring and then the sample was mounted in the modified diffusion cell (Figure 1a) which allows for simultaneous measurements by TD and by γ-RAD methods. The sample was saturated with $NaNO_3$ (4 mol/L) solution by immersion (mounted in the Delrin® sleeve) under vacuum for 3 days (Appendix A). The cell was then assembled and 4 mol/L $NaNO_3$ solution was circulated through both ends for 8 additional days. The concentration of the $I^-$ tracer and the scanning parameters (Table 2) were selected to provide sufficient contrast for the γ-RAD method. The TD measurements were conducted according to the methods previously described by Cavé et al. (2010) and Xiang et al. (2013).

**Table 2: γ-RAD Experimental Conditions**

| Sample | Carbon Tan | Queenston shale | Granite |
|---|---|---|---|
| Scan time/point (s) | 35 | 35 | 60 |
| Measurement Step Size (mm) | 1.0 | 0.75 | 0.5 |
| Synthetic Pore Fluid | 1.0 M $NaNO_3$ | S-SPW[a] | 4.0 M $NaNO_3$ |
| Tracer | 1.0 M NaI | 2.0 M $I^-$ in S-SPW[b] | 4.0 M NaI |

[a] Shale synthetic porewater, Table 4; [b] Equal moles of NaCl were substituted by NaI in S-SPW.

### 3.2 RESULTS

The γ-RAD measurements (Figure 5) display a large degree of scatter due to the low porosity and the resulting small mass of tracer contained in the sample. Efforts to enhance the signal to noise ratio (SNR) included the use of long counting times and high tracer concentration (Table 2). Despite the scatter in the data it is possible to identify tracer profiles that advance with time, and an average pore diffusion coefficient ($D_p$) value of $7.2\times10^{-11}$ $m^2/s$ is obtained. For the purpose of comparison, this $D_p$ value can be multiplied by $\phi_I$ (0.0043) (iodide accessible porosity) to obtain a $D_e$ value of $3.1\times10^{-13}$ $m^2/s$ which is consistent with measured diffusion coefficients for crystalline rocks from Manitoba Canada, Sweden and Finland (Table 3). A through-diffusion (TD) experiment was conducted simultaneously, and the early-time trends in the tracer flux and cumulative mass data (<13 days; Figure 6) evolved according to expectations. However, beyond 13 days the tracer flux decreases in a way that is inconsistent with steady-state diffusion. This behaviour is thought to result from gradual occlusion of diffusion pathways due to mineral-water reactions. Although the early time data (<13 days) indicate a $D_e$ value of $3.0\times10^{-13}$ $m^2/s$ which is very close to the value obtained by γ-RAD,

confidence in this result is low because of the unexpected decline in the tracer flux after 13 days.

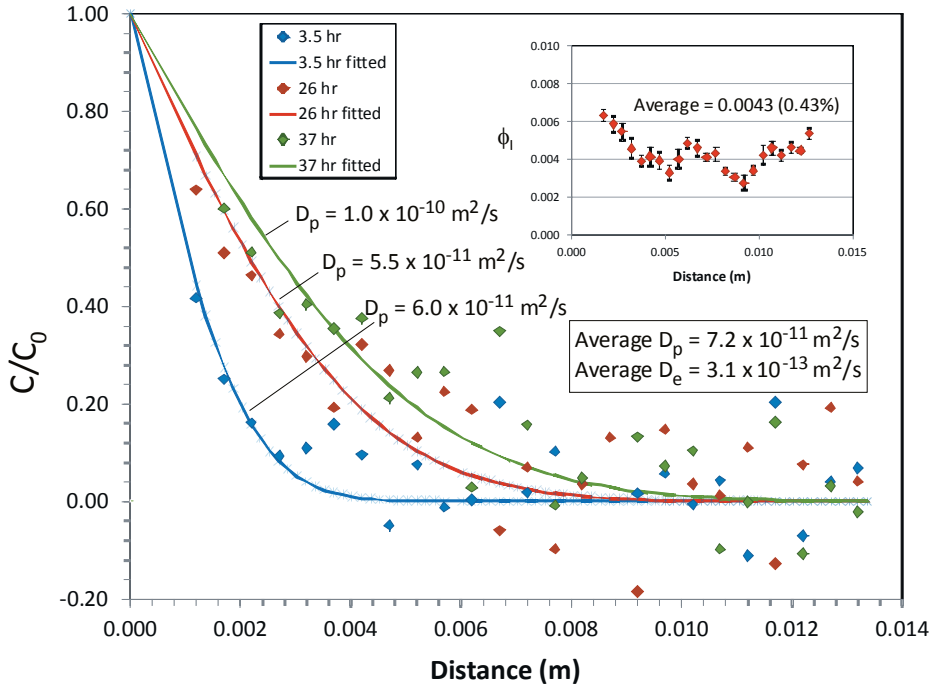



**Figure 5: Diffusion Profiles in Granite Obtained by γ-RAD with 4.0 M NaI Tracer. Inset: $\phi_I$ Profile of the Rock Sample**

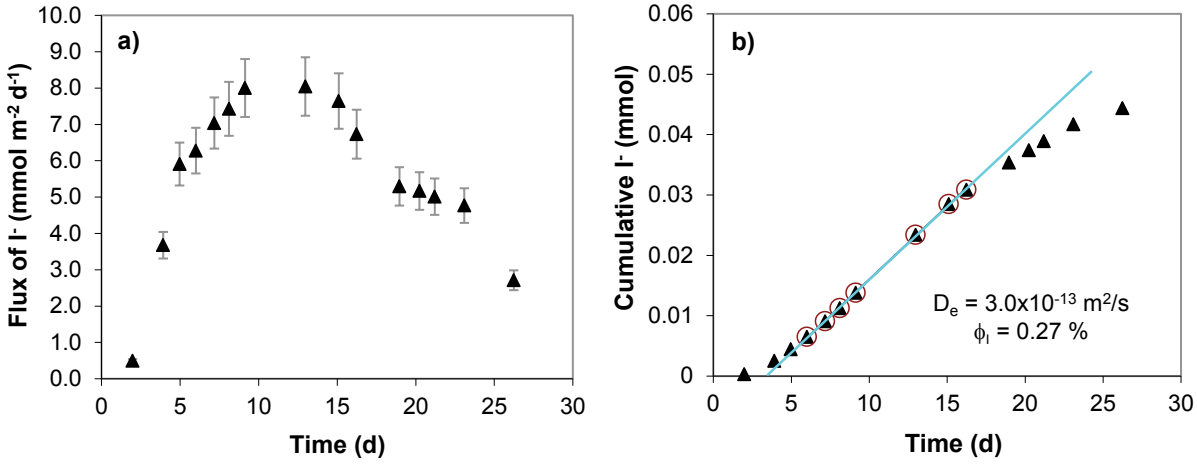



**Figure 6: Results of Through-diffusion Experiment with Granite: (a) Flux of $I^-$ Tracer and (b) Cumulative $I^-$ Quantity as a Function of Time. This Experiment was Conducted Simultaneously with the γ-RAD Experiment (Figure 5)**

**Table 3: Literature Values of Diffusion Properties Obtained by Through-diffusion Experiments for Crystalline Rocks**

| Location | Rock type | Porosity | $D_e$ ($m^2/s$) | Exp. condition | Ref. |
|---|---|---|---|---|---|
| Canada, URL Manitoba | Granite, granodiorite | 0.22-0.28% ($H_2O$ immersion), 0.46 - 0.94% ($I^-$; TD) | $2.1x10^{-12}$ to $1.9x10^{-13}$ | in situ, $I^-$ | a |
| | | | $2.2x10^{-12}$ to $2.7x10^{-12}$ | Lab, $I^-$ | |
| Sweden central, east coast | Granite, granodiorite | | $7.0x10^{-12}$ to $1.3x10^{-13}$ | lab, $I^-$ | b |
| | | | $1.3x10^{-13}$ to $1.8x10^{-13}$ | lab, HTO | |
| Sweden, Aspo lab | Diorite and granite | 0.36 - 0.84% | $1x10^{-13}$ to $9x10^{-13}$ | lab, $I^-$, HTO | c |
| Finland | Tonalite and mica gneiss | 0.1 - 3% (tonalite)<br>0.2% (mica gneiss) | $3.0x10^{-12}$ to $9x10^{-13}$<br>$1.0x10^{-12}$ to $6x10^{-13}$ | lab, TD, HTO<br>lab, TD, $Cl^-$ | d |

[a] Vilks et al. 2003; [b] Skagius and Neretnieks 1986; [c] Xu et al. 2001 and Johansson et al. 1998; [d] Siitari-Kauppi et al 1997.

### 3.3 SUMMARY

The γ-RAD method has been tested for potential use in measurement of $D_e$ values for crystalline rock samples. The result is consistent with the range of values obtained for crystalline rocks elsewhere. The result is also in good agreement with the $D_e$ value obtained with simultaneous measurement by TD on the same sample ($3.0\times10^{-13}$ $m^2 \cdot s^{-1}$ and $3.1\times10^{-13}$ $m^2 \cdot s^{-1}$, respectively). However, there is low confidence in the TD measurement. This is the first and only test of the radiography method on low-porosity crystalline rocks and, although further improvements are possible, the results suggest that it is a viable approach.

## 4. EFFECT OF PARTIAL GAS SATURATION ON DIFFUSION

Results of site characterization studies at the Bruce nuclear site suggest that at some depths in the Ordovician shales and limestones the porewater saturation may be less than 100% and the pore volume may be occupied by a mixture of porewater and gas (Intera, 2011). Partial gas saturation may result from the formation of methane by thermogenic or biogenic mechanisms. Pore-scale changes in the volume ratio of gas and porewater are expected to affect $D_e$ for both aqueous solutes and gases (Savoye et al. 2010).

In this study, our objectives are:

- to develop a method to create partial saturation in rock samples for use in testing of the γ-RAD technique;
- to determine the degree of the partial saturation using the γ-RAD technique; and,
- to investigate the effect of partial saturation on $D_e$ in low permeability rocks.

Sedimentary rocks may contain highly saline porewater, and experimental methods for generating partial saturation must not cause dewatering which could lead to the precipitation of salts, occlusion of porosity and artefacts in $D_e$ measurements.

### 4.1 BACKGROUND: CREATING PARTIAL GAS SATURATION

The approach to creating partial-gas-saturated conditions in rock samples uses $N_2$ gas and takes advantage of the variability of $N_2$ solubility versus pressure. The solubility of a gas in aqueous solution at a given temperature is proportional to its partial pressure. This is known as Henry's law:

$$S_i = K_H \bullet P_i \qquad (4)$$

where $S_i$ is the solubility of gas i (mol/L) in an aqueous solution; $K_H$ is the Henry's law constant ($mol \bullet L^{-1} \bullet atm^{-1}$ or M/atm) for gas i in the solution; $P_i$ is the partial pressure of gas i (atm). The constant $K_H$ is dependent on the gas, the temperature and the solution composition. The partial saturation experiments described herein are conducted at 25 °C using $N_2$ gas and synthetic porewater solution (1.0 mol/L $NaNO_3$ solution for the Carbon Tan sandstone and shale synthetic porewater, S-SPW, for the Queenston Formation shale, Table 2). The composition of S-SPW (Table 4) was adapted from previous work on shale samples (Al et al. 2010, 2012; Cavé et al. 2010; Loomer et al. 2013b; Xiang et al. 2013). The solubility of $N_2$ at 25 °C as a

function of partial pressure ($P_{N2}$; Figure 7) was calculated with the empirical model reported by Mao and Duan (2006) for $N_2$ solubility in NaCl solutions up to 5.3 mol/L. Model calculations were conducted using 1.0 mol/L NaCl solution as a proxy for the 1.0 mol/L $NaNO_3$ Carbon Tan sandstone porewater. Model calculations for the Queenston shale porewater were conducted at the 5.3 mol/L (NaCl solution) limit of the model although the S-SPW is actually a Na-Ca-Cl solution with 5.8 mol/L $Cl^-$. As a result, the model calculations do not fully represent the experimental system, and particularly for the S-SPW case, it is expected that the $N_2$ solubility in S-SPW will be overestimated by the model.

**Table 4: Composition of Synthetic Porewater (SPW) Solutions Used at UNB**

| | S-SPW (mol/kg) | L-SPW (mol/kg) |
|---|---|---|
| $Na^+$ | 2.71 | 2.18 |
| $K^+$ | 0.56 | 0.49 |
| $Ca^{2+}$ | 1.36 | 0.53 |
| $Mg^{2+}$ | 0.28 | 0.22 |
| $Cl^-$ | 6.55 | 4.16 |
| $SO_4^{2-}$ | 0.001 | 0.005 |
| Ionic Strength | 8.2 | 4.9 |

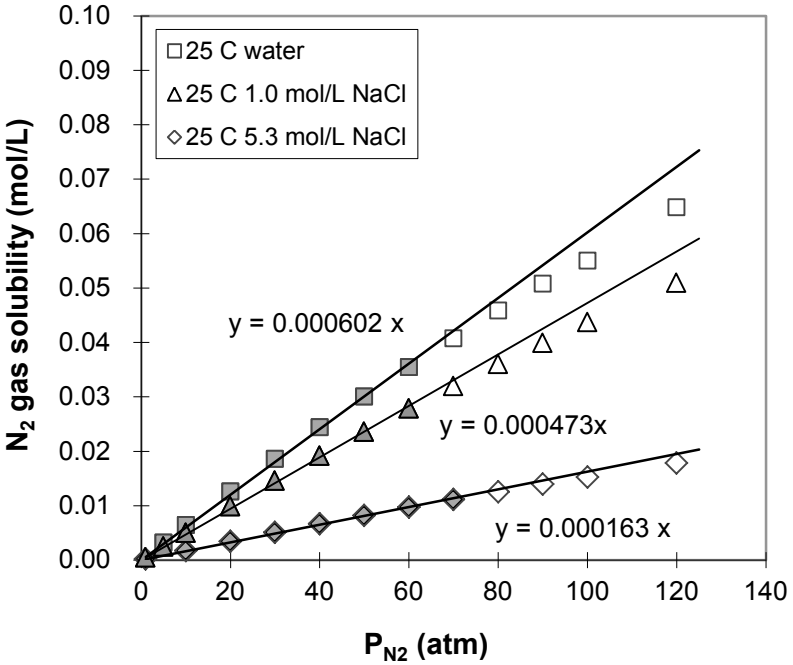



**Figure 7: Henry's Law Plots for $N_2$ Gas at 25 ˚C in Water, 1.0 mol/L NaCl and 5.3 mol/L NaCl Solutions Calculated Using the Empirical Model Reported by Mao and Duan (2006). The Slopes Correspond to the Henry's Law Constants ($K_H$)**

Data in Figure 7 indicate that $N_2$ solubility in 1.0-5.3 mol/L NaCl brines obeys Henry's law up to a partial pressure of 60-70 atm (filled symbols), after which (open symbols) there is a slight departure from linearity. The $K_H$ values determined are 0.000473 M/atm for 1.0 mol/L NaCl brine and 0.000163 M/atm for 5.3 mol/L NaCl.

When a brine system undergoes a change in $N_2$ partial pressure from high ($P_1$) to low ($P_2$), the solubility of $N_2$ decreases correspondingly from $S_1$ to $S_2$. As a result, gas bubbles will form in the solution. For the brine solution occupying the pore spaces in a rock sample, gas bubbles should form in the pore spaces, causing partial brine saturation. Assuming equilibrium is established at $P_2$, the moles of $N_2$ bubbles, n, can be calculated according to:

$$\mathbf{n_{bubble} = K_H V_p (P_1 - P_2)} \qquad \mathbf{(5)}$$

where $V_p$ is the volume of the rock pores (L) initially occupied by brine. The volume of the gas bubbles ($V_{bubble}$) formed at $P_2$ can be calculated using the ideal gas law:

$$\mathbf{V_{bubble} = n_{bubble} RT/P_2 = K_H V_p (P_1 - P_2) RT/P_2} \qquad \mathbf{(6)}$$

The bubble volume calculated by this method was compared to the bubble volume calculated using Van der Waal's equation for non-ideal gases. A maximum difference between two methods of 0.07% was noted under the experimental conditions. Assuming bubbles are formed and remain in the rock pores (the volume change is accounted for by expulsion of brine from the pores), the relative pore volume occupied by gas (% gas saturation) will be:

$$\mathbf{\% \text{ gas saturation} = [K_H (P_1 - P_2) RT/P_2] \times 100\%} \qquad \mathbf{(7)}$$

Experiments were designed so that $P_2$ was equal to 1 atm of $N_2$ (moisturized). Values for the % gas saturation as a function of $P_1$ (Table 5) were calculated using Equation 7. The calculations included $P_1$ values beyond the linear region in Figure 7 (>60-70 atm) assuming Henry's law still applies.

**Table 5: Relationship between % Gas Saturation and Initial $N_2$ Pressure ($P_1$)**

| | 1.0 M NaCl | | 5.3 M NaCl | |
|---|---|---|---|---|
| % gas sat. | $P_1$ (atm) | $P_1$ (kPa) | $P_1$ (atm) | $P_1$ (kPa) |
| 2 | 2.6 | 268 | 5.8 | 591 |
| 5 | 5.2 | 522 | 13.1 | 1329 |
| 10 | 9.3 | 947 | 25.3 | 2560 |
| 20 | 17.7 | 1795 | 49.6 | 5022 |
| 25 | 21.9 | 2219 | 61.7 | 6253 |
| 30 | 26.1 | 2643 | 73.9 | 7484 |
| 35 | 30.3 | 3068 | 86.0 | 8715 |
| 40 | 34.5 | 3492 | 98.2 | 9946 |
| 45 | 38.6 | 3916 | 110.3 | 11177 |
| 50 | 42.8 | 4340 | 122.5 | 12408 |
| 55 | 47.0 | 4765 | 134.6 | 13639 |
| 60 | 51.2 | 5189 | 146.8 | 14870 |
| 70 | 59.6 | 6037 | 171.1 | 17332 |
| 80 | 68.0 | 6886 | 195.4 | 19794 |
| 90 | 76.3 | 7734 | 219.7 | 22256 |

[a]Data were calculated using Equation 7 under the following conditions: T = 25 ˚C, $P_2$ = 1.0 atm $N_2$, 1.0 mol/L or 5.3 mol/L NaCl brine with a $K_H$ constant of 0.000473 mol $L^{-1}$ $atm^{-1}$ or 0.000163 mol $L^{-1}$ $atm^{-1}$ (Figure 7), respectively.

Estimates of % gas saturation from Equation 7 represent the maximum attainable values. The actual degree of partial saturation achieved by experiment is expected to be lower because some $N_2$ may be lost from the system by diffusion while the system re-equilibrates from $P_1$ to $P_2$. The actual degree of partial saturation is determined by the $\gamma$-RAD method.

## 4.2 EXPERIMENTAL PROCEDURES

Samples used in the investigation of partial gas saturation include one sample of Carbon Tan sandstone that was used in two experiments, one after the other (CT-6A and CT-6B) and a sample of Queenston Formation shale (DGR3-472). The experimental procedures are as follows:

- The samples were saturated according to the methods described in Appendix A using a synthetic pore fluid (1.0 mol/L $NaNO_3$ for the Carbon Tan sandstone and S-SPW for the Queenston Formation shale), installed in a Delrin® diffusion cell (Figure 1b).
- The initial reference scan was conducted prior to the introduction of tracer, which provides a measure of the $\gamma$ attenuation properties of the brine–saturated rock ($\mu_{brine}$).
- The samples were submerged in the tracer solution (Table 2) and allowed to saturate with $I^-$ tracer after which $\gamma$-RAD scans were conducted to measure the $\gamma$ attenuation properties of the tracer–saturated rock ($\mu_{tracer}$).

- The solution containing the samples was then placed in a chamber pressurized with $N_2$ gas ($P_1$, Table 6). The system was allowed to equilibrate for up to 27 days, after which time the $N_2$ pressure in the chamber was decreased to one atmosphere ($P_2$), the sample was removed from the tracer solution and the diffusion cell was quickly re-assembled (<15 minutes).
- Moisturized $N_2$ gas (~1 atm) was pumped through both reservoirs (~15 mL/min) and radiography scans were recorded to monitor the displacement of tracer solution from the sample due to formation of $N_2$ gas bubbles. It took between five and ten hours for this process to stabilize in the Carbon Tan sandstone sample, and 48 hours in the Queenston shale sample.
- Fresh tracer solution (1.0 M $I^-$ for Carbon Tan sandstone and 2.0 M $I^-$ for Queenston Formation shale) was then allowed to circulate through both reservoirs for up to eleven days to ensure that the brine/gas saturation states had stabilized. Three scans were conducted before starting the diffusion experiment and the average of these scans ($\mu_{PS\text{-}tracer}$) provides a reference for the diffusion experiment to measure $D_e$ for the partially saturated sample. This measurement was conducted as an "out-diffusion" experiment whereby synthetic pore fluid was introduced to one reservoir and tracer was allowed to diffuse out of the sample.
- After the out-diffusion measurement, the remaining $I^-$ tracer was removed by circulating synthetic pore fluid through both reservoirs while recording radiography scans periodically to confirm complete removal.
- After tracer removal, three final scans were recorded ($\mu_{PS\text{-}brine}$) to complete the multi-step experiment.

A quantitative measure of the degree of partial gas saturation is obtained as:

$$\% \text{ gas saturation} = \left(1 - \frac{\Delta\mu_{ps}}{\Delta\mu_S}\right)100\% \quad (8)$$

Where subscripts *ps* and *S* indicate partially-saturated and saturated conditions respectively.

For the purpose of comparison, an in-diffusion experiment was conducted following the out-diffusion experiment (CT-6A and CT-6B respectively).

**Table 6: Experimental Conditions Used for Partial Gas Saturation Experiments**

| **Experiment ID** | CT-6A | CT-6B | DGR3-472 |
|---|---|---|---|
| **$P_1$ (kPa)** | 4400 | 6600 | 7000 |
| **T (°C)** | 23 ± 2 | 22.5 ± 0.5 | 23 ± 1 |
| **Predicted % gas saturation (from Table 5)** | 50 | 80 | 28 |

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Partial Gas Saturation

#### 4.3.1.1 Carbon Tan Sandstone

One-dimensional profiles of $\Delta\mu$ that reflect the distribution of $I^-$ tracer mass in the rock samples are compared before and after establishment of partial gas saturation (Figure 8a). The concentration of $I^-$ in the porewater remains constant so the systematic shift of the profiles to lower $\Delta\mu$ values is consistent with a decrease in porewater volume. Profiles of $\Delta\mu$ have been converted to that of $\phi_I$ (Figure 8b) using the calibration function of the $\gamma$-RAD method (Section 2.1). These results demonstrate that there is a near-uniform displacement of pore fluid due to formation of a discrete gas phase. Measurements indicate that the average partial gas saturation is 15.2% (84.8% brine) for experiment CT-6A and 13.5% (86.5% brine) for experiment CT-6B calculated by equation 8 (Table 7). These percentages are much lower than the predictions (50% and 80% respectively; Table 6). The discrepancy between predicted and measured values may be explained by non-ideal effects that are not accounted for in the ideal-gas law or the Van der Waal equation. Perhaps most importantly, the tendency to form a discrete gas phase in the pore space will be limited by the permeability, which controls the rate of pore fluid displacement by the expanding gas bubbles.

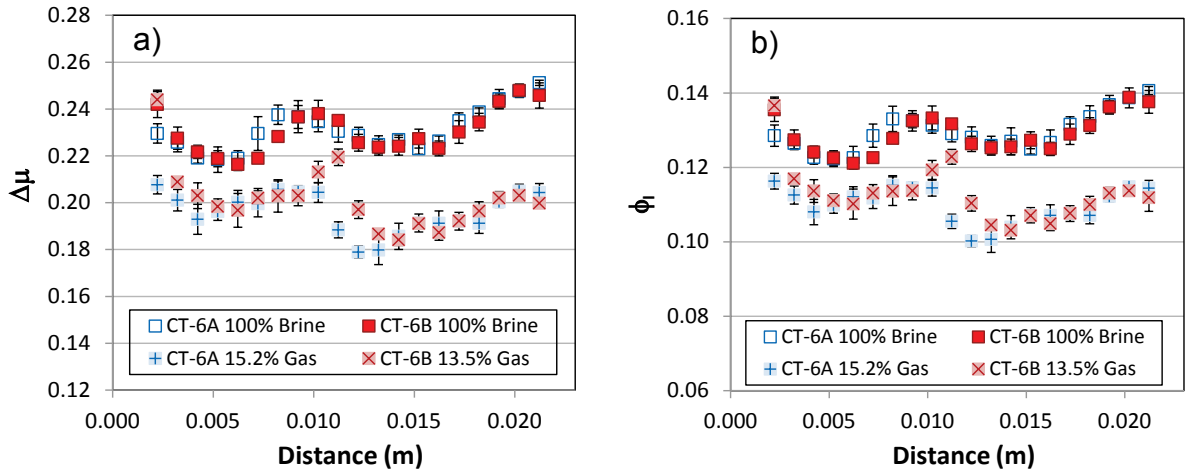



**Figure 8: One Dimensional Profiles of a) $\Delta\mu$ and b) $\phi_I$ of 1 M $I^-$ Tracer in Carbon Tan Sandstone (Experiments CT-6A and CT-6B) before and after Establishment of Partial Gas Saturation. Error Bars Represent the Standard Deviation Measured on Replicate Scans over a Period of up to 7 Days**

**Table 7: Properties of Variably Saturated Carbon Tan Sandstone**

| Experiment | CT-6A | CT-6A-PS[a] | CT-6B | CT-6B-PS[a] |
|---|---|---|---|---|
| **Δμ (1 M $I^-$)** | 0.231 | 0.196 | 0.230 | 0.199 |
| **$\phi_I$ (brine)[b]** | 0.129 | 0.110 | 0.129 | 0.111 |
| **% Brine Saturation** | 100 | 84.8 | 100 | 86.5 |
| **% Gas Saturation** | 0 | 15.2 | 0 | 13.5 |
| **$D_p$ ($m^2/s$)** | 4.1E-10 | 3.9E-10[c] | 4.8E-10 | 2.4E-10 |
| **$D_e$ ($m^2/s$)** | 5.3E-11 | 4.2E-11[c] | 6.2E-11 | 2.7E-11 |

[a] PS indicates samples with partial gas saturation; [b] brine-filled porosity determined by γ-RAD;
[c] average of values determined by in- and out-diffusion experiments.

4.3.1.2 Queenston Formation Shale

Profiles representing the distribution of $I^-$ tracer in the shale sample before and after establishment of partial gas saturation (Figure 9) indicate a general shift to lower $I^-$ mass, in a similar manner to the sandstone samples. Unfortunately, data in Figure 9 also indicate that sample breakage occurred at a distance of 0.015 m. The sample separated along the bedding plane, presumably due to the build-up of gas pressure that could not be relieved by pore fluid displacement because of the low permeability of the rock. This problem can be avoided with some minor modifications to the diffusion cell design. Results of measurements reported in Table 8 for this partially-gas saturated sample were obtained from the data collected in the 0-0.015 m portion of the sample. Measurement of the degree of partial gas saturation indicates 14.6% (85.4% brine). Once again, this percentage is lower than predicted (28%, Table 6).

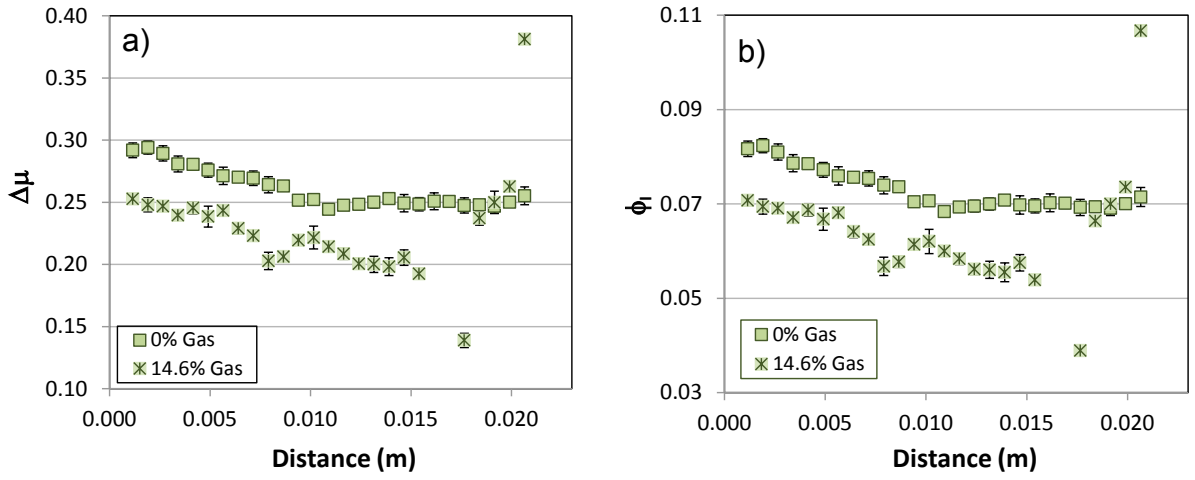



**Figure 9: One Dimensional Profiles of a) Δμ and b) $\phi_I$ of 2 M $I^-$ Tracer in Queenston Shale Sample (DGR3-472) before and after Establishment of Partial Gas Saturation. Error Bars Represent the Standard Deviation Measured on Replicate Scans over a Period of 4 Days**

**Table 8: Properties of Variably Saturated Queenston Formation Shale**

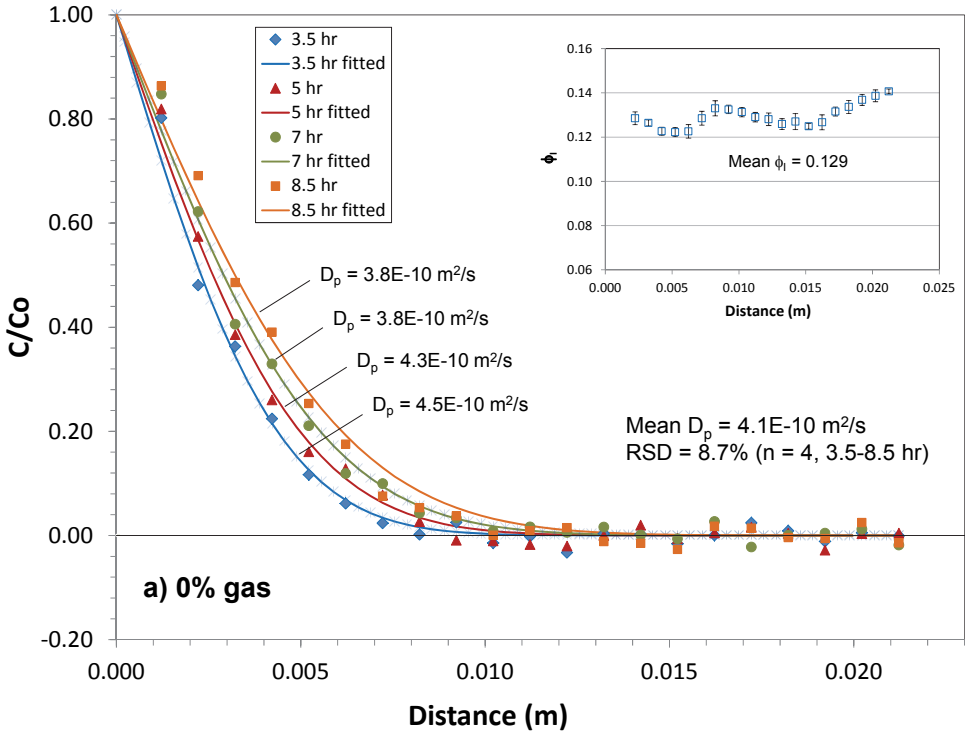
| **Sample** | DGR3-472 | DGR3-472-PS[a] |
|---|---|---|
| **Δμ (2 M $I^-$)** | 0.261 | 0.223 |
| **$\phi_l$ (brine)[b]** | 0.073 | 0.063 |
| **% Brine Saturation** | 100 | 85.4 |
| **% Gas Saturation** | 0 | 14.6 |
| **$D_p$ ($m^2/s$)** | 4.4E-11 | 2.3E-11 |
| **$D_e$ ($m^2/s$)** | 3.2E-12 | 1.5E-12 |

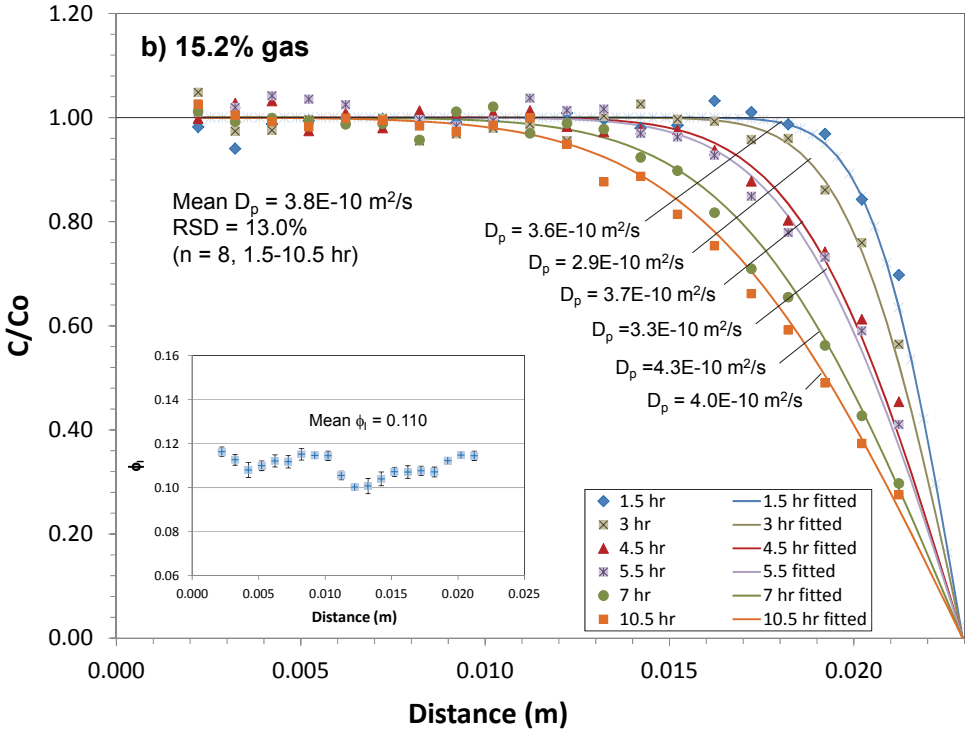
[a] PS indicates samples with partial gas saturation; [b] brine-filled porosity determined by $\gamma$-RAD.

### 4.3.2 Effect of Partial Gas Saturation on Diffusion Coefficients

#### 4.3.2.1 Carbon Tan Sandstone

Measurements for experiment CT-6A indicate that $D_p$ for $I^-$ tracer in a 100% brine-saturated sample is 4.1 x $10^{-10}$ $m^2/s$ (Figure 10a), and at 15.2% gas saturation the $D_p$ value decreases to 3.9 x $10^{-10}$ $m^2/s$ (average of results from out-diffusion and in-diffusion experiments; Figure 10b,c). These results suggest that the effect of approximately 15% gas is small - only a 5% decrease in $D_p$. In contrast, data for experiment CT-6B indicate a 50% decrease in $D_p$ for the same sample at a slightly lower gas saturation (13.5%; Figure 11a, b). The large difference between two measurements using the same rock sample is surprising and suggests an unidentified source of error or a difference in the gas distribution at the pore scale that is not apparent in the $\phi_l$ profiles (Figures 8, 10 and 11). For example, a predominance of gas bubbles in the pore throats for experiment CT-6B could contribute to a relative decrease in the tortuosity factor ($\tau_f$) and explain the lower $D_p$ value observed for the partially saturated sandstone. The $D_e$ values for aqueous solutes are further affected by the decrease in brine-filled porosity (Table 7) such that partial gas saturation resulted in decreases in $D_e$ of 21% and 56% for experiments CT-6A and CT-6B respectively. The addition of a gas phase to the pores is also expected to cause an increase in diffusion coefficients for gases (Reardon and Moddle 1985), but this effect has not been quantified in these experiments.


3.5 hr
3.5 hr fitted
5 hr
5 hr fitted
7 hr
7 hr fitted
8.5 hr
8.5 hr fitted
$D_p$ = 3.8E-10 m²/s
$D_p$ = 3.8E-10 m²/s
$D_p$ = 4.3E-10 m²/s
$D_p$ = 4.5E-10 m²/s
Mean $D_p$ = 4.1E-10 m²/s
RSD = 8.7% (n = 4, 3.5-8.5 hr)
Mean $\phi_I$ = 0.129
$\phi_I$
Distance (m)
a) 0% gas
C/Co
Distance (m)


b) 15.2% gas
Mean $D_p$ = 3.8E-10 m²/s
RSD = 13.0%
(n = 8, 1.5-10.5 hr)
$D_p$ = 3.6E-10 m²/s
$D_p$ = 2.9E-10 m²/s
$D_p$ = 3.7E-10 m²/s
$D_p$ =3.3E-10 m²/s
$D_p$ =4.3E-10 m²/s
$D_p$ = 4.0E-10 m²/s
Mean $\phi_I$ = 0.110
$\phi_I$
Distance (m)
1.5 hr
1.5 hr fitted
3 hr
3 hr fitted
4.5 hr
4.5 hr fitted
5.5 hr
5.5 fitted
7 hr
7 hr fitted
10.5 hr
10.5 hr fitted
C/Co
Distance (m)

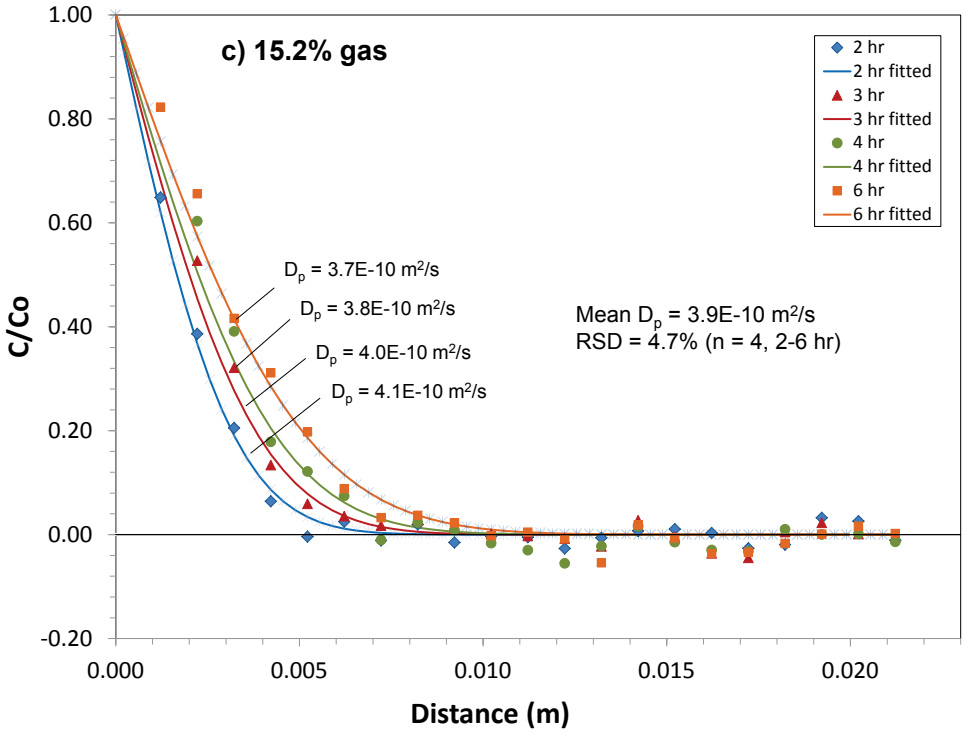



**Figure 10: Diffusion Profiles Obtained for Experiment CT-6A Using γ-RAD with 1.0 M NaI Tracer: a) In-Diffusion with 100% Brine (0% Gas) Saturation, b) Out-Diffusion with 15.2% Gas Saturation, and c) In-Diffusion following b). Inset Images are $\phi_I$ Profiles of the Rock Sample with $I^-$ Tracer at Each Condition**

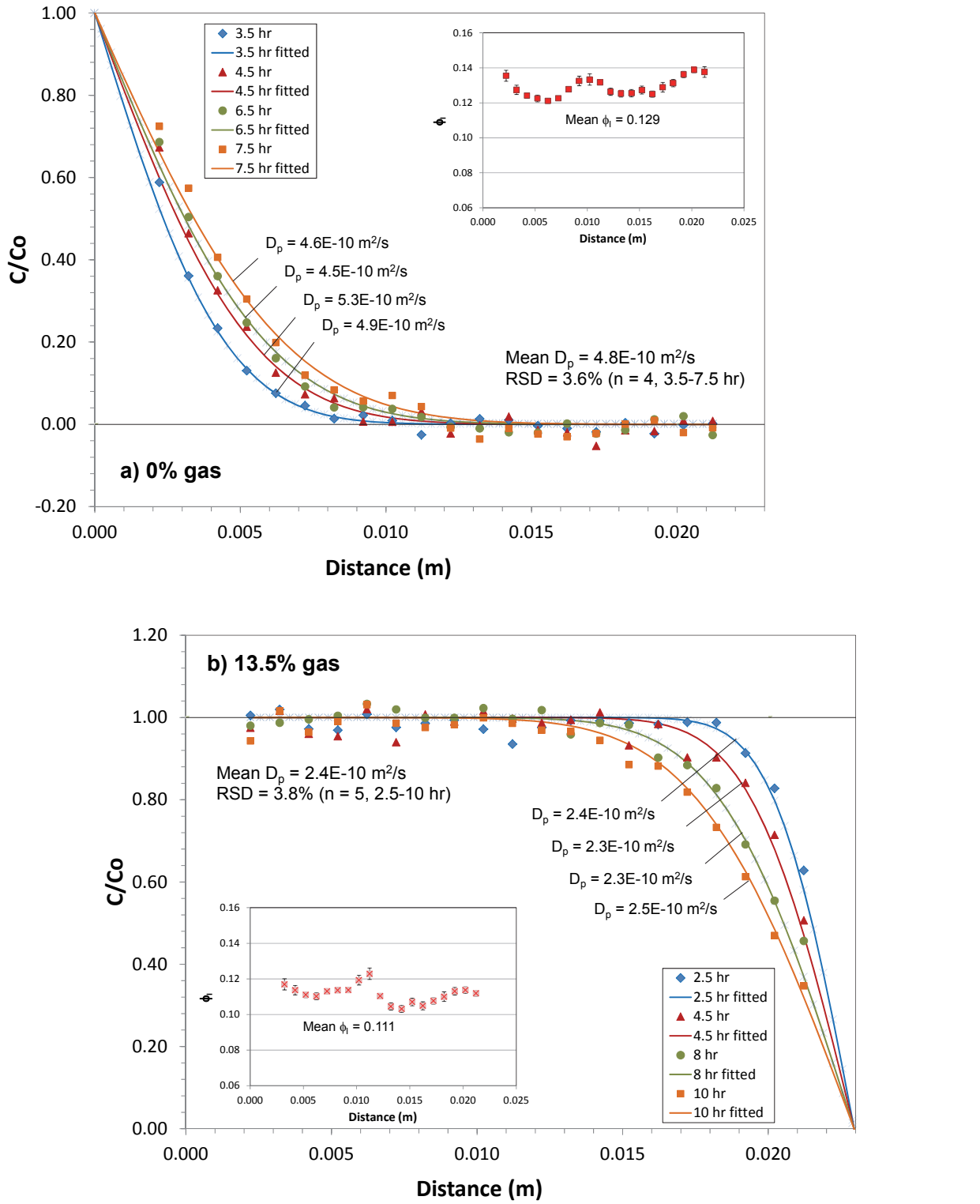



**Figure 11: Diffusion Profiles Obtained for Experiment CT-6B Using γ-RAD with 1.0 M NaI Tracer: a) In-Diffusion with 100% Brine (0% Gas) Saturation, b) Out-Diffusion with 13.5% Gas Saturation. Inset Images are $\phi_I$ Profiles of the Rock Sample with $I^-$ Tracer at Each Condition**

#### 4.3.2.2 Queenston Formation Shale

Measurements with the Queenston Formation shale (DGR3-472) are preliminary and must be viewed with caution because the problems experienced with sample breakage. The results indicate that $D_p$ for $I^-$ tracer at 100% brine-saturation is 4.4 x $10^{-11}$ $m^2/s$ (Figure 12a) which is consistent with the range of values obtained by previous studies (Al et al. 2010, 2012; Cavé et al. 2010; Xiang et al. 2013). Measurements on the intact portion of the broken sample indicate that $D_p$ decreases to 2.3 x $10^{-11}$ $m^2/s$ at 14.6% gas saturation (Figure 12b). In terms of $D_e$, 14.6% gas saturation causes a decrease of 53%, from 3.2 x $10^{-12}$ $m^2/s$ to 1.5 x $10^{-12}$ $m^2/s$ (Table 8). This decrease is lower than that observed by Savoye et al. (2010) who report a 96.5% decrease in $D_e$ for $I^-$ in the Callovo-Oxfordian argillite at 14% gas saturation. Assuming these results can be supported by further work, it is apparent that the degree of partial saturation is one of the more important controls on the magnitude of aqueous diffusion coefficients. For comparison, previous work studying the effect of changes in confining pressure on $D_e$ noted a maximum decrease in $D_e$ of 44% for Georgian Bay Formation shale measured at ambient laboratory pressure versus a confining pressure of 15.1 MPa (Loomer et al. 2013a).

## 4.4 SUMMARY

A new method has been developed to generate partial gas and brine saturated conditions in rock samples containing highly concentrated brine without causing changes to the porosity and pore structure from precipitation of salts. The method is based on the relationship between $N_2$ gas solubility and pressure. The porewater system is equilibrated with $N_2$ gas at high pressure and then the pressure is rapidly decreased to atmospheric pressure. This causes a corresponding decrease in gas solubility, resulting in exsolution of $N_2$ to form gas bubbles in the pore spaces. The actual degree of partial gas saturation cannot be predicted accurately by calculations using theoretical P-V-T relationships for gases, but it can be quantified by $\gamma$-RAD. Results of $D_e$ measurements for $I^-$ tracer on partially saturated sandstone with gas fractions of 15.2% and 13.5% indicate decreases of 21% and 56% respectively. Preliminary results of measurements on the low-permeability Queenston Formation shale indicate a decrease in $D_e$ from 3.2 x $10^{-12}$ $m^2/s$ at 100% brine saturation to 1.5 x $10^{-12}$ $m^2/s$ at 14.6% gas (85.4% brine) for an overall decrease of 53%.

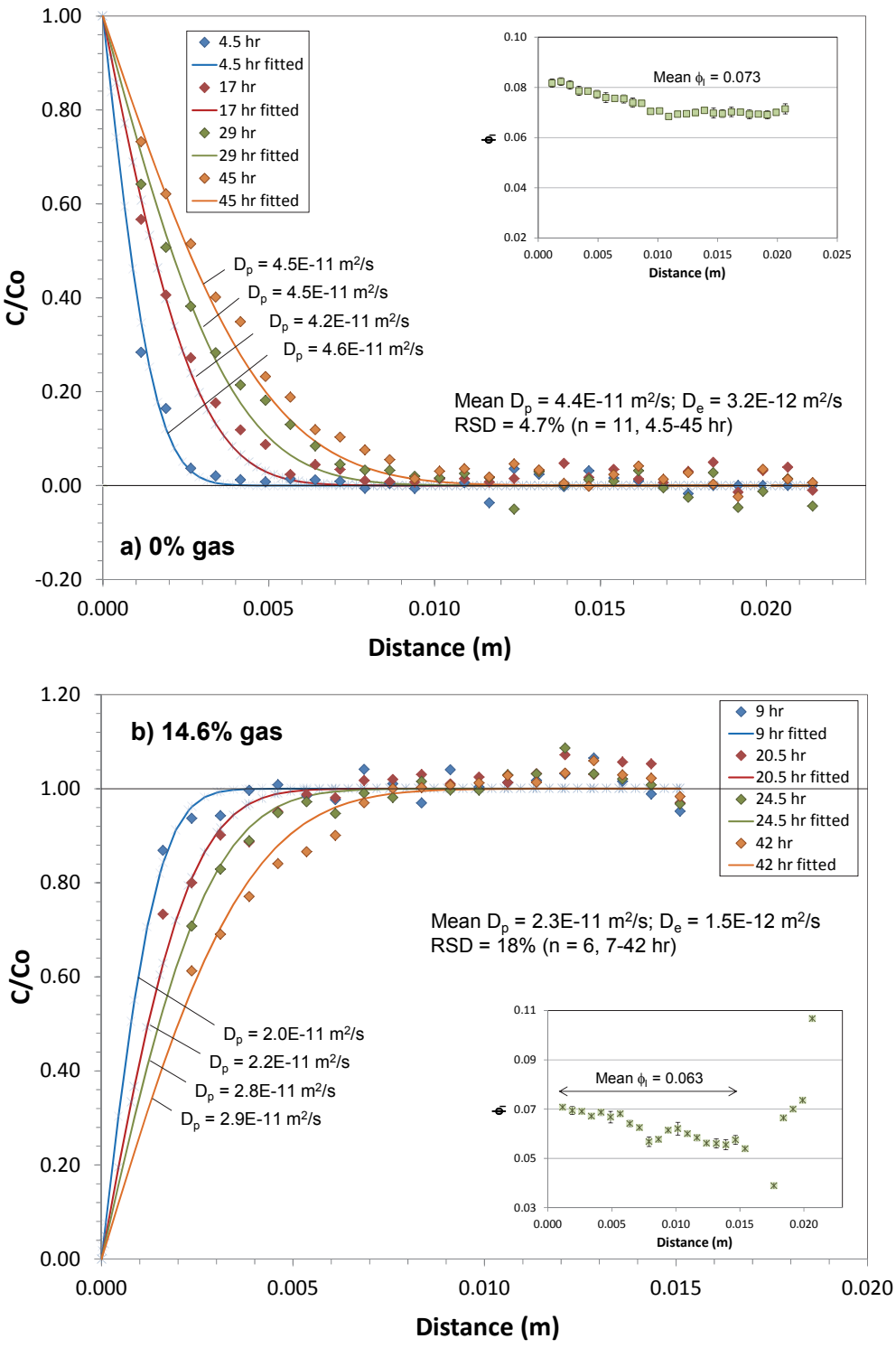



**Figure 12: Diffusion Profiles Obtained for Sample DGR3-472 Using γ-RAD with 2.0 M NaI Tracer: a) In-Diffusion with 100% Brine (0% Gas) Saturation, b) Out-Diffusion with 14.6% Gas Saturation. Inset Images are $\phi_I$ Profiles of the Rock Sample with $I^-$ Tracer at Each Condition**

## 5. PH MEASUREMENT IN HIGH IONIC STRENGTH BRINE SOLUTIONS

Solution pH is a fundamental parameter for understanding the geochemical behaviour of many solutes in groundwater. Reliable pH measurements are important to support studies of speciation, solubility and sorption of radionuclides related to a deep geological repository (DGR) for radioactive nuclear waste. In Canada, Ordovician rocks in the Michigan Basin have been evaluated as possible host rocks for a DGR for low- and intermediate-level waste, and similar rocks are also under consideration as the possible host for a spent nuclear fuel repository. The porewater in these formations is highly saline (up to 28 wt% salinity), with ionic strengths up to 8 mol/kg or higher. The conventional potentiometric method for pH measurement is commonly used for dilute solutions (0.1 m or less), and there is a need for an evaluation of available methods for pH measurements in high salinity brine solutions.

Originally, pH was defined simply as the negative logarithm of the hydrogen ion concentration (mH) without consideration of ion interactions in the solution (Equation 9; Jensen 2004). The definition was subsequently modified to the negative logarithm of the $H^+$ activity (aH), but in practice, mH is easier to work with. Many researchers then created application-specific pH scales by adjusting mH to account for certain known interactions between anions and the $H^+$ ion in concentrated solutions (Covington and Ferra 1994; Dickson 1984; Hansson et al. 1973; Millero et al. 1993). This has led to multiple alternative pH scales and some confusion when comparing pH values reported in the published literature. Three common pH scales include the free hydrogen ion scale ($pH_F$), which is simply based on the concentration of free, or uncomplexed, $H^+$ ions (mH; Equation 9); the total hydrogen ion scale ($pH_T$), which accounts for hydrogen ion complexation with sulphate (Equation 10); and the seawater scale ($pH_{SWS}$), which accounts for $H^+$ interactions with both sulphate and fluoride ions (Equation 11) (Millero et al. 1993).

$$\mathbf{pH_F = -\log mH} \quad \textbf{(9)}$$

$$\mathbf{pH_T = -\log mH^* \text{ , where } mH^* = mH + mHSO_4^-} \quad \textbf{(10)}$$

$$\mathbf{pH_{SWS} = -\log mH^{**}, \text{ where } mH^{**} = mH + mHSO_4^- + mHF^-} \quad \textbf{(11)}$$

In 2002, the International Union of Pure and Applied Chemistry (IUPAC; Buck et al. 2002) provided an official definition of pH based on the activity of $H^+$:

$$\mathbf{pH = -\log aH = -\log(mH\gamma H/m^\circ)} \quad \textbf{(12)}$$

where γH is the molal activity coefficient of the hydrogen ion, $H^+$, and m° is the standard molality (1 mol/kg). In dilute solutions γH approaches 1 and, therefore mH ≈ aH. However, as solutions become more saline and ion interactions become more important, γH changes and the difference between mH and aH increases.

The following discussion provides a brief introduction to the definition and measurement of pH as it was described by Buck et al. (2002).

The activity of the single $H^+$ ion in water cannot be measured. Instead, it is estimated from measurements of the combined activity of $H^+$ and $Cl^-$. The Harned cell (Harned and Owen 1958) is the only method for pH measurement that meets the IUPAC criteria for a primary method. The Harned cell is made up of the standard hydrogen electrode (SHE) coupled with a silver/silver-chloride electrode. It contains a standard buffer and chloride ions – in the form of potassium or sodium chloride (Figure 13). The Harned cell does not involve a liquid junction and, therefore, is not subject to the uncertainty resulting from variable liquid junction potentials.

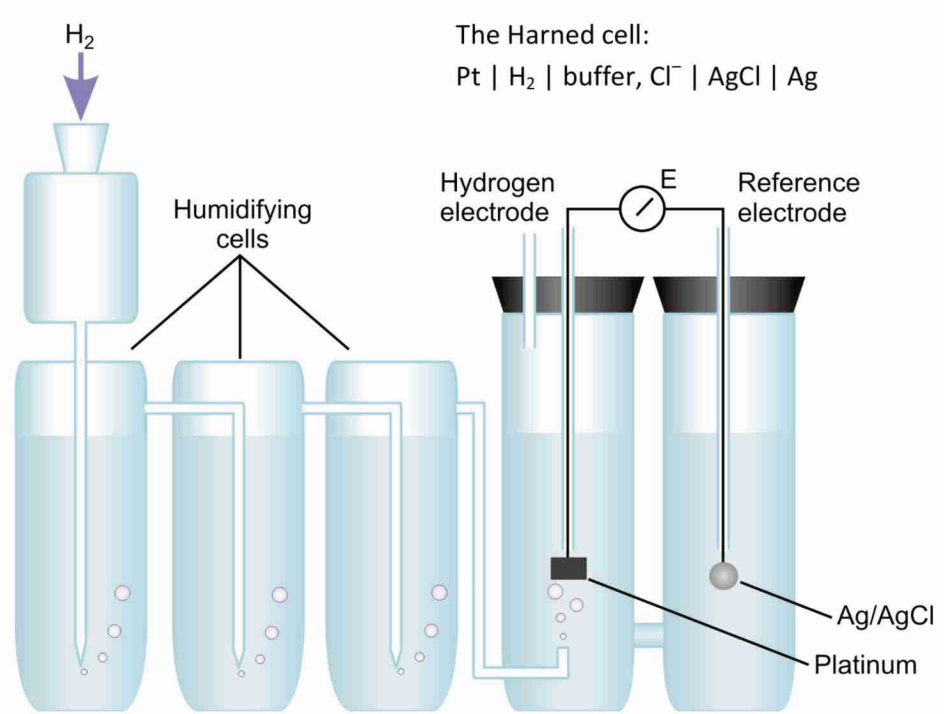



**Figure 13: Schematic Example of a Modern Harned Cell, Based on the Diagram of Maksimov et al. (2008)**

Potentiometrically, pH is determined according to the Nernst Equation:

$$E = E^o - 2.3RT/F \log aH \qquad (13)$$

where E is the voltage of the cell, $E^o$ is the standard voltage of the cell, R is the universal gas constant, F is the Faraday constant, and T is the temperature in degrees Kelvin. In the Harned cell, the Nernst equation is modified to:

$$E = E° - 2.3(RT/F) \log[(mH\gamma H/m°)(mCl\gamma Cl/m°)] \qquad (14)$$

The standard potential difference of the silver/silver-chloride electrode, E°, is determined from a Harned cell in which only HCl is present at a fixed molality (e.g., m = 0.01 mol/kg).

Pt | $H_2$ | mHCl | AgCl | Ag

Application of the Nernst equation to the HCl cell, written in a form convenient for pH determination is:

$$-\log[aH \cdot \gamma Cl] = \frac{E - E^{o}}{\frac{2.3RT}{F}} + \log\left[\frac{mCl}{m^{o}}\right] \quad (15)$$

To obtain a pH value, it is necessary to evaluate log γCl by independent means. This is done in two steps: (i) determination of the value of log(aH γCl) at zero chloride molality, log(aHγCl)°, and (ii) calculation of a value for the activity coefficient of the chloride ion at zero Cl molality, γ°Cl. The activity coefficient of chloride is also an immeasurable quantity. However, in solutions of low ionic strength (I < 0.1 mol/kg), it is possible to calculate the activity coefficient of the chloride ion using the Debye–Hückel theory. This assumes that γ°Cl is given by the expression:

$$\log\gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba_i\sqrt{I}} \quad (16)$$

where A and B are solvent parameters that are dependent on density, dielectric constant and temperature; z is the ionic charge, å is the mean distance of closest approach of the ions (ion size parameter), and I is the ionic strength of the buffer. In practice, Bå is set equal to 1.5 $(mol/kg)^{-1/2}$ at all temperatures in the range of 5–50 °C. While recognizing the importance of ion interaction approaches (e.g., Pitzer 1991) for determining pH (Covington and Ferra 1994; Buck et al. 2002), the IUPAC uses the Debye-Hückle ion-association approach because it has very small experimental uncertainty while the Pitzer ion-interaction approach involves more uncertainty that is difficult to assess in practical applications (Meinrath 2002; Spitzer et al. 2011). By employing the Debye-Hückle approach, the IUPAC (Buck et al. 2002) has limited the standard measurement of pH to solutions with ionic strengths less than 0.1 mol/kg.

Institutes worldwide, such as the National Institute of Standards and Technology (NIST), use the Harned cell to develop primary pH buffers. Chemical companies then use the primary buffers to make secondary, NIST-traceable, commercial pH buffers (NIST buffers) for general laboratory use.

The Harned cell is not practical for everyday laboratory pH measurements and more convenient methods are typically used. One conventional method is potentiometric measurement using glass combination electrodes (Figure 14). The potentiometric cell consists of a pH-sensitive glass electrode, a reference electrode (Ag/AgCl) and an inert filling solution (3.0 M KCl) that functions as a salt bridge connecting the two cells. The glass membrane responds to the $H^+$ activity in a solution (Pehrsson et al. 1976). The presence of the salt bridge introduces a liquid junction potential between the reference cell and the solution being measured. The magnitude of this potential is a function of the solution composition, temperature and ionic mobilities (Mesmer and Holmes 1992).

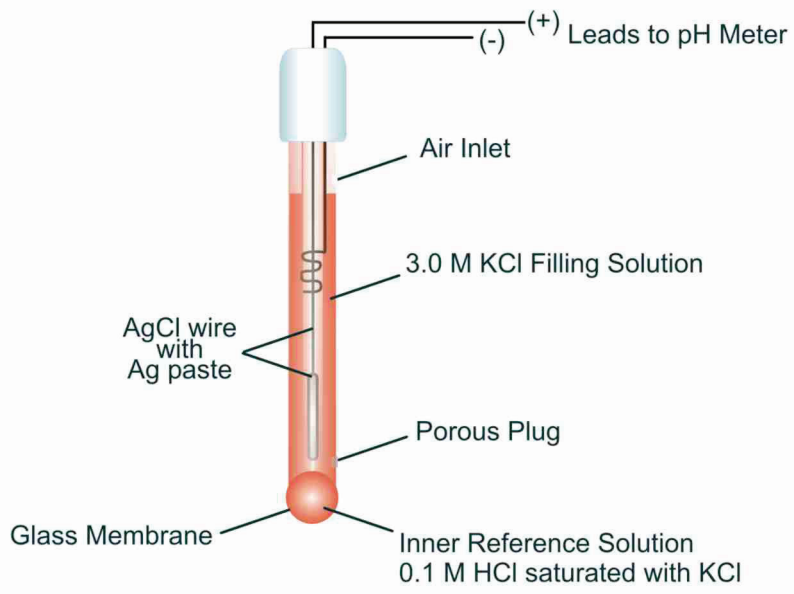



**Figure 14: Glass Combination pH Electrode**

The electrode is connected to a high impedance voltmeter. If the electrode behavior is Nernstian, for every unit change in pH, there should be a 59.16 mV response from the electrode. The conversion from millivolts to pH units is typically done internally by the meter based on calibration with standard, NIST-traceable buffers.

The experimental uncertainty for a typical primary pH (Harned Cell) measurement is of the order of ±0.004 pH units, while the uncertainty arising from the use of the Debye-Hückle approach to determine γCl is ±0.01 pH units (Buck et al. 2002). It is acknowledged that typical pH measurement using a glass electrode can have an error of up to ±0.03 pH units. Sources of error that contribute to this uncertainty include the uncertainty in the NIST calibration buffers (±0.01–0.02 pH units), the precision and accuracy of the electrode (±0.02 and ±0.03 pH units, respectively) and the error in the meter (±0.01 pH units). An additional source of error depends on the resolution of the temperature adjustment for the meter.

When measuring pH with a glass electrode, it is assumed that the liquid junction potential between the reference cell and the buffer is the same as the potential between the reference cell and the solution to be measured. However, this assumption is violated if there is a significant difference in the ionic strengths of the buffer solutions and the solution to be measured.

Ionic strengths as high as 8 mol/kg have been reported for porewaters in Ordovician rocks in the Michigan Basin in southern Ontario (Hobbs et al. 2011). At the University of New Brunswick (UNB), two synthetic porewater (SPW) formulations are commonly used when working with Michigan Basin drill core samples (Al et al. 2010, 2012; Cavé et al. 2010). The Shale SPW (S-SPW) has ionic strength (I) equal to 8.2 mol/kg and the Limestone SPW (L-SPW) has ionic strength equal to 4.9 mol/kg (Table 4). There must then be a difference in liquid junction potential for measurements in the SPW versus the NIST buffers that would add systematic error to potentiometric pH measurements in these solutions. One alternative to the use of NIST buffers for measuring pH in high ionic strength solutions is to calibrate the electrode in terms of

mH rather than aH using a Gran plot (Gran 1950, 1952; Hansson 1973). In this application, the Gran plot involves the titration of a solution of known strong-acid concentration with a solution of known strong base concentration in the presence of a relatively high concentration of background electrolyte. The background electrolyte allows the assumption of constant $\gamma H^+$ during the titration. The Gran plot provides a calibration for an electrode that can be used for pH measurements in solutions with the same electrolyte composition as the calibration solution, assuming negligible electrode drift between the titration and the measurements. However, this method is time consuming and impractical for everyday laboratory and field applications, and it is prone to complication in the presence of weak acids (Pehrsson et al. 1976). Furthermore, if defining pH in terms of mH rather than aH, the measured pH would not be consistent with geochemical models that are employed within the DGR context such as PHREEQC (Parkhurst and Appelo 1999, 2013) or MIN3P (Mayer et al. 2002; Bea et al. 2010, 2011). For this study, it was decided to evaluate pH measurement in brine solutions as a function of aH, consistent with IUPAC recommendations (Buck et al. 2002) and standard geochemical practice.

Solution pH can also be measured spectrophotometrically. Spectrophotometric measurements using colorimetric indicators have been used as an alternative to potentiometric measurements by a variety of researchers (King and Kester 1989; Martz et al. 2003; Millero et al. 2009; Raghuraman et al. 2006a,b). Colorimetric pH indicators are weak acids or bases – analogous to pH buffers – and are sensitive to the activity, rather than the concentration of $H^+$. With colorimetric indicators such as phenol red, the acid (A) and base (B) forms of the indicator, absorb light at different wavelengths (Figure 15). Spectrophotometric pH measurements take advantage of the change in absorbance ratio, or optical density ratio (ODR), between the basic and acidic peaks as pH changes. Raghuraman et al. (2006a) have applied the spectrophotometric method to the measurement of pH in NaCl brines up to an ionic strength of 3.0 mol/kg. In this work, we follow their approach, but extend the range of $pK'_a$ measurements to higher ionic strengths and more complex solutions.

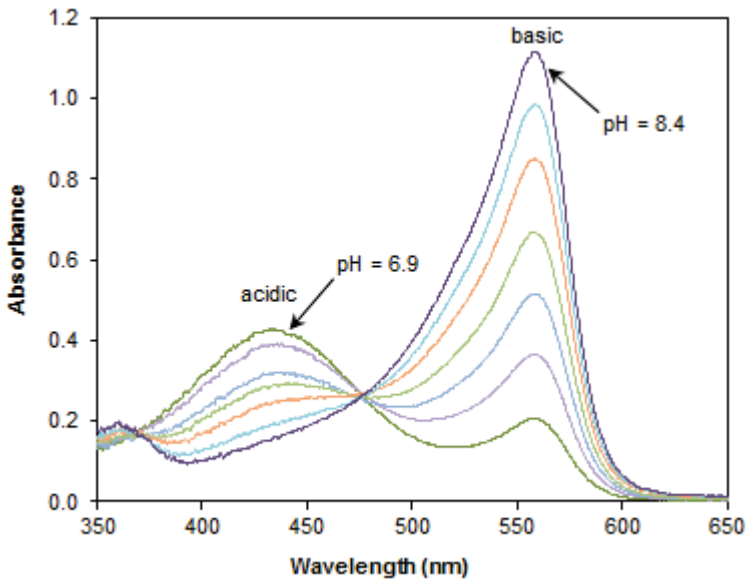



**Figure 15: Absorbance Spectra with Changing pH for Phenol Red in L-SPW Tris Buffer Solutions**

In spectrometry, the pH of a solution can be determined based on: (1) the thermodynamic disassociation constant ($pK_a$) of the indicator, a weak acid (HA) or base ($A^-$) and its disassociation equilibrium is represented as $HA \Leftrightarrow A^- + H^+$; and (2) the ratio of basic to acid peaks in the spectra (Figure 15).

$$\mathbf{pH = pK_a + \log\frac{[\gamma_B]}{[\gamma_A]} + \log\frac{[B]}{[A]}} \qquad \mathbf{(17)}$$

where $\gamma_A$ and $\gamma_B$ are the activity coefficients of the acid (A) and base (B) forms of the indicator. Equation 17 can be rewritten such that pH is a function of the measured concentration ratio for the acid (A) and base (B) forms of the indicator, and the conditional disassociation constant $pK'_a$ which varies with $\gamma_A$ and $\gamma_B$.

$$\mathbf{pH = pK'_a + \log\frac{[B]}{[A]}} \qquad \mathbf{(18)}$$

The $pK'_a$ is therefore a function of ionic strength, temperature and pressure (King and Kester 1989; Raghuraman et al. 2006a). Pitzer ion interaction coefficients for the phenol red indicator are not available in the published literature and its $pK'_a$ values in high ionic strength solutions can not be determined by geochemical modelling. Therefore, it is necessary to empirically determine the variation of $pK'_a$ with ionic strength and solution composition. A common method involves the collection of spectra to measure log [B]/[A] over a range of pH. The $pK'_a$ of an indicator is then determined at the pH value where log [B]/[A] = 0 in a straight-line plot of log [B]/[A] versus pH. This method was described in detail by Raghuraman et al. (2006a).

The objectives of this work were to: 1) characterize the glass electrode response in increasingly saline solutions; 2) evaluate a spectrophotometric approach as a possible alternative method for pH measurements in brine solutions; and 3) present an approach for improved confidence in pH determination when working with brine solutions. The approach developed to meet these objectives was to create high-ionic-strength buffers with known pH to: a) test the glass electrode response in solutions of varying ionic strength; and b) determine the ionic-strength dependence of the association constant ($pK'_a$) for a colorimetric pH indicator.

## 5.1 HIGH-IONIC-STRENGTH BUFFERS

The standard NIST buffers have low ionic strength (<0.1 mol/kg) and there are no NIST-certified high-ionic-strength pH buffers commercially available. A pH buffer is an aqueous solution consisting of a mixture of a weak acid (HA) and its conjugate base (A-) or a weak base and its conjugate acid. The equilibrium between the acid and base (Equation 19) resists changes in pH in response to minor changes in solution composition.

$$\mathbf{HA \leftrightarrow H^+ + A^- \ \ and \ \ K_a = \frac{aH^+ \cdot aA^-}{aHA}} \qquad \mathbf{(19)}$$

As noted above, determination of single-ion activity coefficients with the Debye-Hückle ion-association model makes it possible to assign a pH value to a buffer solution, but that method is not suitable for solutions with ionic strength much greater than 0.1 mol/kg. In order to extend pH measurement to high-ionic-strength solutions, the ion interaction approach (Pitzer 1991), is

required. Several geochemical speciation codes (e.g. PHREEQC, MIN3P-THCm) implement the Pitzer equations for ion activity calculations (Bea et al. 2011; Parkhurst and Appelo 1999, 2013; Wall et al. 2006).

The publicly available geochemical code PHREEQC (Parkhurst and Appelo 1999, 2013; USGS 2013) includes the numerical implementation of the Pitzer equations of Plummer et al. (1988) and a limited thermodynamic database containing virial Pitzer coefficients. PHREEQC Interactive, version 3.0.6.7757, was used in this work. The buffer protonation-deprotonation reaction is an association-disassociation reaction. The geochemical equilibrium code is used to calculate a conditional disassociation constant ($pK'_a$) according to Equation 20.

$$\mathbf{pK'_a = pK_{a(thermodynamic)} \cdot \frac{\gamma(reactants)}{\gamma(products)}} \qquad \mathbf{(20)}$$

Two pH buffers were chosen for this work: acetate – acetic acid (acetate; pH ≈ 4) and Tris-[hydroxymethyl]aminomethane – Tris-[hydroxymethyl]aminomethane hydrochloride (Tris and TrisHCl; pH ≈ 8). The Pitzer ion interaction coefficients for these buffer components were added to the PHREEQC-Pitzer database (pitzer.dat). The choice of these buffers was constrained by the need to avoid buffers that react with the components of the brine. For example, citrate and phosphate buffers are not recommended for solutions with significant concentrations of Ca because of the significant complexation with Ca and the insolubility of Ca-phosphate complexes. Tris is known to be compatible with Ca- and Mg- containing solutions (ANGUS Chemical Company 2000; McFarland and Norris 1958; Mohan 2006). Tris is also highly soluble in aqueous solutions, chemically stable and readily available in purified form. Furthermore, Tris has low hygroscopicity, does not readily absorb $CO_{2(g)}$ from the atmosphere and has insignificant light absorbance characteristics between 240 nm and 700 nm, so its use will not interfere in colorimetric measurements (ANGUS Chemical Company 2000). Another benefit to using Tris is that the base and acid forms are both salts, and therefore, there is no dilution from adding acidic or basic solutions to adjust the pH of a buffer. However, the Tris association reaction is such that changing the relative Tris:TrisHCl concentrations results in variable ionic strength for a given buffer series.

In addition, the Tris buffer is temperature sensitive. In dilute buffer solutions the pH changes ±0.03 pH units/°C inversely with temperature (AppliChem 2008). Foti et al. (1999) and Millero et al. (2009) reported the same temperature dependency of the Tris buffer system (±0.03 pH unit/°C) in the temperature range 0-100 °C for ionic strengths ranging from 0-5 mol/kg NaCl solution. Because of the limitations in the availability of verifiable Pitzer parameters in the peer-reviewed literature, the Pitzer ion interaction coefficients added to the PHREEQC-Pitzer database for Tris buffer are limited to a temperature of 25 °C.

Multiple references were considered and included in the modified Pitzer database (pitzerUNB; Appendix B.1) and the modified database was verified against published $pK'_a$ data (Figure 16a; Figure 17a). The parameters (or combination of parameters) that could best reproduce the published $pK'_a$ data have been activated in the database (Table 9). The maximum difference between the PHREEQC-calculated and the literature values (Millero et al. 1987) for the $pK'_a$ of Tris was 0.02 units. Novak et al. (1996) reported Pitzer coefficients for the acetate-NaCl system and was the main source used for model calculations involving the acetate buffer. The maximum difference in the $pK'_a$ of acetate calculated with PHREEQC and the values reported by Novak et al. (1996) was 0.03 units (Figure 16). Mesmer et al. (1989) and Mizera et al. (1999) also measured the $pK'_a$ of acetate in NaCl solutions and their results were included in

the model verification. The $pK'_a$ values calculated using PHREEQC were similar to those from Mesmer et al. (1989) and Mizera et al. (1999) (Figure 17) with a maximum difference in $pK'_a$ of 0.06 units.

The MacInnes convention for scaling activity coefficients is the default in PHREEQC. It was not used in this work, either for verification of results against literature values or for any other PHREEQC calculations. The MacInnes convention (MacInnes 1919) assumes that $\gamma K^+ = \gamma Cl^- = \gamma \pm KCl$. With this assumption one can determine the single-ion activity coefficients of other salts in a KCl solution by substitution. While the MacInnes convention is recognized as being convenient and is widely used, the IUPAC (Bates and Robinson 1974) have stated that the assumption that $Cl^-$ will have a constant activity coefficient at a given ionic strength across a range of solution compositions is implausible. There is a considerable difference in calculated pH if the MacInnes convention is used in PHREEQC (Nordstrom et al., 2000; Figure 16b; Figure 17b), highlighting the sensitivity of the calculated pH values to the convention used.

The Pitzer interaction parameters for the acetate buffer are well characterized in NaCl solutions (up to an ionic strength of 5 mol/kg) and for the Tris buffer in NaCl, KCl, $CaCl_2$ and $MgCl_2$ solutions (up to an ionic strength of 6 mol/kg). However, Millero et al. (1987) indicated that for solutions with ≥1 mol/kg Ca there is increasing uncertainty in the Pitzer parameters for Tris, and that additional parameters may be required. These ionic strength and Ca-concentration limitations place constraints on the use of Tris buffer in pH measurement for brine from the Michigan Basin which commonly contains $Ca^{2+}$ in excess of 1 mol/kg, and in some cases has ionic strength greater than 6 mol/kg (Al et al. 2010; Hobbs et al. 2011; Koroleva et al. 2009).

There are few data for Pitzer parameters in Ca-acetate buffer solutions, and none were found for Mg-acetate solutions, which limits the use of PHREEQC to calculate the pH of acetate buffer solutions at high ionic strength. Loos et al. (2004) determined interaction parameters for Ca with acetate but they did not report pH values, therefore modelled pH values for Ca-acetate buffer solutions cannot be verified. Because of these limitations, it was decided not to use the acetate buffer for this work, but it is recognized that the acetate buffer can be used reliably in NaCl solutions.

**Table 9: Additions Made to the PHREEQC v. 3.0.6 PITZER Database (pitzerUNB)**

| Name | Master Species | Alkalinity | FWT (Formula Weight) |
|---|---|---|---|
| Tris | Tris | 1 | 121.138 |
| Acetate | $Acetate^-$ | 1 | 59.045 |

| Solution Species | $pK_a$[1] | Temperature (˚C) | Delta H (kcal) | Ref |
|---|---|---|---|---|
| $Tris + H^+ = (Tris)H^+$ | 8.075 | 25 | 11.36 kcal | 1 |
| $H^+ + Acetate^- = H(Acetate)$ | 4.757 | 25 | 0.098 | 2 |
| $Na^+ + Acetate^- = Na(Acetate)$ | -0.18 | 25 | 2.87 | 2 |
| $K^+ + Acetate^- = K(Acetate)$ | -0.1955 | 25 | 1 | 2 |
| $Ca^{+2} + Acetate^- = Ca(Acetate)^+$ | 1.18 | 25 | 0.96 | 2 |
| $Mg^{+2} + Acetate^- = Mg(Acetate)^+$ | 1.27 | 25 | 0 | 2 |

**Binary Pitzer ion-interaction coefficients:**

| Ion-pair | | $B_0$ | $B_1$ | $C_0$ | θ | λ | Ref |
|---|---|---|---|---|---|---|---|
| $(Tris)H^+$ | $Cl^-$ | 0.0395 | 0.20978 | -0.00236 | - | - | 3 |
| $(Tris)H^+$ | $SO_4^{2-}$ | 0.09393 | 0.59829 | -0.004316 | - | - | 3 |
| $(Tris)H^+$ | $H^+$ | - | - | - | 0.0027 | - | 3 |
| $Na^+$ | Tris | - | - | - | - | 0.0239 | 8 |
| $K^+$ | Tris | - | - | - | - | 0.0262 | 8 |
| $Mg^{2+}$ | Tris | - | - | - | - | -0.0594 | 8 |
| $Ca^{2+}$ | Tris | - | - | - | - | -0.2327 | 8 |
| $H^+$ | $Acetate^-$ | 0 | 0 | 0 | - | - | 4 |
| $Na^+$ | $Acetate^-$ | 0.1426 | 0.3237 | -0.00629 | - | - | 4/5 |
| $K^+$ | $Acetate^-$ | 0.155 | 0.3 | -0.005 | - | - | 6 |
| $Ca^{+2}$ | $Acetate^-$ | 0.269 | 1.134 | -0.031 | - | - | 7 |
| $Acetate^-$ | $Cl^-$ | - | - | - | -0.09 | - | 4 |

**Ternary Pitzer ion-interaction coefficients:**

| Ion group | | | ζ | ψ | Ref |
|---|---|---|---|---|---|
| Tris | $Na^+$ | $Cl^-$ | 0 | - | 8 |
| $H^+$ | $(Tris)H^+$ | $Cl^-$ | - | -0.013 | 8 |
| $Na^+$ | $H^+$ | $Acetate^-$ | - | 0 | 4 |
| $Na^+$ | $Acetate^-$ | $Cl^-$ | - | 0.01029 | 4 |

[1]Zero ionic strength $pK_a$; PHREEQC calculates $pK'_a$ internally.

References: 1. Foti et al. (1999); 2. PHREEQC v. 3.0.6 minteq.v4 database (Parkhurst and Appelo 2013); 3. Bates and Macaskill (1985); 4. Novak et al. (1996); 5. Pitzer and Mayorga (1973); 6. Spitzer et al. (2011); 7. Loos et al. (2004); 8. Millero et al. (1987).

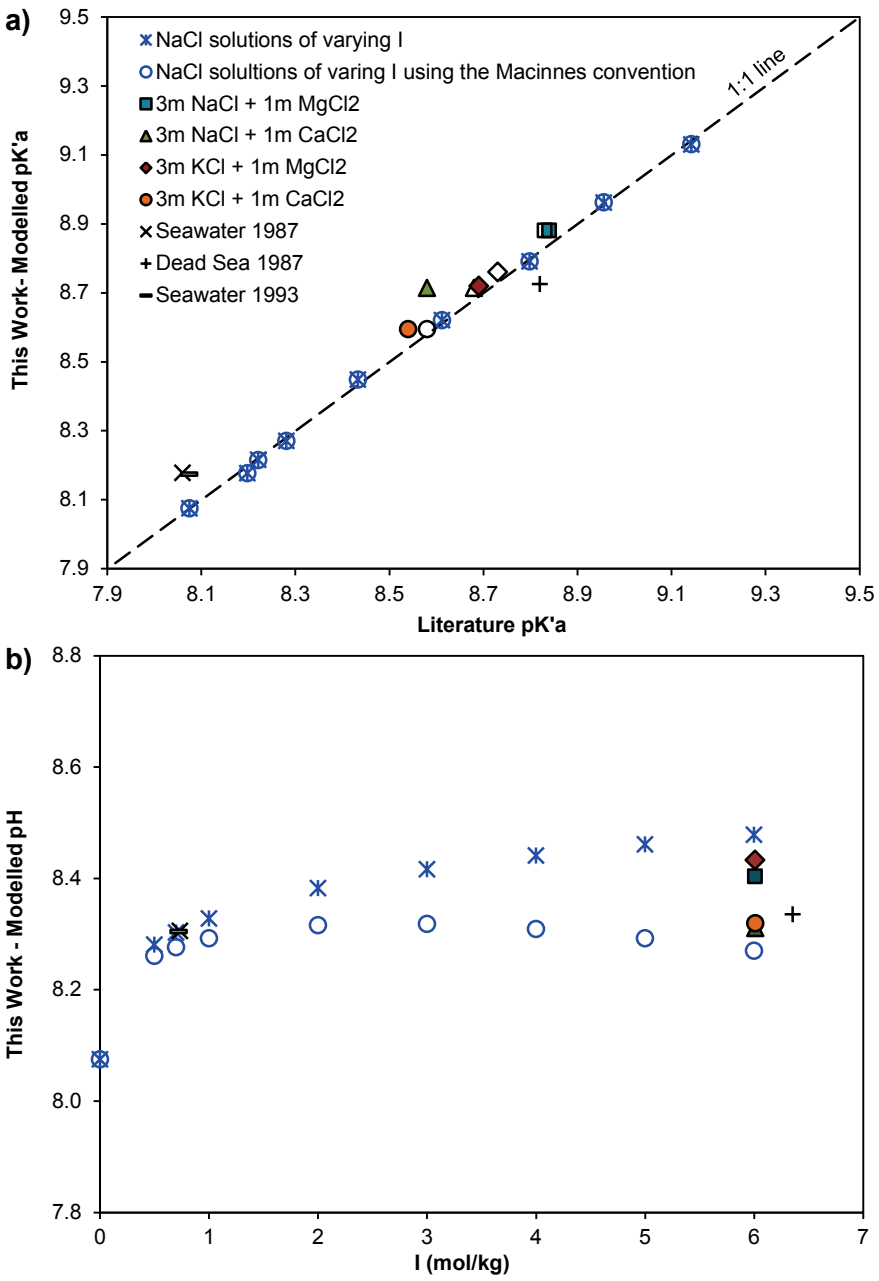



**Figure 16: Tris Buffer Data: a) Comparison of the pK'$_a$ for Tris in Electrolyte Solutions Calculated Using PHREEQC (pitzerUNB Database) with Measured Values for Seawater and the Dead Sea from Millero et al. (1987, 1993). "MacInnes Convention" Means it was Used for Calculating pH in PHREEQC. The Filled Symbols Represent Measured Values and the Hollow Symbols Represent the Corresponding Calculated Values (Millero et al. 1987); (b) The Modelled pH of a 0.02 mol/kg Tris Buffer in the Same Solutions Shown in (a)**

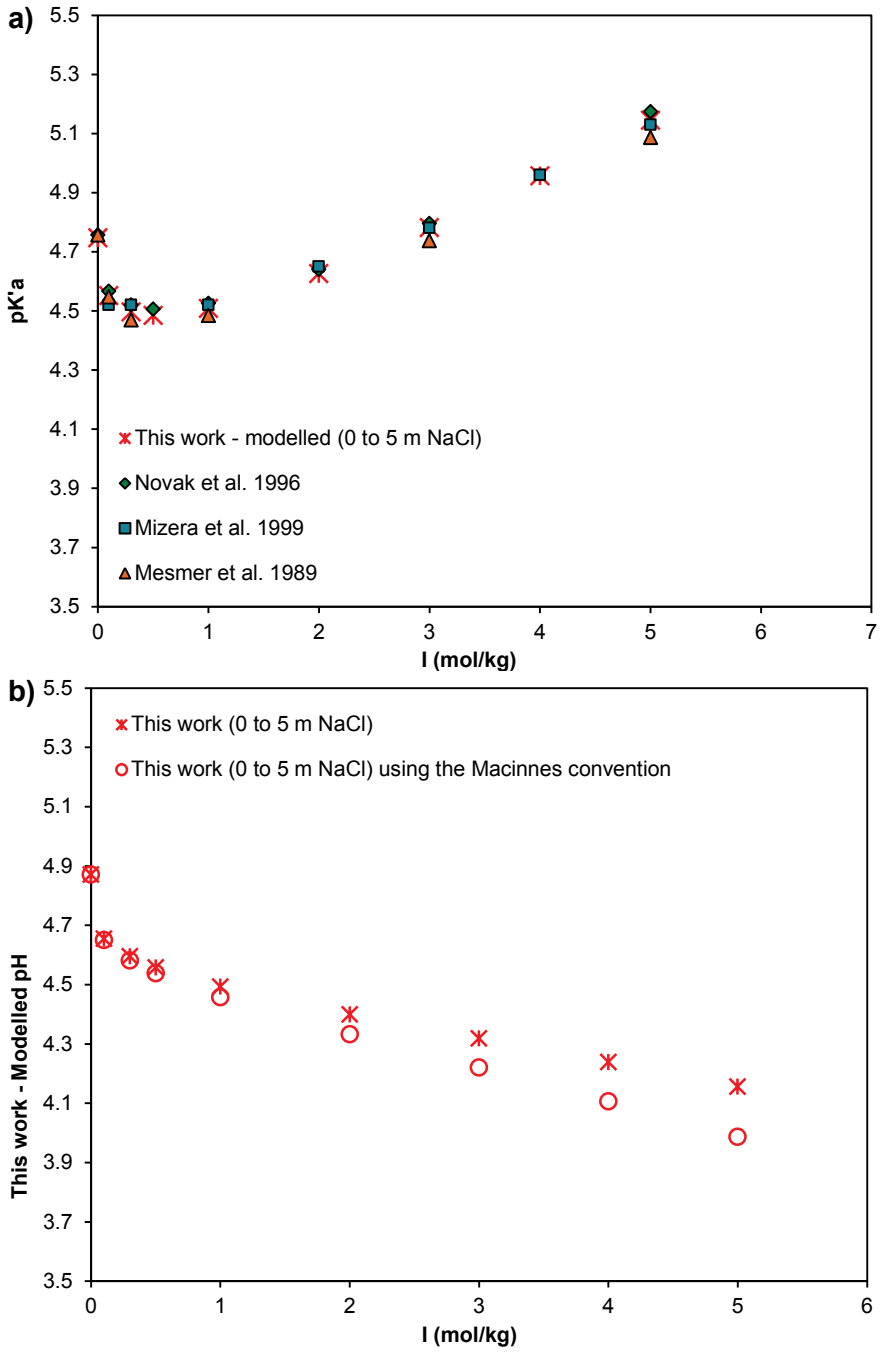



**Figure 17: Acetate Buffer Data: (a) Comparison Between the Acetate pK'$_a$ Calculated Using PHREEQC (pitzerUNB Database) and Values from Published Literature; (b) The Modelled pH of a 0.002 mol/kg Acetate Buffer in NaCl Solutions of Varying Ionic Strength. "MacInnes Convention" Means the MacInnes Convention was Used for Calculating pH in PHREEQC**

## 5.2 EXPERIMENTAL METHODS

### 5.2.1 Preparation of High Ionic Strength Buffers

Buffered solutions at varying ionic strengths and solution compositions were developed by using PHREEQC with the pitzerUNB database. The buffer solutions were designed to simultaneously test the glass electrode response (potentiometric pH measurements) and collect the spectral data necessary to determine the $pK'_a$ of the phenol red indicator for spectrophotometric pH measurements.

The $pK_a$ (infinite dilution) at 25 °C for the Tris buffer is 8.075 (Foti et al. 1999). The $pK_a$ (infinite dilution) at 25 °C for the phenol red (phenolsulfonphthalein) indicator is 8.0 (Drummond et al. 1989). The MERK Index (MERK 2014) lists a $pK_a$ of 7.9 for phenolsulfonphthalein, but does not specify a temperature and the relevant references in the monograph date back to the late 1800's or early 1900's. Therefore, the Drummond et al. (1989) value is considered the more reliable of the two. Both pH buffers and pH-sensitive colorimetric indicators are reliable within ±1 pH unit of their $pK_a$. Therefore, it is appropriate to use Tris and phenol red in the pH range 7 to 9, and in this work we extended the working range down to pH 6.5.

Tris buffers were prepared with total Tris concentrations of 0.05 or 0.06 mol/kg which is near the lower limit of Tris concentrations that are reliable for maintaining the desired pH (Millero et al. 2009). The range of pH values was achieved by varying the relative proportions of Tris and TrisHCl. A series of 5-8 Tris buffers were prepared for each ionic strength. On average, the effect of the Tris on ionic strength across a series of Tris buffers was 0.03 mol/kg, with a maximum effect of 0.06 mol/kg.

The Tris buffers were prepared in 4 types of aqueous media: pure water, NaCl solutions of varying ionic strength, concentrated and diluted forms of L-SPW solution with varying ionic strength, and S-SPW dilutions of varying ionic strength. All salts used for the buffer solutions were ACS grade: NaCl, KCl, $CaCl_2{\cdot}2H_2O$, $MgCl_2{\cdot}6H_2O$, $CaSO_4$, Tris and TrisHCl.

The range in difference between the measured and calculated Tris $pK'_a$ in mixed electrolyte solutions reported by Millero et al. (1987) was 0.01 to 0.1 unit, with the maximum discrepancy reported from a solution of 3 mol/kg NaCl + 1 mol/kg $CaCl_2$ (Figure 16a). Millero et al. (1987) suggested that $Ca^{2+}$-Tris-$Na^+$ and $Ca^{2+}$-$Trish^+$-$Na^+$ ternary Pitzer coefficients would be necessary to account for the $Ca^{2+}$-Tris interactions. Such ternary Pitzer coefficients are not available in the published literature. However, there is debate in the literature about whether the ternary Pitzer coefficients are statistically different from zero (Meinrath 2002; Spitzer et al. 2011). Without the ternary Pitzer parameters it was decided that this work would focus on L-SPW solution because of its relatively low Ca content relative to that of the S-SPW (Table 4).

One goal of the work was to extend the colorimetric $pK'_a$ determinations and potentiometric pH measurements from ionic strength of ≈0.1 mol/kg to 8.2 mol/kg, the ionic strength of the S-SPW. To do this, the L-SPW matrix was either diluted or concentrated while maintaining the relative proportions of the major ions. The one exception is the $SO_4^{2-}$ concentration which was held to a maximum of 0.001 mol/kg to prevent gypsum precipitation.

The L-SPW-based pH buffers covered a wide range of ionic strengths, from 0.09-7.67 mol/kg. At most, the buffer was 1.6 times more concentrated than L-SPW, with a Ca concentration of

0.81 mol/kg, less than the 1 mol/kg limitation discussed by Millero et al. (1987). The Ca concentration in S-SPW is higher than the measurements reported by Millero et al. (1987) and, therefore, greater uncertainty in the modelled pH values for S-SPW is unavoidable. Four buffer series based on dilutions of S-SPW were also prepared. All buffers were undersaturated with respect to halite and gypsum.

Example PHREEQC input and output files are provided in Appendices B.2 and B.3. The solution compositions, modelled pH values and ionic strengths are provided in Appendix B.4. In the modelling, the pH of the solutions was calculated by assuming that there was no effect from $CO_{(2)}$ in the solutions and also by equilibrating the solutions with $CO_{2(g)}$ (log $PCO_2$ = -3.4; equivalent to the 2012 global average atmospheric concentration of 393 ppm; Dlugokencky and Tans 2014).

The solutions were prepared in deionized water (18 MΩ•cm) which had been bubbled vigorously with $N_{2(g)}$ for 1.5 to 3.0 hours to remove $CO_{2(g)}$. The Tris buffers were made by adding the appropriate amounts of Tris and TrisHCl to the solution. This approach ensured that the only difference within a series of Tris buffers was the relative proportions of Tris and TrisHCl. Each buffer series consisted of 5-8 buffer solutions of varying pH. A series of Tris buffers made up in pure deionized water (Just Tris; ionic strength = 0.04 ± 0.01 mol/kg) was also prepared.

After the Tris buffers were made, a phenol red indicator solution (made from phenol red sodium salt, ACS grade; Amresco®) was added. Because the colorimetric method is based on the ratio of base to acid peaks in the spectra, measurements are independent of the concentration of the indicator (King and Kester 1989; Raghuraman 2006b). However, low indicator concentrations (2-3 x $10^{-6}$ mol/L) were used in order to stay within the linear range of the spectrophotometer, to prevent changes in the pH of the solutions from the indicator itself, and to reduce the risk of indicator dimerization (King and Kester 1989). The same stock indicator solution, 3.2x$10^{-3}$ mol/L, was used for most of the $pK'_a$ determinations which were performed over a period of 6 months. The stock solution was stored in a double-sealed amber glass bottle at room temperature. Replicate $pK'_a$ measurements using both freshly made and 6-month-old phenol red indicator stock solution gave the same value, within the uncertainty of the $pK'_a$ measurements.

The buffer solutions were made, the indicator added, spectra collected and pH measured potentiometrically on the same day. The buffers were then measured at least twice more at 1 to 3 day intervals. The pH of one set of L-SPW buffers was monitored potentiometrically over a period of 2 months to assess buffer stability with time. The buffer solutions were capped and stored at room temperature between measurements.

Replicate solutions were prepared as part of the quality assurance/quality control (QAQC) protocol. Three complete Tris buffer series were prepared in duplicate. Eight individual solutions within buffer series were prepared in either duplicate or triplicate and 15 phenol red additions to the buffer solutions were performed in duplicate.

To test the range in linearity of the potentiometric electrodes, five sets of low pH (pH = 1.4-3.4) HCl buffers were prepared in high-ionic-strength matrices (Appendix B.4). The buffering capacity of HCl is strongest below a pH of 2. The pH of the solutions was adjusted using either standardized 0.0101 mol/kg hydrochloric acid (HCl) or concentrated HCl (≈16.6 mol/kg) as the buffering agent. The Pitzer coefficients for ions in HCl systems have been well characterized

and are included in the standard PHREEQC-PITZER database. Dilution of high ionic strength solutions with the 0.0101 mol/kg HCl solution was accounted for in the modelling.

### 5.2.2 Potentiometric pH Measurements

pH measurements were made with two electrode/meter combinations: an Orion Ross 815600 electrode (Ross 815600) with a Barnant 20 meter and a Ross Sureflow 8165BNWP electrode (Sureflow) with a Jenco M-5005 meter. Both electrodes have low-sodium error and are suitable for use with the Tris buffer. The Sureflow electrode is recommended by the manufacturer for pH measurements in high ionic strength solutions because the flowing junction should reduce the liquid junction potential compared to a standard porous-plug junction (Ross 815600).

The meters were calibrated using low-ionic strength pH 4 and pH 7 NIST buffers immediately before each set of measurements. The linear range of the calibration was checked using a pH 9.18 commercial buffer. The stability of calibration was checked by re-measuring the calibration buffers after the measurements were completed. In all cases, both the pH and the mV reading were recorded. Ambient laboratory temperature was recorded and the pH measurements were made with manual temperature compensation.

### 5.2.3 Spectrophotometric pH Measurements

Absorbance measurements were made using an Ocean Optics USB4000 spectrophotometer coupled with an Ocean Optics deuterium-halogen light source. The spectrophotometric measurements were in a FIAlab® Instruments SMA Z-flow cell with a 10-cm path length. Dark spectra and reference spectra were collected immediately prior to each set of measurements. For a consistent background matrix between reference and test solution spectra, the reference spectrum for each series of measurements was collected using one of the test solutions without the addition of the phenol red indicator. Spectra were collected in triplicate for all of the Tris buffer solutions. The spectrophotometer operating conditions are summarized in Table 10.

**Table 10: Spectrophotometer Operating Conditions**

| | |
|---|---|
| Integration Time (µsec): | 15000 |
| Spectra Averaged: | 10 |
| Boxcar Smoothing: | 2 |
| Correct for Electrical Dark: | No |
| Strobe/Lamp Enabled: | No |
| Correct for Detector Non-linearity: | No |
| Correct for Stray Light: | No |
| Number of Pixels in Processed Spectrum: | 3648 |

The phenol red molal absorption coefficients, $\varepsilon$, for the acid and base forms were measured at their maximum absorbance wavelengths 431 nm ($\lambda_1$) and 559 nm ($\lambda_2$), respectively. To do this, spectra were acquired for phenol red when it was 99.9% in its acid form (3 pH units below $pK'_a$)

and also 99.9% in its base form (3 pH units above $pK'_a$) (King and Kester 1989). In L-SPW and S-SPW, an increase of 3 pH units resulted in the formation of precipitates and the ε measurements are not possible. As a result, ε measurements were determined in NaCl solutions only, at three ionic strengths: 0.05, 1.0, and 5.0 mol/kg. The maximum difference in a calculated $pK'_a$, if based on ε values determined at either the 0.05, 1.0 or 5.0 mol/kg ionic strength solutions, was small (0.03 units). Therefore, the average values of the ε measurements (acid and base forms) were used for the $pK'_a$ calculations at all ionic strengths. This approach is consistent with that of King and Kester (1989) and Raghuraman et al. (2006b).

## 5.3 RESULTS AND DISCUSSION

The mean ambient laboratory temperature for all measurements was 24.9 °C, and ranged between 23.5 and 25.8 °C. The mean variation in ambient temperature over the course of a single experiment was 0.4 °C and the maximum variation was 1.5 °C. Any change in the solution temperature during an experiment would be less than these values. For both the potentiometric pH measurements and the phenol red $pK'_a$ determinations, the modelled pH values were corrected (±0.03 unit/°C; Millero et al. 2009) by post modelling to account for the difference between the mean laboratory temperature and 25.0 °C.

### 5.3.1 Potentiometric pH Measurements

The glass electrode is linear across a modelled pH range of 1.4 to 9.1 (Figure 18) and the linearity of the electrode response is consistent over the range of ionic strengths tested (Figure 19). The measured pH values from the Ross 815600 and the Sureflow electrodes are the same within error, ±0.03 units (Figure 19; Appendix B.5). Despite the expectation that uncertainty increases with Ca concentration (Section 5.2.1), the linear response observed for the S-SPW across the pH range suggests that the modelled values are reasonable.

There is a linear relationship between mV and modelled pH ($R^2$ = 0.9997) when $CO_2$ is not included in the model calculations. In contrast, if equilibration with $CO_{2(g)}$ is accounted for, the relationship is nonlinear (Figure 18 Inset) because of the increase in $CO_2$ solubility at high pH. The linearity observed in the experimental data across the pH range of 1.4 to 9.1 suggests that any influence on the solution pH from atmospheric $CO_{2(g)}$ in these solutions over the course of the experiments was negligible.

Although the electrode response is linear, an offset from the NIST buffer calibration line is observed with increasing ionic strength for all solutions (Figure 19, Figure 20). Measured pH values are either equal to (within error) or lower than modelled values. The 0.2 pH unit offset for the 5 mol/kg NaCl buffers is consistent with the finding of Hinds et al. (2009), who compared glass electrode pH measurements against the standard hydrogen electrode (SHE) in NaCl solutions. The magnitude of the offset is not only affected by ionic strength, but also by the solution composition. For example, the offset in the 4.89 mol/kg L-SPW solution is 0.39 units, double that of the NaCl solution of similar ionic strength. The offset is even greater, 0.45 units, with the S-SPW diluted to an ionic strength of 4.95 mol/kg. These differences indicate that the offset is a function of both ionic strength and solution composition.

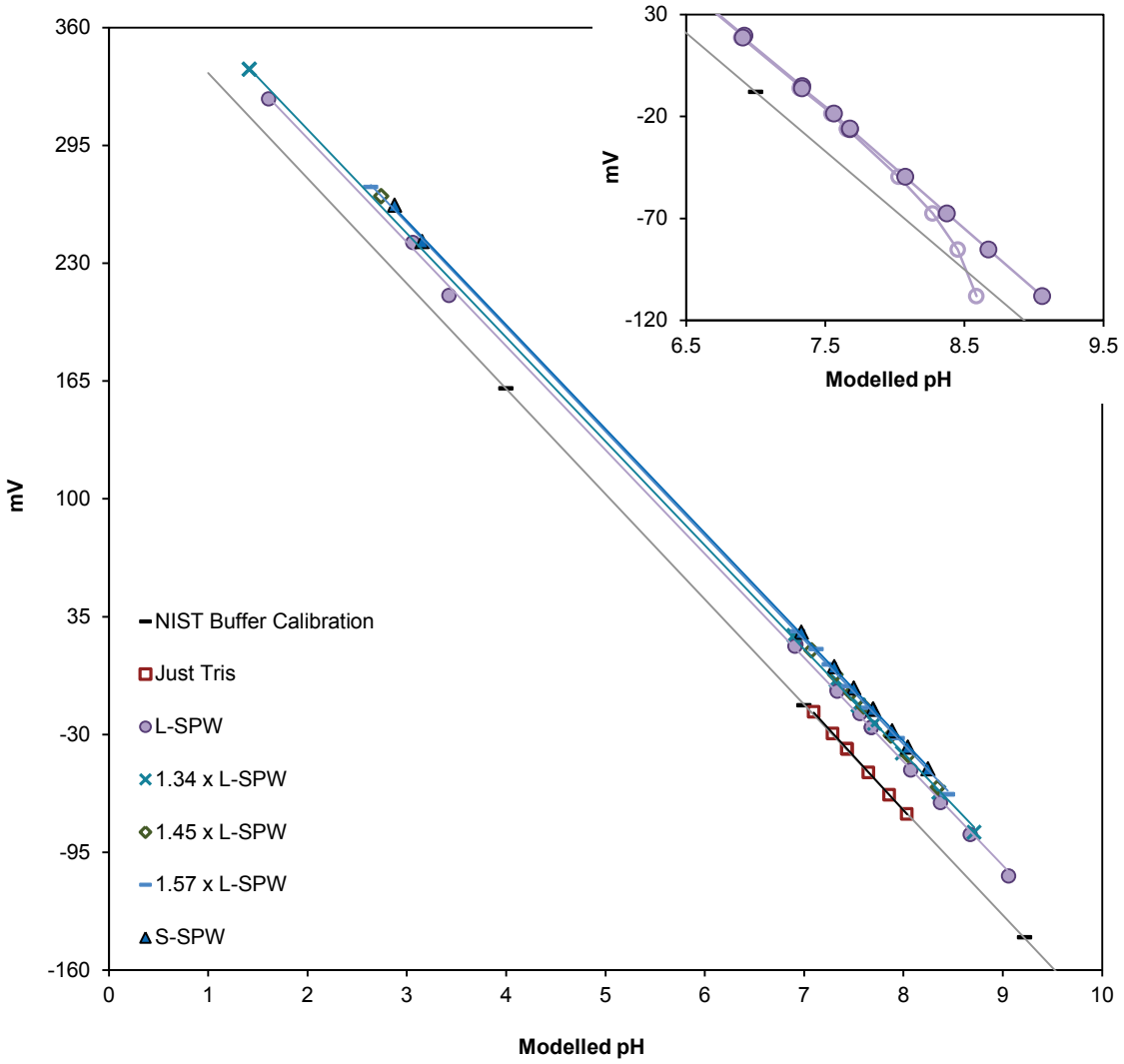



**Figure 18: Electrode Response to Changing pH for Selected Tris and HCl Buffer Solutions. Modelled pH Values Assume no Equilibrium with Atmospheric $CO_{2(g)}$. Inset: Filled Symbols Represent L-SPW Tris Buffer with No $CO_{2(g)}$ and Hollow Symbols Represent Modelled pH Assuming Solution Equilibration with $CO_{2(g)}$ (log $PCO_2$ = -3.4)**

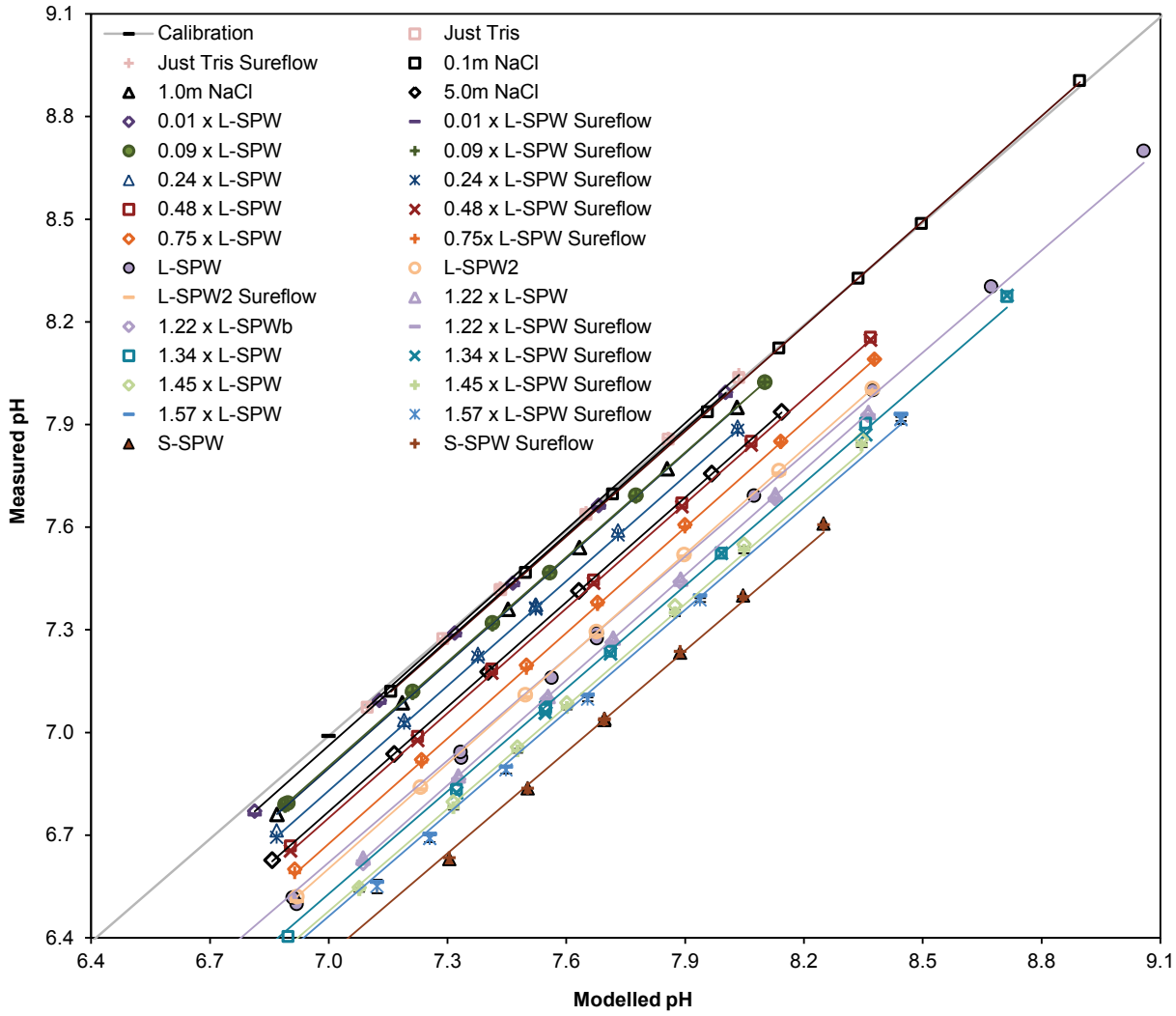



**Figure 19: Modelled Versus Measured pH for the Tris Buffer Data Set. Modelled pH Values Assume no Equilibrium with Atmospheric $CO_{2(g)}$. Data Series with the Identifier "Sureflow" were Measured with the Sureflow Electrode. Otherwise, the pH was Measured Using the Ross 815600 Electrode**

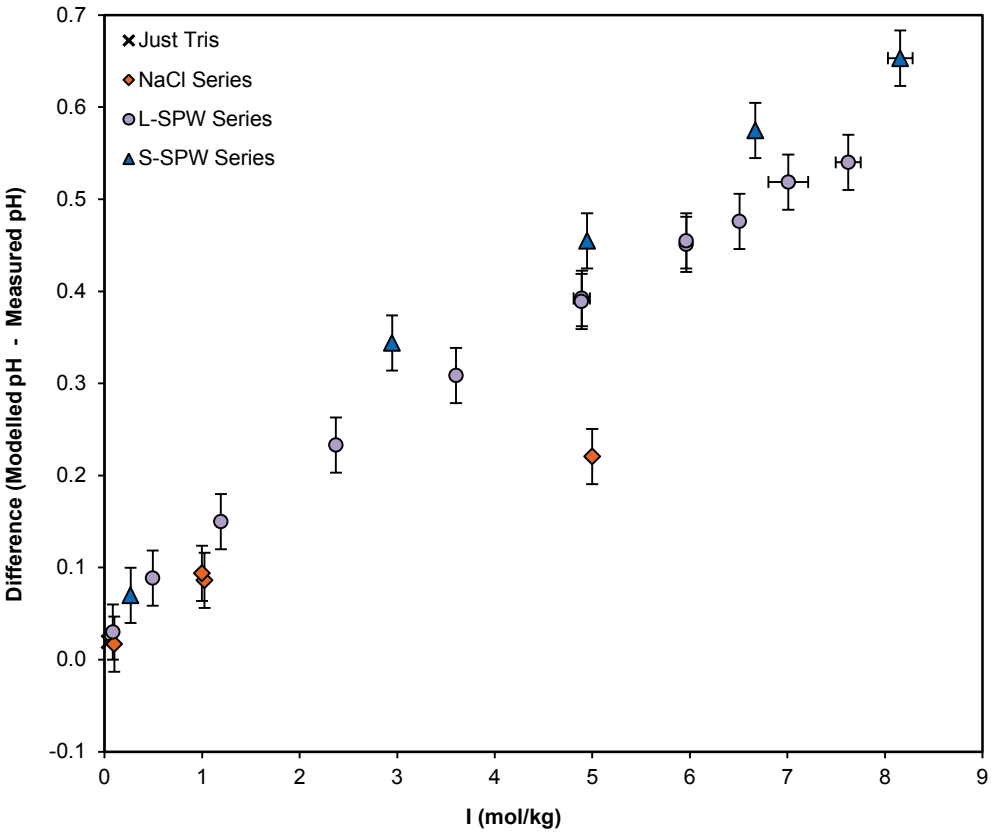



**Figure 20: The Difference Between Modelled pH and Potentiometrically Measured pH with Changing Ionic Strength and Solution Composition. Modelled Values Do Not Include Equilibration With Atmospheric $CO_{2(g)}$. Vertical Error Bars Represent the Standard Error in Potentiometric pH Measurements, ±0.03 pH Units. Horizontal Error Bars Represent the Standard Deviation in Ionic Strength Across a Buffer Series; Where Not Visible, the Variation is Smaller than the Symbol**

Periodic pH measurements for a Tris buffer series stored over a period of 60 days display very little change (standard deviation = 0.02; Figure 21), indicating that the Tris buffers are stable over that amount of time. Millero et al. (1993) also reported that the Tris buffer is stable over similar time periods.

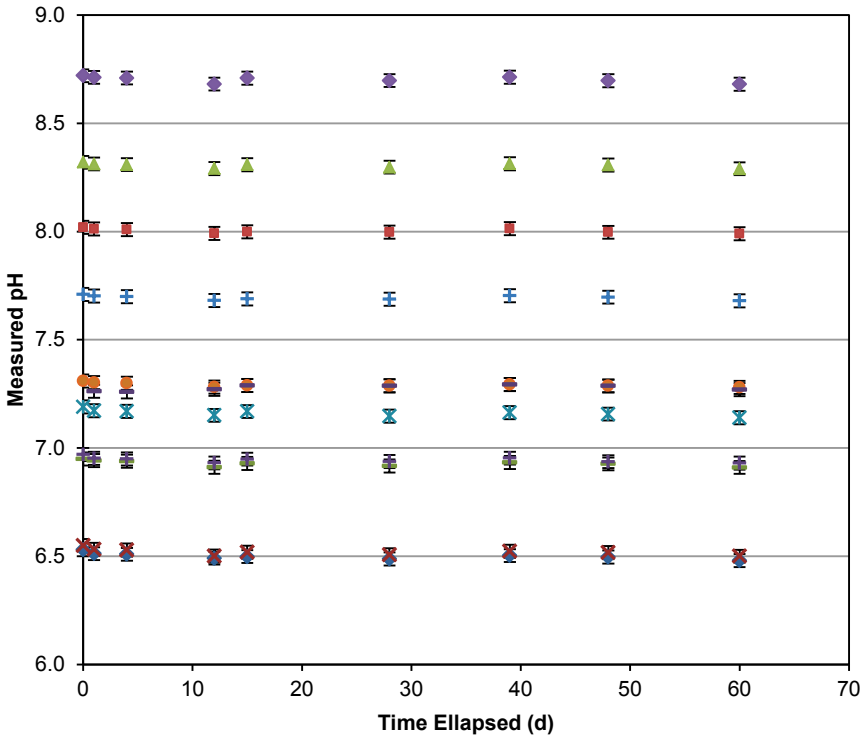



**Figure 21: Measured pH of a L-SPW Tris Buffer Series Over Time. The Data Have Been Normalized to 25 °C. Error Bars Represent the Standard Error in Potentiometric pH Measurements, ±0.03 pH Units**

The time series measurements, the agreement between the two pH electrodes used in this study and the results of replicate pH measurements all suggest that the offsets are consistent and reproducible. The millivolt response and the $E^o$ of the potentiometric cells are different with different electrode/meter combinations and will change over time; they are not reproducible. However, as long as the composition of the buffers used to calibrate the potentiometric cell is consistent, the measured pH values will also be consistent.

In practice, when working in the laboratory, the composition of test solutions will be known and, provided model parameters are available for all solution components, calibration buffers can be prepared to match the matrix. In cases where the test-solution composition is not known, such as with field sampling of groundwater, there may be a mismatch between the ionic strength and composition of the calibration buffers and the test solution. The magnitude of these mismatches will determine any offset (error) in the measurement (Figure 18, Figure 20) that is over and above the standard error of ±0.03 pH units. A field measurement strategy that includes collection of the raw data (mV) for any calibrations and for the test solutions would make it possible to make corrections to field measurements at a later time, after the composition and ionic strength of the solution becomes known.

Two-point calibrations are required for reliable pH measurement. Therefore, in practice, one Tris buffer and one HCl buffer should be prepared in the same matrix as the test solutions. The buffers should be prepared so that the pH is well within their effective range; for Tris this means

using Tris and TrisHCl salts at or near equal molar quantities. This would give, for example, a pH of 8.25 in S-SPW (Appendix B.4). The HCl buffer should have a pH <2.0.

### 5.3.2 Spectrophotometric pH Measurements

The measured molar absorptivities for the phenol red indicator (Table 11) are not the same as those reported by Raghuraman et al. (2006b) because different wavelengths were used. Raghuraman et al. (2006b) used 445 nm and 570 nm wavelengths, and 431 nm and 559 nm wavelengths were used in this work. Furthermore, Raghuraman (2006b) used different instrumentation and it has also been reported that impurities in indicators, which can vary by manufacture and even by batch, can affect the molar absorptivities of the indicator and result in differences in measured pH by up to 0.01 unit (Yao et al. 2007). To put it in context, that magnitude of error from indicator impurities is similar to the magnitude of error associated with commercial NIST pH buffers. If required, the error from indicator impurities can be reduced by taking extra steps to purify each dye batch used (Liu et al. 2011), or molar absorptivities can be measured each time a new batch of indicator is used. The $pK'_a$ for phenol red in 0.1 mol/kg NaCl was recalculated at the wavelengths used by Raghuraman et al. (2006b) and with the molar absorptivities they reported. Raghuraman et al. (2006b) reported a $pK'_a$ of 7.79 at 20 °C and the corresponding $pK'_a$ measured in this study would be 7.74 at 25 °C. The uncertainty in the method developed by Raghuraman et al. (2006b) is ±0.1 unit. Therefore, the effect of differences in measured ε values between the studies is considered negligible.

**Table 11: Measured Molar Absorptivities for Phenol Red in NaCl Solutions**

| | 0.05 mol/kg NaCl | | 1.0 mol/kg NaCl | | 5.0 mol/kg NaCl | | **All Measurements** | |
|---|---|---|---|---|---|---|---|---|
| | Mean | σ | Mean | σ | Mean | σ | **Mean** | **σ** |
| $\varepsilon_{559,B}$ | 59,975 | 279 | 59,170 | 1,477 | 55,823 | 583 | **58,323** | **2,039** |
| $\varepsilon_{559,A}$ | 74 | 29 | -11 | 63 | 66 | 75 | **43** | **69** |
| $\varepsilon_{431,B}$ | 4,077 | 78 | 3,529 | 135 | 3,771 | 201 | **3,792** | **269** |
| $\varepsilon_{431,A}$ | 19,303 | 205 | 20,246 | 1,367 | 19,393 | 440 | **19,647** | **914** |

ε in units of $(mol/kg)^{-1}cm^{-1}$; σ is standard deviation

The effect of equilibration with atmospheric $CO_{2(g)}$ on plots of log[B]/[A] versus modelled pH is presented in (Figure 22). The addition of $CO_{2(g)}$ adds a small degree of nonlinearity at the higher pH values, and this in-turn would contribute to error on the order of 0.02 to 0.03 in the $pK'_a$ measurement (intercept with the X axis). However, on the basis of arguments presented in Section 5.3.1, any effect from the presence of $CO_{2(g)}$ is expected to be negligible and all $pK'_a$ determinations were made with pH values obtained from the model without equilibrating with atmospheric $CO_{2(g)}$ (Appendix B.6).

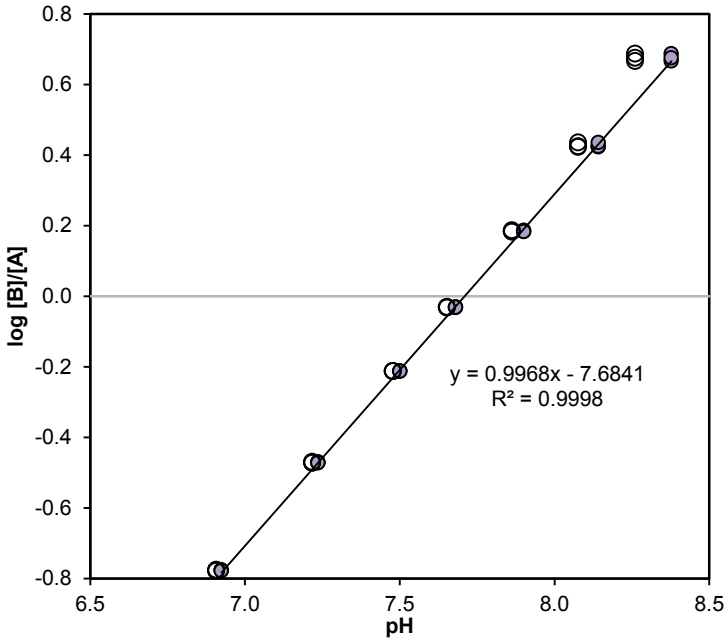



**Figure 22: Plot of the Phenol Red Absorbance Ratio Versus pH in L-SPW. Filled Symbols Represent Modelled pH Assuming no Equilibrium with Atmospheric $CO_{2(g)}$; Hollow Symbols Represent Modelled pH with Solutions at Equilibrium with Atmospheric $CO_{2(g)}$ (log $PCO_2$ = -3.4)**

The $pK'_a$ of phenol red is sensitive to the ionic strength of the solution, but the data indicate that it is not sensitive to solution composition (Figure 23; Appendix B.6). With increasing ionic strength there is a rapid drop from the $pK'_a$ of 8.0 (Drummond et al. 1989) to a $pK'_a$ of 7.8 at 0.04 mol/kg. There is a minimum ($pK'_a$ = 7.6) in the ionic strength range of 1.0 to 2.5 mol/kg and then a gradual increase back to a $pK'_a$ of 7.8 at 8.2 mol/kg. This indicates that the maximum possible error in measured pH would be 0.2 units if the ionic strength of the test solution did not match the ionic strength of the buffer solutions. Therefore, the maximum error in pH measured spectrophotometrically is lower than that from potentiometric measurements (Section 5.3.1). Furthermore, there is an advantage in that the spectrophotometric measurements are not sensitive to variations in ionic composition. In this case, the difference in the measured $pK'_a$ for three solutions of similar ionic strength (~5.0 mol/kg) but different composition ranged from 0.01 to 0.04 (Figure 23).

The useful range for the phenol red indicator is approximately ±1 pH unit from the $pK'_a$ value (Figure 22) and the measurement is therefore a function of ionic strength. The pH range for the spectrophotometric method in high-ionic-strength solutions could be extended by developing similar datasets for $pK'_a$ for multiple indicators that cover a broad pH range. Raghuraman (2006b) used a combination of colorimetric indicators in NaCl solutions, however NaCl buffer solutions limit the upper end of ionic strength to approximately 6 mol/kg. To extend the ionic strength range beyond 6 mol/kg requires the use of divalent cation salts, but this is only possible for a limited range of conditions because the Pitzer ion interaction parameters are not available to model pH for all buffers and for solutions with high Ca and Mg concentrations (Section 5.1, Figure 20). For DGR-related work it is desirable to have the ability to measure pH

in the range 4 to 9 and, until additional spectrophotometric datasets become available, the only available option is to use the potentiometric approach as outlined in Section 5.3.1.

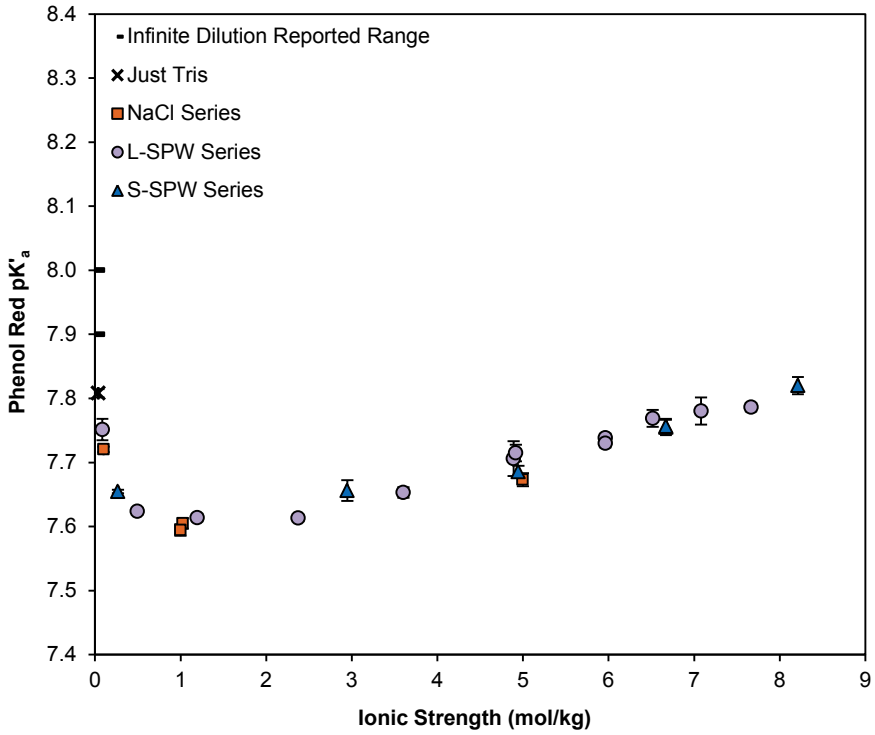



**Figure 23: Variation in Phenol Red pK'$_a$ with Ionic Strength and Solution Composition. Vertical Error Bars Represent 1σ. Horizontal Error Bars Represent the Standard Deviation in Ionic Strength Across a Tris Buffer Series; Where Not Visible, the Variation is Smaller than the Symbol**

### 5.3.3 Uncertainty Assessment

To evaluate what effect weighing errors could have had on the buffer pH, and therefore on the measured pK'$_a$, a sensitivity analysis was conducted. The L-SPW2 buffer series was modelled for an additional 4 times considering:

- The maximum discrepancy that could occur if the actual mass of Tris and TrisHCl was in error by a factor of 5 times the precision of the balances used to weigh the Tris salts; and
- +5% and -5% of the molal values for the components of the L-SPW2 matrix ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$ and $SO_4^{2-}$).

The differences in both buffer pH and pK'$_a$ were apparent at the third decimal point, less than the resolution of the glass electrodes, ± 0.01 unit. The pK'$_a$ for phenol red in L-SPW2 ranged from 7.705 to 7.709 – a difference of 0.004 units. This is almost an order of magnitude smaller

than the standard deviation from replicate $pK'_a$ measurements, which was up to 0.03 units. Therefore, effects from possible errors in solution preparation are considered negligible.

## 5.4 SUMMARY

Pitzer coefficients for two buffers, Tris and acetate, were added to the PHREEQC-Pitzer database and the model-calculated $pK'_a$ values were verified against literature data. The Pitzer coefficient data were more complete and considered more reliable for the Tris buffer – effective pH range of 6.5-9.0 – than for the acetate data – effective pH range of 3.0-5.6 units. pH buffers were also prepared using HCl. The Pitzer coefficients for the HCl system are well known and included in the standard PHREEQC-Pitzer database. It was decided to use Tris and HCl buffers to evaluate two methods for pH ($-\log a_H$) measurement in brine solutions: potentiometric measurements with glass electrodes, and spectrophotometric measurements using the colorimetric indicator phenol red ($pK_a = 8.0$). The experiments involved a range of ionic strengths from 0.04 to 8.2 mol/kg, and solution compositions ranging from NaCl to the more complex S-SPW. Uncertainty in the modelled pH values for the buffer solutions increases for ionic strengths >6.0 mol/kg and for solutions that are more complex than just NaCl because Pitzer parameters for the Tris and acetate buffers have not been measured in such conditions. Extrapolation beyond these conditions could result in errors in modelled pH of up to 0.1 pH unit.

The potentiometric pH electrode response is linear over a pH range from 1.4 to 9.1 and for ionic strengths up to 8.2 mol/kg. However, there is a systematic offset with increasing ionic strength such that an electrode calibrated with low ionic strength buffers will underestimate the pH of the highest ionic strength solution tested (8.2 mol/kg) by 0.6 to 0.7 pH units. For any given ionic strength, the potentiometric measurement is also sensitive to the ionic composition of the solution. Despite these effects, accurate potentiometric measurements are possible if the composition of the calibration buffers is similar to the test solution.

The results of spectrophotometric measurements indicate that the stoichiometric disassociation constant ($pK'_a$) of the phenol red indicator is sensitive to ionic strength but virtually insensitive to the composition of the solution. A maximum error of 0.2 units is possible for pH measured spectrophotometrically, if the ionic strength of the buffers does not match the ionic strength of the test solution. Because of the lower sensitivity of the spectrophotometric data to both ionic strength and solution composition, spectrophotometric measurements may prove more reliable than potentiometric measurements in unknown solutions, e.g., for pH measured in the field. However, the measurement range of phenol red is limited to pH ≈7-9. Additional indicators can be combined to increase the effective range of the spectrophotometric approach. The choice in additional indicators must be considered in the context of the availability and reliability of the appropriate Pitzer ion interaction coefficient data for the buffer as well as the logical combination of indicators to extract unique pH values from multi-indicator spectra (Raghuraman et al. 2006b).

Both methods for pH measurement, potentiometric and spectrophotometric, can be adapted to reliably measure pH in high ionic strength solutions. The two methods offer distinct advantages and limitations. Therefore, the selection of which method to use will depend on the application.

## 6. CONCLUDING REMARKS

A $\gamma$-RAD technique has been established for use in measurement of $D_e$ and $\phi_l$ values for low-permeability sedimentary and crystalline rock samples. The $\gamma$-RAD method is free of beam-hardening artefacts and a linear calibration function is obtained that is essentially independent of background matrix.

The $\gamma$-RAD method has been tested for measurement of porosity and diffusion coefficients of granite (<1% porosity; $D_e = 3.1\times10^{-13}$ $m^2/s$) using an experimental design that allows for simultaneous TD (through-diffusion) measurements ($D_e = 3.0\times10^{-13}$ $m^2/s$). Only one test has been conducted to date and the results of the two techniques are in good agreement, but there were problems identified in the TD experiment probably due to gradual occlusion of diffusion pathways by mineral-water reactions and the SNR (signal to noise ratio) is low for the $\gamma$-RAD measurements. These results demonstrate that the $\gamma$-RAD technique will be viable for crystalline rocks but further method development is required to demonstrate full confidence.

A new method has been developed to generate partial gas saturation conditions in low-permeability rocks. The method is based on the relationship between gas solubility and pressure, whereby a rock sample that is initially 100% brine saturated is equilibrated with $N_2$ gas at high pressure (up to 7000 kPa), and then the pressure is rapidly decreased to atmospheric pressure. This causes a corresponding decrease in gas solubility, resulting in exsolution of $N_2$ to form gas bubbles in the pore spaces. The degree of partial saturation is determined by $\gamma$-RAD. During method development, the initial partial saturation work has been conducted on sandstone (13.0% porosity). Results of repeat experiments on the same sandstone sample display decrease in $D_e$ values ranging from 21-56% for very similar degrees of partial saturation (15% and 13.5%, respectively). This is an unexpected result and it suggests that there is either an unidentified source of error in the measurements, or an effect from pore-scale variations in the distribution of the gas phase that cannot be resolved in the $\gamma$-RAD measurements. A preliminary result from Queenston Formation shale indicates a 53% decrease in $D_e$ as a result of 14.6% partial gas saturation. This method shows great potential for evaluating the effect of partial saturation on diffusion in the Michigan Basin rocks that contain very high salinity porewater. However, these are challenging, multistep experiments and the technique requires further testing and development in order to gain full confidence in the results.

Two techniques for measuring pH were evaluated – potentiometric and spectrophotometric pH measurement – in the context of high-ionic-strength brines. As part of the study, Pitzer coefficients for two buffers, Tris and acetate, were added to the PHREEQC-Pitzer database to calculate the pH of high-ionic-strength buffers. Using these buffers, it was found that the potentiometric measurement is sensitive to both the ionic strength and the ionic composition of the solution. Despite these effects, accurate potentiometric measurements are possible if the composition of the calibration buffers is similar to the test solution. The results of spectrophotometric measurements indicate that the association constant ($pK'_a$) of the phenol red indicator is sensitive to ionic strength but virtually insensitive to the composition of the solution. The magnitude of the possible error in pH measurement using unmatched calibration buffers is larger for the potentiometric method than the spectrophotometric method. However, the range of pH that can be measured using the spectrophotometric method is limited by the narrow working range of the colorimetric indicators, whereas the potentiometric method is

applicable across the pH range. From this work, we have determined that both methods for pH measurement can be adapted to reliably measure pH in high ionic strength solutions. The two methods offer certain advantages and limitations. Therefore, the selection of which method to use will depend on the application.

## ACKNOWLEDGEMENTS

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# APPENDIX A: METHOD FOR ENSURING 100% BRINE SATURATION

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# APPENDIX A: METHOD FOR ENSURING 100% BRINE SATURATION

In conducting measurements of diffusion coefficients under partially brine-saturated conditions, the 100% brine-saturated condition represents a baseline against which all data will be compared.

Saturation of a rock sample with a background brine solution is required for measurements of water-accessible porosity ($\phi_w$) and $D_e$. The method for brine saturation used in previous work (Al et al. 2010, 2012; Cavé et al. 2009; Loomer et al. 2013b; Xiang et al. 2013; Xiang and Al, in prep.) involves submersing the sample in a brine solution followed by evacuation of the head space in a large (5 L) desiccator. This step is intended to remove the gas (air) initially present in the system, including dissolved air in the aqueous phase and trapped air in the rock pore spaces, and thereby maximize brine saturation of the sample.

## A.1 SAMPLE DESCRIPTION

### A.1.1 Sandstones

Well characterized natural sandstone (Carbon Tan from Utah from Ohio) was purchased from Kocurek Industries, Inc. (Caldwell, TX). The porosities of the sandstone were reported to be 12.2-17.7% for Carbon Tan at purchase. They were used previously in our research lab as calibration matrices for the X-ray radiography method (Loomer et al. 2013a). The water-loss porosity measured at UNB was 12.8% for Carbon Tan , which is in the reported range.

### A.1.2 Queenston Formation Shale

The Queenston Formation shale sample (DGR3-472) used in this study was prepared from a preserved core segment obtained during a drilling and coring program for characterization of the Deep Geologic Repository (DGR) site for low- and intermediate-level waste at the Bruce nuclear site near Tiverton, Ontario. Samples from the Queenston Formation are dominantly red-brown shale with minor green and grey shale. Clay minerals comprise 50-60% of these shales, 70-80% of which are illite and illite-smectite mixed layers. Chlorite is also present. Carbonates (calcite and dolomite, 30-40%) and quartz (approximately 10%) are the other major mineral components in these shales (Koroleva et al., 2009). The previously measured $\phi_w$ value for sample DGR3-472 was 8.6%.

## A.2 IMPROVED EXPERIMENTAL PROCEDURES FOR ENSURING 100% BRINE SATURATION

Modification of the saturation procedure involves use of a smaller (approximately 100 mL) vacuum chamber to minimize water mass lost to evaporation (Figure A.1). Such a system allows the following two equilibria to be established and maintained.

1) $Air_{(aq)} \leftrightarrow Air_{(g,\ head\ space)}$
2) $Air_{(g,\ rock\ pores)} \leftrightarrow Air_{(aq)}$

If a vacuum is maintained in the headspace by removal of $Air_{(g,\ head\ space)}$ these coupled equilibria lead to removal of pore gas from the rock.

### A.2.1 Sandstones

The first step was to replace air in the rock pore space with a water soluble gas, $CO_2$. Dry sandstone samples were placed in the vacuum chamber and the system was evacuated to approximately 90 kPa below atmospheric pressure (capacity of the pump) for an hour, after which $CO_2$ gas was introduced and allowed to flow through the chamber for 10-20 min. The $CO_2$ source was removed and the rock samples were allowed to equilibrate with the $CO_2$ atmosphere for approximately 30 min. The chamber was then evacuated. This procedure of adding $CO_2$ followed by evacuation of the chamber was repeated 3 times to ensure complete replacement of the air.

After $CO_2$ treatment, tap water was introduced into the chamber under vacuum to a level approximately 1/4 of the sample height (Figure A.1a), following which the chamber was evacuated. Within 30 minutes, the sandstone samples appeared wet as a result of capillary rise of water in the pores (Figure A.1b). Additional water was added under vacuum to completely submerge the samples, and then the system was allowed to sit in vacuum for 7 days. After water saturation, the $\phi_w$ values for the replicates of Carbon Tan sample were measured using the method outlined in Al et al. (2010, 2012) and Loomer et al. (2013a).

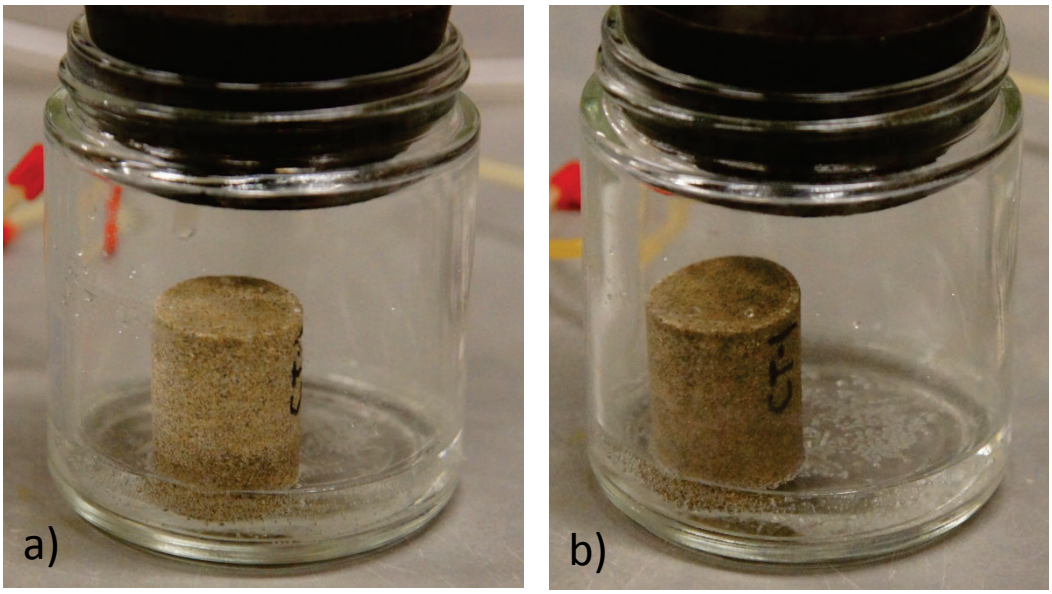



**Figure A.1: Carbon Tan Sandstone Sample Partially Immersed in Water in a Vacuum Chamber: a) Immediately after Adding Water; and b) 30 min Later**

### A.2.2 Queenston Formation Shale

Triplicates of DGR3-472 were prepared from preserved drill cores. During the preparation it is expected that some water loss occurs from the surface of the samples. In order to resaturate them they were placed in the 100-mL vacuum chamber and the chamber was evacuated to approximately 90 kPa below atmospheric pressure for 1 hour. Shale synthetic porewater (S-SPW, Table 4) was introduced into the chamber under vacuum to reach approximately 1/4 of

the sample height. Partially immersed samples were allowed to sit in vacuum until samples were visibly wet – this commonly required 5-6 hours. Additional S-SPW was added under vacuum to submerse the samples completely. Submerged samples were allowed to sit in vacuum for 19 days, during which time the S-SPW solution was replaced 3-4 times with fresh solution to ensure constant concentration.
After brine saturation, the $\phi_w$ values were measured using the method outlined in Al et al. (2010, 2012); Xiang and Al (in prep).

## A.3 RESULTS

Measurements of $\phi_w$, using this method are 9.0% for Queenston Formation shale, and 13.0% for Carbon Tan sandstone. Comparison of these values with those previously reported (Al et al. 2010, 2012; Loomer et al. 2013a; Xiang and Al, in prep.) indicates that the new porosity values are 2-4 % higher (Table A.1). The fact that the present results consistently display higher values suggests some improvement in the method of saturating samples.

**Table A.1: Water-Loss Porosity Data**

| **Sample ID** | DGR3-472 | | Carbon Tan | |
|---|---|---|---|---|
| **Description** | Queenston shale | | Sandstone | |
| **Method** | Ref[a] | This work | Ref[b] | This work |
| **Porosity, $\phi_w$ (%)** | 8.6 ± 0.1 | 9.0 ± 0.03 | 12.8 ± 0.2 | 13.0 ± 0.1 |
| $\phi_{w\,(Ref)}/\phi_{w\,(This\ work)}$ | | 0.96 | | 0.98 |

[a] Xiang and Al, in prep.; [b] Loomer et al. 2013a.

# APPENDIX B: PH MEASUREMENT IN BRINE SOLUTIONS

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## B.1 MODIFIED PHREEQC-PITZER DATABASE

The PHREEQC-PITZER database as modified at UNB (pitzerUNB.dat). “#” marks in front of an entry indicate that the entry is inactive (ignored) in the file.

```
# PHREEQCI v.3.0.0-7430 PITZER database modified to include the Tris and Acetate buffer system and Cesium Pitzer parameters
# Date: 22 March 2013
# Personnel: Diana Loomer (DL), UNB Fredericton
# Parameter values listed after a "#" were considered and are included here for reference but the parameters (or combination of)
# that resulted in the best fit and/or could be verified best are set as active in the file.
# Data were verified with literature using "macinnes=false" which must be specified in input file.
# The Pitzer parameters for TRISHCl and TRIS are only known at 25 °C(Millero 2009).
# Millero et al. 1987 indicate reduced reliability in the Ca+2 and Mg+2 Pitzer parameters and/or that additional parameters
# are required to fully define a solution with 1(or greater) mol/kg Ca or Mg.
# For Millero's SO4 considerations, his calculations included using Harvie et al. 1984 values which are the same used in the
# PHREEQC-Pitzer database.
# Generally, Millero's data could be best reproduced for Tris and is considered the best for use.
# Tishchenko 2000 determined several temp dependant Tris Pitzer parameters (included here) based on the same eqn PHREEQC
# uses, but did not extend to the last 2 PHREEQC coefficients so PHREEQC would assume are zero.
# Generally, it was found Novak's acetate data could be reproduced best for acetate.
#
# Using "analytic" instead of delta h for Tris pK temperature dependence
#
# Pitzer.DAT for calculating pressure dependence of reactions, with
#   molal volume of aqueous species and of minerals, and
#   critical temperatures and pressures of gases used in Peng-Robinson's EOS.
# Details are given at the end of this file.
SOLUTION_MASTER_SPECIES
Tris                Tris                1.0                 121.138   121.138#DL
Acetate             Acetate-  1.0                59.045    59.045              #DL - From minteq.v4
Cs      Cs+         0.0    132.91  132.91                                 #DL
H           H+          -1.    H                1.008
H(1)    H+              -1.    0.0
E           e-          0.0    0.0              0.0
O           H2O         0.0    O                16.00
O(-2)   H2O             0.0    0.0
Ca      Ca+2            0.0    Ca               40.08
Mg      Mg+2            0.0    Mg               24.305
Na      Na+             0.0    Na               22.9898
K           K+          0.0    K                39.0983
Fe      Fe+2            0.0    Fe               55.847
Mn      Mn+2            0.0    Mn               54.938
Ba      Ba+2            0.0    Ba               137.33
Sr      Sr+2            0.0    Sr               87.62
Cl      Cl-     0.0     Cl              35.453
C           CO3-2       2.0    HCO3             12.0111
C(4)    CO3-2           2.0    HCO3             12.0111
Alkalinity CO3-2    1.0     Ca0.5(CO3)0.5   50.05
S           SO4-2       0.0    SO4              32.064
S(6)    SO4-2           0.0    SO4
B           B(OH)3      0.0    B        10.81
Li      Li+     0.0     Li              6.941
Br      Br-     0.0     Br              79.904
# redox-uncoupled gases
Hdg                 Hdg     0       Hdg     2.016 # H2 gas
Oxg                 Oxg     0       Oxg     32 # Oxygen gas
Mtg                 Mtg     0.0     Mtg     16.032 # CH4 gas
Sg                  H2Sg    1.0     H2Sg    34.08
Ntg                 Ntg     0       Ntg     28.0134 # N2 gas

SOLUTION_SPECIES
Tris = Tris                             #DL
            log_k               0.0     #DL
Tris + H+ = (Tris)H+            #DL
#           log_k               8.075   #DL - zero ionic strength pKa @ 25 deg C - Bates and Hetzer 1961: J. Phys. Chem.
65.667-67 1
            log_k               8.070   #DL - zero ionic stregth pKa @ 25 deg C - Foti et al. 1999: Ann. di Chim. 89, 87-98
(recommended value from compiled references)
```

```
#           delta_h    11.377  kcal          #DL - zero ionic strength delta h @ 25 deg C = 47,600 J/mol valid 0-50 deg C - Bates and
Hetzer 1961: J. Phys. Chem. 65.667-67 1
            delta_h    11.36       kcal      #DL - zero ionic stregth pKa @ 25 deg C - Foti et al. 1999: Ann. di Chim. 89, 87-98
(recommended value from compiled references)
#           delta_h    11.395  kcal          #DL - Tishchenko 2000
#           -analytic  75.6853   0.0153422            -4884.31  -29.0765
Acetate- = Acetate-                 #DL - From minteq.v4
            log_k                   0.0       #DL - From minteq.v4
H+ + Acetate- = H(Acetate)    #DL - acetic acid
            log_k                   4.757     #DL - From minteq.v4 (zero ionic strength pKa for acetate/acetic acid (0.001m))
#           log_k                   4.756     #DL - From Handbook of Chemistry and Physics, 93rd Ed., 2012-2013
            delta_h    0.098 kcal           #DL - From minteq.v4
            -gamma     0.0          0.0     #DL - From minteq.v4 (Debye-Hückel a, Debye-Hückel b coefficients - not relevant here)
                       #DL -              Id:   3309921
                       #DL -        log K source:        NIST46.4
                       #DL -       Delta H source:       NIST46.4
                       #DL - T and ionic strength:       0.00 25.0
#           log_k                   4.757     #DL - From Mesmer et al.: J. Phys. Chem. 1989, 93, 7483-7490(ionic strength 0 m NaCl;
25 deg C)
#           delta_h    -0.12 kcal #DL - From Mesmer et al.: J. Phys. Chem. 1989, 93, 7483-7490(ionic strength 0 m NaCl; 25 deg C -
different at different temperatures)
Na+ + Acetate- = Na(Acetate) #DL - From minteq.v4
            log_k                   -0.18     #DL - From minteq.v4 -0.18: corrected to zero ionic strength, if necessary. Original NIST
database now discontinued
            delta_h    2.87 kcal  #DL - From minteq.v4
                       #DL -                Id:              5009920
                       #DL -        log K source:        NIST46.4
                       #DL -       Delta H source:       NIST46.4
                       #DL - T and ionic strength:       0.00 25.0
K+ + Acetate- = K(Acetate)    #DL - From minteq.v4
            log_k                   -0.1955   #DL - From minteq.v4
            delta_h    1            kcal      #DL - From minteq.v4
            -gamma     0            0         #DL - From minteq.v4
                       #DL -                Id:              4109921
                       #DL -        log K source:        NIST46.4
                       #DL -       Delta H source:       NIST46.2
                       #DL - T and ionic strength:       0.10 25.0
Ca+2 + Acetate- = Ca(Acetate)+          #DL - From minteq.v4
            log_k                   1.18      #DL - From minteq.v4
            delta_h    0.96 kcal  #DL - From minteq.v4
            -gamma     0            0         #DL - From minteq.v4
                       #DL -                Id:              1509920
                       #DL -        log K source:        NIST46.4
                       #DL -       Delta H source:       NIST46.4
                       #DL - T and ionic strength:       0.00 25.0
Mg+2 + Acetate- = Mg(Acetate)+          #DL - From minteq.v4
            log_k      1.27                              #DL - From minteq.v4
            delta_h    0            kcal                 #DL - From minteq.v4
            -gamma     0            0         #DL - From minteq.v4
                       #DL -               Id: 4609920
                       #DL -        log K source:        NIST46.4
                       #DL -       Delta H source:       NIST46.2
                       #DL - T and ionic strength:       0.00 25.0
Cs+ = Cs+                               #DL
      log_k      0.000                  #DL
     -gamma           1.81        0.01  #DL - a,b parameters from Parkhurst 1990 cited in Langmuir 1997 p 133
H+ = H+
            -dw          9.31e-9
e- = e-
H2O = H2O
Li+ = Li+
            -dw          1.03e-9
            -Vm    -.0237   -.0690   11.5800   -2.7761 .4862 6 # supcrt
Na+ = Na+
            -dw          1.33e-9
             -Vm  1.403  -2.285  4.419  -2.726  -5.125e-5  4.0  0.162  47.67  -3.09e-3  0.725 # supcrt modified
# for calculating densities (rho) when I > 3...
#            -Vm  1.403  -2.285  4.419  -2.726  -5.125e-5  2.0  0.162  47.67  -3.09e-3  0.4
K+ = K+
            -dw          1.96e-9
```

```
        -Vm  3.322  -1.473  6.534  -2.712  9.06e-2  3.5  0  29.70  0  1 # supcrt modified
Mg+2 = Mg+2
        -dw         0.705e-9
        -Vm  -1.410  -8.6  11.13  -2.39  1.332  5.5  1.29  -32.9  -5.86e-3  1 # supcrt modified
Ca+2 = Ca+2
        -dw         0.793e-9
        -Vm  -0.3456  -7.252  6.149  -2.479  1.239  5  1.60  -57.1  -6.12e-3  1 # supcrt modified
Sr+2 = Sr+2
        -dw         0.794e-9
        -Vm  -1.57e-2  -10.15  10.18  -2.36  0.860  5.26  0.859  -27.0  -4.1e-3  1.97 # supcrt modified
Ba+2 = Ba+2
        -dw         0.848e-9
        -Vm  2.063  -10.06  1.9534  -2.36  0.4218  5  1.58  -12.03  -8.35e-3  1 # supcrt modified
Mn+2 = Mn+2
        -dw         0.688e-9
        -Vm   -.1016   -8.0295   8.9060   -2.4471  1.4006 6 # supcrt
Fe+2 = Fe+2
        -dw         0.719e-9
        -Vm  -0.3255  -9.687  1.536  -2.379  0.3033  5.5  -4.21e-2  37.96  0  1 # supcrt modified
Cl- = Cl-
        -dw         2.03e-9
        -Vm  4.465  4.801  4.325  -2.847  1.748  0  -0.331  20.16  0  1 # supcrt modified
CO3-2 = CO3-2
        -dw         0.955e-9
        -Vm  5.052 0  0  -5.447  4.927  0  0.103  94.9  -1.30e-2  1 # supcrt modified
SO4-2 = SO4-2
        -dw         1.07e-9
        -Vm  5.0  9.06  -8.36  -3.14  3.773  0  6.61  -27.9  -6.32e-2  0.428 # supcrt modified
B(OH)3 = B(OH)3
        -dw         1.1e-9
        -Vm 7.0643   8.8547   3.5844   -3.1451 -.2000  # supcrt
Br- = Br-
        -dw         2.01e-9
        -Vm  5.2690   6.5940   4.7450   -3.1430 1.3858 # supcrt
# redox-uncoupled gases
Hdg = Hdg # H2
        -dw         5.13e-9
        -Vm 6.52  0.78  0.12 # supcrt
Oxg = Oxg # O2
        -dw         2.35e-9
        -Vm   5.7889  6.3536  3.2528  -3.0417   -0.3943 # supcrt
Mtg = Mtg # CH4
        -dw         1.85e-9
        -Vm 7.7 # CH4 solubility, 25-100C, 1-700atm
Ntg = Ntg # N2
        -dw         1.96e-9
        -Vm 7 # Pray et al., 1952, IEC 44. 1146
H2Sg = H2Sg # H2S
        -dw         2.1e-9
        -Vm  7.81  2.96  -0.46 # supcrt
# aqueous species
H2O = OH- + H+
        -analytic  68.547  0  -6199.8  -24.955
        -dw         5.27e-9
        -Vm  1.776  0.0738  1.417  -2.782  2.347  0  0.906  0  0  1 # supcrt modified
CO3-2 + H+ = HCO3-
        log_k          10.3393
        delta_h -3.561  kcal
        -analytic    107.8975    0.03252849  -5151.79   -38.92561    563713.9
        -dw         1.18e-9
        -Vm  8.625  0  -11.90  0  1.695  0  0  124  0  1 # supcrt modified
CO3-2 + 2 H+ = CO2 + H2O
        log_k          16.6767
        delta_h     -5.738  kcal
        -analytic    464.1965    0.09344813  -26986.16       -165.75951   2248628.9
        -dw         1.92e-9
        -Vm   21.78  -49.4  -91.7  31.96 # supcrt modified
SO4-2 + H+ = HSO4-
        log_k          1.979
        delta_h 4.91    kcal
```

```
            -analytic   -5.3585   0.0183412   557.2461
            -dw          1.33e-9
            -Vm 8.2 9.2590   2.1108   -3.1618 1.1748  0 -0.3 15 0 1 # supcrt modified
H2Sg = HSg- + H+
            log_k       -6.994
            delta_h 5.30           kcal
            -analytical  11.17   -0.02386  -3279.0
            -dw          2.1e-9
            -Vm 5.0119   4.9799   3.4765   -2.9849 1.4410 # supcrt
B(OH)3 + H2O = B(OH)4- + H+
            log_k         -9.239
            delta_h 0   kcal
3B(OH)3 = B3O3(OH)4- + 2H2O + H+
            log_k         -7.528
            delta_h 0   kcal
4B(OH)3 = B4O5(OH)4-2 + 3H2O + 2H+
            log_k         -16.134
            delta_h 0   kcal
Ca+2 + B(OH)3 + H2O = CaB(OH)4+ + H+
            log_k         -7.589
            delta_h 0   kcal
Mg+2 + B(OH)3 + H2O = MgB(OH)4+ + H+
            log_k         -7.840
            delta_h 0   kcal
#Ca+2 + CO3-2 = CaCO3
#             log_k         3.151
#             delta_h 3.547   kcal
#             -analytic    -1228.806   -0.299440    35512.75   485.818
#             -dw 4.46e-10          # complexes: calc'd with the Pikal formula
#             -Vm  -.2430   -8.3748   9.0417   -2.4328  -.0300 # supcrt
Mg+2 + H2O = MgOH+ + H+
            log_k         -11.809
            delta_h 15.419 kcal
Mg+2 + CO3-2 = MgCO3
            log_k         2.928
            delta_h 2.535   kcal
            -analytic   -32.225   0.0             1093.486    12.72433
            -dw 4.21e-10
            -Vm  -.5837   -9.2067   9.3687   -2.3984  -.0300 # supcrt

PHASES
CsCl                                        #DL
      CsCl = Cs+ + Cl-                      #DL
      log_k         1.515                   #DL - Hu et al 2007 CCPDTC 31:541-544 (note: they give solubility as ln Ksp, not log K - to
convert: log K = ln K/2.303 =  3.488/2.303 = 1.515)
CsBr                                        #DL
            CsBr = Cs+ + Br-  #DL
      log_k         0.817                   #DL - Hu et al 2007 CCPDTC 31:541-544 (note: they give solubility as ln Ksp, not log K - to
convert: log K = ln K/2.303 = 1.881/2.303 = 0.817)
Anhydrite
            CaSO4 = Ca+2 + SO4-2
            log_k         -4.362
            -anal  87.836  0  -3136.79  -32.953 # 50 - 160oC, 1 - 1e3 atm, anhydrite dissolution, Blount and Dickson, 1973, Am.
Mineral. 58, 323.
            -Vm 46.1 # 136.14 / 2.95
Aragonite
            CaCO3 = CO3-2 + Ca+2
            log_k         -8.336
            delta_h -2.589 kcal
            -analytic    -171.8607   -.077993    2903.293    71.595
            -Vm 34.04
Arcanite
            K2SO4  =  + 1.0000 SO4-- + 2.0000 K+
            log_k         -1.776
            -analytic    2.823    0.0          -1371.2
            -Vm 65.5
Bischofite
            MgCl2:6H2O  =  + 1.0000 Mg++ + 2.0000 Cl- + 6.0000 H2O
            log_k         4.455
            -analytic    3.524    0.0          277.6
```

```
        Vm 127.1
Bloedite
        Na2Mg(SO4)2:4H2O  =  + 1.0000 Mg++ + 2.0000 Na+ + 2.0000 SO4-- + 4.0000 H2O
        log_k         -2.347
        -delta_H  0               # Not possible to calculate enthalpy of reaction Bloedite
        Vm 147
Brucite
        Mg(OH)2  =  + 1.0000 Mg++ + 2.0000 OH-
        log_k         -10.88
        -delta_H  4.85    kcal/mol
#       -analytic -1.0280e+002 -1.9759e-002 9.0180e+003 3.8282e+001 1.4075e+002
#    -Range:  0-300
        Vm 24.6
Burkeite
        Na6CO3(SO4)2  =  + 1.0000 CO3-2 + 2.0000 SO4-- + 6.0000 Na+
        log_k         -0.772
        Vm 152
Calcite
        CaCO3 = CO3-2 + Ca+2
        log_k         -8.406
        delta_h -2.297 kcal
        -analytic    -171.8329    -0.077993    2839.319    71.595
        -Vm 36.9
Carnallite
        KMgCl3:6H2O  =  K+ + Mg++ + 3Cl- + 6H2O
        log_k         4.330
        Vm 173.7
Celestite
        SrSO4 = Sr+2 + SO4-2
        log_k         -6.630
        -analytic  -7.14 6.11E-03  75 0 0 -1.79E-05  # Howell et al., 1992, JCED 37, 464.
        -Vm 46.4
Dolomite
        CaMg(CO3)2 = Ca+2 + Mg+2 + 2 CO3-2
        log_k         -17.083
        delta_h -9.436 kcal
        -Vm 64.5
Epsomite
        MgSO4:7H2O  =  Mg+2 + SO4-2 + 7 H2O
        log_k         -1.881
        -analytical   1.718     0.0          -1073.
        Vm 147
Gaylussite
        CaNa2(CO3)2:5H2O = Ca+2 + 2 CO3-2 + 2 Na+ + 5 H2O
        log_k         -9.421
Glaserite
        NaK3(SO4)2 =  Na+ + 3K+ + 2SO4-2
        log_k         -3.803
Glauberite
        Na2Ca(SO4)2  =  Ca+2 + 2 Na+ + 2 SO4-2
        log_k         -5.245
        Vm 99
Gypsum
        CaSO4:2H2O = Ca+2 + SO4-2 + 2 H2O
        log_k         -4.581
        delta_h -0.109 kcal
        -analytic    90.318    0.0          -4213.    -32.641
        -Vm 73.9
Barite
        BaSO4 = Ba+2 + SO4-2
        log_k       -9.97
        delta_h  6.35 kcal
        -analytic   136.035   0.0          -7680.41  -48.595
        -Vm 51.9
Halite
        NaCl  =  Cl- + Na+
        log_k         1.570
        -analytic -713.4616   -.1201241   37302.21    262.4583    -2106915.
        -Vm 27.1
Hexahydrite
```

```
        MgSO4:6H2O  =  Mg+2 + SO4-2 + 6 H2O
        log_k         -1.635
        -analytic     -62.666   0.0          1828.     22.187
        Vm 132
Kainite
        KMgClSO4:3H2O  =  Cl- + K+ + Mg+2 + SO4-2 + 3 H2O
        log_k         -0.193
Kalicinite
        KHCO3  =  K+ + H+ + CO3-2
        log_k         -10.058
Kieserite
        MgSO4:H2O  =  Mg+2 + SO4-2 + H2O
        log_k         -0.123
        Vm 53.8
Labile_S
        Na4Ca(SO4)3:2H2O = 4Na+ + Ca+2 + 3SO4-2 + 2H2O
        log_k         -5.672
Leonhardite
        MgSO4:4H2O = Mg+2 + SO4-2 + 4H2O
        log_k         -0.887
Leonite
        K2Mg(SO4)2:4H2O  =  Mg+2 + 2 K+ + 2 SO4-2 + 4 H2O
        log_k         -3.979
Magnesite
        MgCO3 =  CO3-2 + Mg+2
        log_k         -7.834
        delta_h    -6.169
        Vm 28.3
Mirabilite
        Na2SO4:10H2O  =  SO4-2 + 2 Na+ + 10 H2O
        log_k         -1.214
        -analytic     -3862.234   -1.19856    93713.54    1577.756    0.
        Vm 216
Misenite
        K8H6(SO4)7  =  6 H+ + 7 SO4-2 + 8 K+
        log_k         -10.806
Nahcolite
        NaHCO3  =  CO3-2 + H+ + Na+
        log_k         -10.742
Natron
        Na2CO3:10H2O = CO3-2 + 2 Na+ + 10.0000 H2O
        log_k         -0.825
Nesquehonite
        MgCO3:3H2O =  CO3-2 + Mg+2 + 3 H2O
        log_k         -5.167
Pentahydrite
        MgSO4:5H2O  =  Mg+2 + SO4-2 + 5 H2O
        log_k         -1.285
Pirssonite
        Na2Ca(CO3)2:2H2O = 2Na+ + Ca+2 + 2CO3-2 + 2 H2O
        log_k         -9.234
Polyhalite
        K2MgCa2(SO4)4:2H2O  = 2K+ +  Mg+2 + 2 Ca+2 + 4SO4-2 + 2 H2O
        log_k         -13.744
        Vm 218
Portlandite
        Ca(OH)2 =  Ca+2 + 2 OH-
        log_k         -5.190
Schoenite
        K2Mg(SO4)2:6H2O  =  2K+ + Mg+2 + 2 SO4-2 + 6H2O
        log_k         -4.328
Sylvite
        KCl  = K+ + Cl-
        log_k          0.900
        -analytic     3.984     0.0          -919.55
        Vm 37.5
Syngenite
        K2Ca(SO4)2:H2O  =  2K+ + Ca+2 + 2SO4-2 + H2O
        log_k         -7.448
Trona
```

```
        Na3H(CO3)2:2H2O =  3 Na+ + H+ + 2CO3-2 + 2H2O
        log_k       -11.384
        Vm 106
Borax
        Na2(B4O5(OH)4):8H2O + 2 H+  =  4 B(OH)3 + 2 Na+ +  5 H2O
        log_k       12.464
        Vm 223
Boric_acid,s
        B(OH)3  =  B(OH)3
        log_k       -0.030
KB5O8:4H2O
        KB5O8:4H2O + 3H2O + H+ = 5B(OH)3 + K+
        log_k       4.671
K2B4O7:4H2O
        K2B4O7:4H2O + H2O + 2H+ = 4B(OH)3 + 2K+
        log_k       13.906
NaBO2:4H2O
        NaBO2:4H2O + H+ = B(OH)3 + Na+ + 3H2O
        log_k       9.568
NaB5O8:5H2O
        NaB5O8:5H2O + 2H2O + H+ = 5B(OH)3 + Na+
        log_k       5.895
Teepleite
        Na2B(OH)4Cl + H+ = B(OH)3 + 2Na+ + Cl- + H2O
        log_k       10.840
CO2(g)
        CO2 = CO2
        log_k     -1.468
        delta_h -4.776 kcal
        -analytic  119.87356  2.185434e-2  -7337.8 -44.7652    669371
        -T_c  304.2 # critical T, K
        -P_c   72.80 # critical P, atm
        -Omega 0.225 # acentric factor
H2O(g)
        H2O = H2O
        log_k  1.506; delta_h -44.03 kJ
        -T_c  647.3 # critical T, K
        -P_c  217.60 # critical P, atm
        -Omega 0.344 #  acentric factor
        -analytic   -16.5066 -2.0013E-3  2710.7  3.7646  0 2.24E-6
# redox-uncoupled gases
Oxg(g)
        Oxg = Oxg
        -analytic -7.5001 7.8981e-003 0.0 0.0 2.0027e+005
        T_c  154.6 ; -P_c   49.80 ; -Omega 0.021
Hdg(g)
        Hdg = Hdg
        -analytic   -9.3114e+000    4.6473e-003   -4.9335e+001    1.4341e+000    1.2815e+005
        -T_c  33.2 ; -P_c   12.80 ; -Omega 0.225
Ntg(g)
        Ntg = Ntg
        -analytic -58.453 1.81800E-03  3199  17.909 -27460
        T_c  126.2 ; -P_c   33.50 ; -Omega 0.039
Mtg(g)
        Mtg = Mtg
        -analytic -2.4027e+001 4.7146e-003 3.7227e+002 6.4264e+000 2.3362e+005
        T_c  190.6 ; -P_c   45.40 ; -Omega 0.008
H2Sg(g)
        H2Sg  =  H+ + HSg-
        -analytic -9.7354e+001 -3.1576e-002 1.8285e+003 3.7440e+001 2.8560e+001
        T_c  373.2 ; -P_c  88.20 ; -Omega 0.1

PITZER
-B0
(Tris)H+  Cl-     0.0395          #DL - Bates and Macaskill 1985: J. Solution Chem. 1985, 14, 723–734.
(Tris)H+  SO4-2   0.09393         #DL - Bates and Macaskill 1986: J. Chem. Eng. Data 31, 416-418.
#         (Tris)H+  Cl-         0.03574   0           0           0.00013   #DL - Tishchenko 2000: Russ. Chem. Bull. 49, No 4, April,
2000
#         H+        Cl-         0.17527               #DL - Bates and Macaskill 1985: J. Solution Chem. 14, 723–734 (Tris)
#         Na+       Cl-         0.075373 #DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115 (acetate)
```

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        H+      OH-     0                       #DL - not litsted, so same in PHREEQC Pitzer database, Novak et al 1996:
Radiochimica Acta 74, 111-116 (acetate)
        H+      Acetate-        0       #DL - Novak et al 1996: Radiochimica Acta 74, 111-116
        Na+     Acetate-        0.1426  #DL - Novak et al 1996: Radiochimica Acta 74, 111-116/Pitzer and Mayorga
1973: J. Phys. Chem. 77, 2300-2307/Pitzer 1991: Activity Coefficients in Electrolyte Solutions
#       Na+     Acetate-        0.13723 #DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115
#       K+      Acetate-        0.1587  #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307/Pitzer 1991:
Activity Coefficients in Electrolyte Solutions
#       K+      Acetate-        0.15343  #DL - (+/-0.00204)Marshall et al 1995: J. Chem. Eng. Data 40, 1041–1052
#       K+      Acetate-        0.15283 #DL - Kim and Frederick 1988: J. Chem. Eng. Data 33, 177–184
#       K+      Acetate-        0.161   #DL - Ferra et al 2011: J. Chem. Eng. Data 56, 3673–3678
#       K+      Acetate-        0.228   #DL - DeRobertis et al (1999) J. Chem. Eng. Data 1999, 44, 262–270
        K+      Acetate-        0.155   #DL - (+/-0.005)Spitzer et al 2011: Accred. Qual. Assur. 16, 191–198
        Ca+2    Acetate-        0.269   #DL - Loos et al. 2004: Fluid Phase Equilibria 219, 219–229
#       Ca+2    HCO3-           -0.104  #DL - different than PHREEQC Pitzer database: Loos et al 2004: Fluid Phase
Equilibria 219, 219–229 (acetate)
#       Ca+2    SO4-2           0.128   #DL - different in PHREEQC Pitzer database: Loos et al 2004: Fluid Phase
Equilibria 219, 219–229 (acetate)
        Cs+     Cl-             0.030   #DL - Pitzer and Mayorga 1973: J Phys Chem 77, 2300-2307
        Cs+     Br-             0.0279  #DL - Pitzer and Mayorga 1973: J Phys Chem 77, 2300-2307
        Cs+     SO4-2           0.0888  #DL - Pitzer and Mayorga 1973: J Phys Chem 77, 2300-2307
        Cs+     OH-              0.150  #DL - Pitzer and Mayorga 1973: J Phys Chem 77, 2300-2307
 Na+    Cl-     0.0765  -777.03 -4.4706        0.008946  -3.3158E-6
 K+     Cl-     0.04835 0       0               5.794E-4
 Mg+2   Cl-     0.35235 0       0               -1.943E-4
 Ca+2   Cl-     0.3159  0       0               -1.725E-4
 MgOH+  Cl-     -0.1
 H+     Cl-     0.1775  0       0               -3.081E-4
 Li+    Cl-     0.1494  0       0               -1.685E-4
 Sr+2   Cl-     0.2858  0       0               0.717E-3
 Fe+2   Cl-     0.335925
 Mn+2   Cl-     0.327225
 Ba+2   Cl-     0.2628  0       0               0.6405E-3
 CaB(OH)4+      Cl-     0.12
 MgB(OH)4+      Cl-     0.16
 Na+    Br-     0.0973  0       0               7.692E-4
 K+     Br-     0.0569  0       0               7.39E-4
 H+     Br-     0.1960  0       0               -2.049E-4
 Mg+2   Br-     0.4327  0       0               -5.625E-5
 Ca+2   Br-     0.3816  0       0               -5.2275E-4
 Li+    Br-     0.1748  0       0               -1.819E-4
 Sr+2   Br-     0.331125        0       0       -0.32775E-3
 Ba+2   Br-     0.31455 0       0               -0.33825E-3
 Na+    SO4-2   0.01958 0       0               2.367E-3
 K+     SO4-2   0.04995 0       0               1.44E-3
 Mg+2   SO4-2   0.221   0       0               -0.69E-3
 Ca+2   SO4-2   0.2
 H+     SO4-2   0.0298
 Li+    SO4-2   0.136275        0       0       0.5055E-3
 Sr+2   SO4-2   0.200   0       0               -2.9E-3
 Fe+2   SO4-2   0.2568
 Mn+2   SO4-2   0.2065
 Na+    HSO4-   0.0454
 K+     HSO4-   -0.0003
 Mg+2   HSO4-   0.4746
 Ca+2   HSO4-   0.2145
 H+     HSO4-   0.2065
 Fe+2   HSO4-   0.4273
 Na+    OH-     0.0864  0       0               7.00E-4
 K+     OH-     0.1298
 Ca+2   OH-     -0.1747
 Li+    OH-     0.015
 Ba+2   OH-     0.17175
 Na+    HCO3-   0.0277  0       0               1.00E-3
 K+     HCO3-   0.0296  0       0               0.996E-3
 Mg+2   HCO3-   0.329
 Ca+2   HCO3-   0.4
 Sr+2   HCO3-   0.12
 Na+    CO3-2   0.0399  0       0               1.79E-3
 K+     CO3-2   0.1488  0       0               1.788E-3
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 Na+      B(OH)4-  -0.0427
 Na+      B3O3(OH)4- -0.056
 Na+      B4O5(OH)4-2 -0.11
 K+       B(OH)4-   0.035
 K+       B3O3(OH)4- -0.13
 K+       B4O5(OH)4-2 -0.022
-B1
          (Tris)H+          Cl-       0.20978  #DL - Bates and Macaskill 1985: J. Solution Chem. 1985 14, 723–734.
          (Tris)H+          SO4-2     0.59829  #DL - Bates and Macaskill 1986: J. Chem. Eng. Data 31, 416-418.
#         (Tris)H+          Cl-       0.21452          -5875.10          -36.291   0.05613          #DL - The A0 coeff
is a different value in the temp dependance table than for the value listed at 25 deg C (0.21488), Tishchenko 2000 Russ.Chem.Bull.
49, No 4, April, 2000
#         H+        Cl-       0.30197          #DL - Bates and Macaskill 1985: J. Solution Chem. 1985 14, 723–734 (Tris)
#         Na+       Cl-       0.277031 #DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115 (acetate)
          H+        OH-               0        #DL - not listed, so same in PHREEQC Pitzer database, Novak et al 1996:
Radiochimica Acta 74, 111-116 (acetate)
          H+        Acetate-          0        #DL - Novak et al 1996: Radiochimica Acta 74, 111-116/Mesmer et al 1989: J.
Phys. Chem. 93, 7483-7490
#         Na+       Acetate-          0.22     #DL - Novak et al 1996: Radiochimica Acta 74, 111-116/Mesmer et al 1989: J.
Phys. Chem. 93, 7483-7490
          Na+       Acetate-          0.3237   #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307/Pitzer 1991:
Activity Coefficients in Electrolyte Solutions
#         Na+       Acetate-          0.34915 #DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115
#         K+        Acetate-          0.3251   #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307/Pitzer 1991:
Activity Coefficients in Electrolyte Solutions
#         K+        Acetate-          0.34323  #DL - (+/-0.01102)Marshall et al 1995: J. Chem. Eng. Data 40, 1041–1052
#         K+        Acetate-          0.35513  #DL - Kim and Frederick 1988: J. Chem. Eng. Data 33, 177–184
#         K+        Acetate-          0.143    #DL - DeRobertis et al 1999: J. Chem. Eng. Data 44, 262–270
#         K+        Acetate-          0.342    #DL - Ferra et al 2011: J. Chem. Eng. Data 56, 3673–3678
          K+        Acetate-          0.3      #DL - Spitzer et al 2011: Accred. Qual. Assur. 16, 191–198
          Ca+2      Acetate-          1.134    #DL - Loos et al 2004: Fluid Phase Equilibria 219, 219–229
#         Ca+2      HCO3-             1.68     #DL - different in PHREEQC Pitzer database: Loos et al 2004: Fluid Phase
Equilibria 219, 219–229 (acetate)
#         Ca+2      SO4-2             2.76     #DL - different in PHREEQC Pitzer database: Loos et al 2004: Fluid Phase
Equilibria 219, 219–229 (acetate)
          Cs+       Cl-               0.0558   #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
          Cs+       Br-               0.0139   #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
          Cs+       SO4-2             1.11075  #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
          Cs+       OH-               0.30     #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
 Na+      Cl-     0.2664      0         0        6.1608E-5   1.0715E-6
 K+       Cl-     0.2122      0         0        10.71E-4
 Mg+2     Cl-     1.6815      0         0        3.6525E-3
 Ca+2     Cl-     1.614       0         0        3.9E-3
 MgOH+    Cl-     1.658
 H+       Cl-     0.2945      0         0        1.419E-4
 Li+      Cl-     0.3074      0         0        5.366E-4
 Sr+2     Cl-     1.667       0         0        2.8425E-3
 Fe+2     Cl-     1.53225
 Mn+2     Cl-     1.55025
 Ba+2     Cl-     1.49625     0         0        3.2325E-3
 Na+      Br-     0.2791      0         0        10.79E-4
 K+       Br-     0.2212      0         0        17.40E-4
 H+       Br-     0.3564      0         0        4.467E-4
 Mg+2     Br-     1.753       0         0        3.8625E-3
 Ca+2     Br-     1.613       0         0        6.0375E-3
 Li+      Br-     0.2547      0         0        6.636E-4
 Sr+2     Br-     1.7115      0         0        6.5325E-3
 Ba+2     Br-     1.56975     0         0        6.78E-3
 Na+      SO4-2   1.113       0         0        5.6325E-3
 K+       SO4-2   0.7793      0         0        6.6975E-3
 Mg+2     SO4-2   3.343       0         0        1.53E-2
 Ca+2     SO4-2   3.1973      0         0        5.46E-2
 Li+      SO4-2   1.2705      0         0        1.41E-3
 Sr+2     SO4-2   3.1973      0         0        27.0E-3
 Fe+2     SO4-2   3.063
 Mn+2     SO4-2   2.9511
 Na+      HSO4-   0.398
 K+       HSO4-   0.1735
 Mg+2     HSO4-   1.729
 Ca+2     HSO4-   2.53
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 H+       HSO4-     0.5556
 Fe+2     HSO4-     3.48
 Na+      OH-       0.253        0            0            1.34E-4
 K+       OH-       0.32
 Ca+2     OH-       -0.2303
 Li+      OH-       0.14
 Ba+2     OH-       1.2
 Na+      HCO3-     0.0411     0            0            1.10E-3
 K+       HCO3-     -0.013       0            0            1.104E-3
 Mg+2     HCO3-     0.6072
 Ca+2     HCO3-     2.977
 Na+      CO3-2     1.389        0            0            2.05E-3
 K+       CO3-2     1.43         0            0            2.051E-3
 Na+      B(OH)4-   0.089
 Na+      B3O3(OH)4- -0.910
 Na+      B4O5(OH)4-2 -0.40
 K+       B(OH)4-   0.14
-B2
 Mg+2     SO4-2     -37.23       0            0            -0.253
 Ca+2     SO4-2     -54.24       0            0            -0.516
 Sr+2     SO4-2     -54.24       0            0            -0.42
 Fe+2     SO4-2     -42.0
 Mn+2     SO4-2     -40.0
 Ca+2     OH-       -5.72
#          (Tris)H+              Cl-          -1.93        #DL - Tishchenko 2000: Russ. Chem. Bull. 49, No 4, April, 2000
#          Ca+2                  SO4-2        -51.09       #DL - different than PHREEQC Pitzer database: Loos et al 2004: Fluid Phase
Equilibria 219, 219–229 (acetate)
-C0
           (Tris)H+              Cl-      -0.00236        #DL - Bates and Macaskill 1985: J. Solution Chem. 14, 723–734
           (Tris)H+              SO4-2    -0.004316 #DL - Bates and Macaskill 1986: J. Chem. Eng. Data 31, 416-418
#          (Tris)H+              Cl-          -0.000693              251.30       1.775        -0.00313              #DL - The A0 coeff is a
different value in the temp dependance table than for the value listed at 25 deg C (0.000695), Tishchenko 2000 Russ. Chem. Bull.
49, No 4, April, 2000
#          H+         Cl-          0.001467 #DL - Bates and Macaskill 1985: J. Solution Chem. 1985, 14, 723–734 (Tris)
#          Na+        Cl-          0.001407 #DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115 (acetate)
           H+         OH-          0            #DL - not listed so same in PHREEQC Pitzer database, Novak et al 1996: Radiochimica
Acta 74, 111-116 (acetate)
           H+         Acetate-             0            #DL - Novak et al 1996: Radiochimica Acta 74, 111-116
           Na+        Acetate-             -0.00629 #DL - Novak et al 1996: Radiochimica Acta 74, 111-116/Pitzer 1991: Activity
Coefficients in Electrolyte Solutions
#          Na+        Acetate-             -0.00523 #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
#          Na+        Acetate-             -0.00474 #DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115
#          K+         Acetate-             -0.00660 #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307/Pitzer 1991:
Activity Coefficients in Electrolyte Solutions
#          K+         Acetate-             -0.00452 #DL - (+/-0.00058)Marshall et al 1995: J. Chem. Eng. Data 40, 1041–1052
#          K+         Acetate-             -0.00432 #DL - Kim and Frederick 1988: J. Chem. Eng. Data 33, 177–184
#          K+         Acetate-             -0.0021  #DL - Ferra et al 2011: J. Chem. Eng. Data 56, 3673–3678
#          K+         Acetate-             -0.0033     #DL - DeRobertis et al 1999: J. Chem. Eng. Data 44, 262–270 in Ferra et al
2011: J. Chem. Eng. Data 56, 3673–3678
           K+         Acetate-             -0.005       #DL - (+/-0.002)Spitzer et al 2011: Accred. Qual. Assur. 2011 16, 191–198
           Ca+2       Acetate-             -0.031       #DL - Loos et al 2004: Fluid Phase Equilibria 219, 219–229
           Cs+        Cl-                  0.00038  #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
           Cs+        Br-                  0.00004  #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
           Cs+        SO4-2                -0.00599803          #DL - Pitzer and Mayorga 1973: J. Phys. Chem. 77, 2300-2307
 Na+      Cl-       0.00127     33.317       0.09421     -4.655E-5
 K+       Cl-       -0.00084       0            0            -5.095E-5
 Mg+2     Cl-       0.00519        0            0            -1.64933E-4
 Ca+2     Cl-       -0.00034
 H+       Cl-       0.0008         0            0            6.213E-5
 Li+      Cl-       0.00359        0    0       -4.520E-5
 Sr+2     Cl-       -0.00130
 Fe+2     Cl-       -0.00860725
 Mn+2     Cl-       -0.0204972
 Ba+2     Cl-       -0.0193782     0            0            -1.53796E-4
 Na+      Br-       0.00116        0            0            -9.30E-5
 K+       Br-       -0.00180       0            0            -7.004E-5
 H+       Br-       0.00827        0            0            -5.685E-5
 Mg+2     Br-       0.00312
 Ca+2     Br-       -0.00257
 Li+      Br-       0.0053         0            0            -2.813E-5
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 Sr+2     Br-      0.00122506
 Ba+2     Br-     -0.0159576
 Na+      SO4-2    0.00497      0           0          -4.87904E-4
 Mg+2     SO4-2    0.025        0           0           0.523E-3
 H+       SO4-2    0.0438
 Li+      SO4-2   -0.00399338   0           0          -2.33345E-4
 Fe+2     SO4-2    0.0209
 Mn+2     SO4-2    0.01636
 Na+      OH-      0.0044       0           0          -18.94E-5
 K+       OH-      0.0041
 K+       HCO3-   -0.008
 Na+      CO3-2    0.0044
 K+       CO3-2   -0.0015
 Na+      B(OH)4-  0.0114
-THETA
#        H+                Na+       0.0289    #DL - Different than PHREEQC Pitzer database: used in Millero 2009 - ref
Campell et al 1993: Mar. Chem. 44, 221–234: (0.0342-0.000209*25degC =0.0290)(Tris)
         (Tris)H+          H+        0.0027    #DL - Bates and Macaskill 1985: J. Solution Chem. 14, 723–734. Can't tell is
higher-order electrostatic terms were considered, but is from same paper as B and C values
#        (Tris)H+          Na+       -0.00055          -17353.52          -118.9707          0.2031    #DL - The A0 coeff
is a different value in the temp dependance table than for the value listed at 25 deg C (-0.00086), Tishchenko 2000 Russ. Chem.
Bull. 49, No 4, April, 2000
         Acetate-          Cl-       -0.09     #DL - Novak et al 1996: Radiochimica Acta 74, 111-116
#        Acetate-          Cl-       -0.00545  #DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115/Ferra et
al 2011: J. Chem. Eng. Data 56, 3673–3678
         OH-               Acetate-  0         #DL - Novak et al 1996: Radiochimica Acta 74, 111-116
         Na+               Cs+       -0.033    #DL - Pitzer and Kim 1974: J. Am. Chem. Soc. 96, 5701-5707
         K+                Cs+       0.0       #DL - Pitzer and Kim 1974: J. Am. Chem. Soc. 96, 5701-5707
         H+                Cs+       -0.044    #DL - Pitzer and Kim 1974: J. Am. Chem. Soc. 96, 5701-5707
 K+       Na+      -0.012
 Mg+2     Na+       0.07
 Ca+2     Na+       0.07
 Sr+2     Na+       0.051
 H+       Na+       0.036
 Ca+2     K+        0.032
 H+       K+        0.005
 Ca+2     Mg+2      0.007
 H+       Mg+2      0.1
 H+       Ca+2      0.092
 SO4-2    Cl-       0.02
 HSO4-    Cl-      -0.006
 OH-      Cl-      -0.05
 HCO3-    Cl-       0.03
 CO3-2    Cl-      -0.02
 B(OH)4-  Cl-      -0.065
 B3O3(OH)4-  Cl-       0.12
 B4O5(OH)4-2  Cl-      0.074
 OH-      Br-      -0.065
 OH-      SO4-2    -0.013
 HCO3-    SO4-2     0.01
 CO3-2    SO4-2     0.02
 B(OH)4-  SO4-2    -0.012
 B3O3(OH)4-  SO4-2     0.10
 B4O5(OH)4-2  SO4-2     0.12
 CO3-2    OH-       0.1
 CO3-2    HCO3-    -0.04
 B3O3(OH)4-  HCO3-    -0.10
 B4O5(OH)4-2  HCO3-    -0.087
-LAMDA
         Tris      Na+       0.0239    #DL - Millero et al 1987: Geochim. Cosmochim. Acta 51, 707–711
         Tris      Cl-       0         #DL - Millero et al 1987: Geochim. Cosmochim. Acta 51, 707–711
         Tris      K+        0.0262    #DL - Millero et al 1987: Geochim. Cosmochim. Acta 51, 707–711
         Tris      Mg+2      -0.0594   #DL - Lower reliability indicated, Millero et al 1987: Geochim. Cosmochim. Acta 51, 707–
711
         Tris      Ca+2      -0.2327   #DL - Lower reliability indicated, Millero et al 1987: Geochim. Cosmochim. Acta 51, 707–
711
#        Tris      Tris      0.02617           -1692.47           -10.151            0.01524           #DL - The A0 coeff
is a different value in the temp dependance table than for the value listed at 25 deg C (0.02591), Tishchenko 2000: Russ. Chem.
Bull. 49, No 4, April, 2000
#        H+        H(Acetate)        0.08      #DL - Partanen 1998: Acta Chem. Scand. 52, 985-994
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#           Na+         H(Acetate)          0.087       #DL - Partanen 1998: Acta Chem. Scand. 52, 985-994
#           Cl-         H(Acetate)          0           #DL - Partanen 1998: Acta Chem. Scand. 52, 985-994
#           Acetate-    H(Acetate)          -0.09       #DL - Partanen 1998: Acta Chem. Scand. 52, 985-994
#           H(Acetate)          H(Acetate)          -0.06       #DL - Partanen 1998: Acta Chem. Scand. 52, 985-994
#           K+                  H(Acetate)          0.044       #DL - Partanen 1998: Acta Chem. Scand. 52, 985-994/Ferra et al
2011: J. Chem. Eng. Data 56, 3673–3678
#           K+          H(Acetate)          0.094       #DL - DeRobertis et al 1999: J. Chem. Eng. Data 44, 262–270 in Ferra et al
2011: J. Chem. Eng. Data 56, 3673–3678
  Na+       CO2       0.085
  K+                  CO2       0.051
  Mg+2      CO2       0.183
  Ca+2      CO2       0.183
  Cl-       CO2       -0.005
  SO4-2     CO2       0.097
  HSO4-     CO2       -0.003
  Na+       B(OH)3    -0.097
  K+        B(OH)3    -0.14
  Cl-       B(OH)3    0.091
  SO4-2     B(OH)3    0.018
  B3O3(OH)4-  B(OH)3    -0.20
-ZETA
            Tris        Na+         Cl-         0 #DL - Millero et al 1987: Geochim. Cosmochim. Acta 51, 707–711
#           Tris        (Tris)H+    Cl-         -0.02747            2899.40             20.379      -0.03546            #DL - The A0 coeff
is a different value in the temp dependance table than for the value listed at 25 deg C (-0.02741), Tishchenko 2000: Russ. Chem.
Bull. 49, No 4, April, 2000
#           Tris        Na+         Cl-         0.02067             2475.34             17.384      -0.03045            #DL - The A0 coeff
is a different value in the temp dependance table than for the value listed at 25 deg C (0.02097), Tishchenko 2000: Russ. Chem.
Bull. 49, No 4, April, 2000
  H+        Cl-       B(OH)3    -0.0102
  Na+       SO4-2     B(OH)3    0.046
  Na+       SO4-2     CO2       -0.015
-PSI
#   H+      Na+         Cl-         0.0002              #DL - Different than PHREEQC Pitzer database: used in Millero 2009 ref
Campell et al. 1993: Mar. Chem. 44, 221–234: psi HNaCl = 0? (Tris)
#   H+      Na+         Cl-         -0.004              #DL - as listed in PHREEQC Pitzer database: Millero 1983: Geochim.
Cosmochimm. Acta 41, 2121-2129 (Tris)
    H+      (Tris)H+    Cl-         -0.013              #DL - Bates and Macaskill 1985: J. Solution Chem. 14, 723–734. Can't
tell if higher-order electrostatic terms were considered, but is from same paper as B and C values
#   Na+     (Tris)H+    Cl-         -0.00095            3920.1      27.114      -0.04657            #DL - The A0 coeff is a
different value in the temp dependance table than for the value listed at 25 deg C (-0.000405), Tishchenko 2000: Russ. Chem. Bull.
49, No 4, April, 2000
            Na+         H+          OH-         0           #DL - not listed so same in PHREEQC Pitzer database, Novak et al 1996:
Radiochimica Acta 74, 111-116
            Na+         H+          Acetate-                0           # DL - Novak et al 1996: Radiochimica Acta 74, 111-116
            Na+         Acetate-    Cl-         0.01029 #DL - Novak et al 1996: Radiochimica Acta 74, 111-116
#           Na+         Acetate-    Cl-         -0.00205#DL - Manohar and Ananthaswamy 1991: CAN. J. CHEM. 69, 111-115
            H+          Acetate-    Cl-         0           #DL - Novak et al 1996: Radiochimica Acta 74, 111-116
            H+          Cl-         OH-         0           #DL - not listed so same in PHREEQC Pitzer database, Novak et al
1996: Radiochimica Acta 74, 111-116
            Na+         Cs+         Cl-         -0.003      #DL - Pitzer and Kim 1974: J. Am. Chem. Soc. 96, 5701-5707
            K+          Cs+         Cl-         -0.0013     #DL - Pitzer and Kim 1974: J. Am. Chem. Soc. 96, 5701-5707
            H+          Cs+         Cl-         -0.019      #DL - Pitzer and Kim 1974: J. Am. Chem. Soc. 96, 5701-5707
  Na+       K+          Cl-       -0.0018
  Na+       K+          Br-       -0.0022
  Na+       K+          SO4-2     -0.010
  Na+       K+          HCO3-     -0.003
  Na+       K+          CO3-2     0.003
  Na+       Ca+2        Cl-       -0.007
  Na+       Sr+2        Cl-       -0.0021
  Na+       Ca+2        SO4-2     -0.055
  Na+       Mg+2        Cl-       -0.012
  Na+       Mg+2        SO4-2     -0.015
  Na+       H+          Cl-       -0.004
  Na+       H+          Br-       -0.012
  Na+       H+          HSO4-     -0.0129
  K+        Ca+2        Cl-       -0.025
  K+        Mg+2        Cl-       -0.022
  K+        Mg+2        SO4-2     -0.048
  K+        H+          Cl-       -0.011
  K+        H+          Br-       -0.021
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 K+        H+          SO4-2      0.197
 K+        H+          HSO4-     -0.0265
 Ca+2      Mg+2        Cl-       -0.012
 Ca+2      Mg+2        SO4-2      0.024
 Ca+2      H+          Cl-       -0.015
 Mg+2      MgOH+       Cl-        0.028
 Mg+2      H+          Cl-       -0.011
 Mg+2      H+          HSO4-     -0.0178
 Cl-       Br-       K+   0.0000
 Cl-       SO4-2     Na+          0.0014
 Cl-       SO4-2     Ca+2      -0.018
 Cl-       SO4-2     Mg+2      -0.004
 Cl-       HSO4-     Na+       -0.006
 Cl-       HSO4-     H+           0.013
 Cl-       OH-       Na+       -0.006
 Cl-       OH-       K+-0.006
 Cl-       OH-       Ca+2      -0.025
 Cl-       HCO3-     Na+       -0.015
 Cl-       HCO3-     Mg+2      -0.096
 Cl-       CO3-2     Na+          0.0085
 Cl-       CO3-2     K+           0.004
 Cl-       B(OH)4-   Na+       -0.0073
 Cl-       B3O3(OH)4-  Na+       -0.024
 Cl-       B4O5(OH)4-2  Na+    0.026
 SO4-2     HSO4-     Na+       -0.0094
 SO4-2     HSO4-     K+        -0.0677
 SO4-2     HSO4-     Mg+2      -0.0425
 SO4-2     OH-       Na+       -0.009
 SO4-2     OH-       K+        -0.050
 SO4-2     HCO3-     Na+       -0.005
 SO4-2     HCO3-     Mg+2      -0.161
 SO4-2     CO3-2     Na+       -0.005
 SO4-2     CO3-2     K+        -0.009
 OH-       CO3-2     Na+       -0.017
 OH-       CO3-2     K+        -0.01
 OH-       Br-       Na+       -0.018
 OH-       Br-       K+        -0.014
 HCO3-     CO3-2     Na+        0.002
 HCO3-     CO3-2     K+         0.012
#-MU
#          Tris      Tris      Tris      -0.003707          -95.29    -0.854    0.00175   #DL - The A0 coeff is a different value in
the temp dependance table than for the value listed at 25 deg C (-0.003734), Tishchenko 2000: Russ. Chem. Bull. 49, No 4, April,
2000


EXCHANGE_MASTER_SPECIES
          X     X-
EXCHANGE_SPECIES
          X- = X-
          log_k       0.0

          Cs+ + X- = CsX              #DL
#         log_k       1.10      #DL - from Appelo and Postma p160, log K(Na/Cs)
#         log_k       7.239     #DL - K(Vaneslow) for Cs-Na exch on strong sites (illite) at 5M ionic strength from Liu et al
2004 JCH 68 217-238
#         log_k       2.302     #DL - K(Vaneslow) for Cs-Na exch on weak sites at 5M ionic strength from Liu et al 2004
JCH 68 217-238
#         log_k       4.64      #DL - average K(Gaines-Thomas?) for Cs-Na exch on weak sites in Bure mudrock Melkior
et al 2005
          log_k       1.5       #DL - determined at UNB using 1 mol/l Cs+ in Shale SPW through MIN3P-PEST fitting,
Loomer et al 2013: Applied Geochemistry 39, 49–58

          Na+ + X- = NaX
          log_k   0.0

          K+ + X- = KX
          log_k   0.7
          delta_h  -4.3   # Jardine & Sparks, 1984

          Li+ + X- = LiX
```

```
        log_k   -0.08
        delta_h  1.4    # Merriam & Thomas, 1956

        Ca+2 + 2X- = CaX2
        log_k   0.8
        delta_h  7.2    # Van Bladel & Gheyl, 1980

        Mg+2 + 2X- = MgX2
        log_k   0.6
        delta_h  7.4    # Laudelout et al., 1968

        Sr+2 + 2X- = SrX2
        log_k   0.91
        delta_h  5.5    # Laudelout et al., 1968

        Ba+2 + 2X- = BaX2
        log_k   0.91
        delta_h  4.5    # Laudelout et al., 1968

        Mn+2 + 2X- = MnX2
        log_k   0.52

        Fe+2 + 2X- = FeX2
        log_k   0.44

SURFACE_MASTER_SPECIES
        Hfo_s  Hfo_sOH
        Hfo_w  Hfo_wOH
SURFACE_SPECIES
#   All surface data from
#   Dzombak and Morel, 1990
#
#
#   Acid-base data from table 5.7
#
#   strong binding site--Hfo_s,

        Hfo_sOH = Hfo_sOH
        log_k  0.0

        Hfo_sOH  + H+ = Hfo_sOH2+
        log_k  7.29    # = pKa1,int

        Hfo_sOH = Hfo_sO- + H+
        log_k  -8.93   # = -pKa2,int

#   weak binding site--Hfo_w

        Hfo_wOH = Hfo_wOH
        log_k  0.0

        Hfo_wOH  + H+ = Hfo_wOH2+
        log_k  7.29    # = pKa1,int

        Hfo_wOH = Hfo_wO- + H+
        log_k  -8.93   # = -pKa2,int

###############################################
#               CATIONS                       #
###############################################
#
#   Cations from table 10.1 or 10.5
#
#   Calcium
        Hfo_sOH + Ca+2 = Hfo_sOHCa+2
        log_k  4.97

        Hfo_wOH + Ca+2 = Hfo_wOCa+ + H+
        log_k -5.85
#   Strontium
```

```
            Hfo_sOH + Sr+2 = Hfo_sOHSr+2
            log_k  5.01

            Hfo_wOH + Sr+2 = Hfo_wOSr+ + H+
            log_k -6.58

            Hfo_wOH + Sr+2 + H2O = Hfo_wOSrOH + 2H+
            log_k -17.60
#   Barium
            Hfo_sOH + Ba+2 = Hfo_sOHBa+2
            log_k  5.46

            Hfo_wOH + Ba+2 = Hfo_wOBa+ + H+
            log_k  -7.2                     # table 10.5
#
#   Derived constants table 10.5
#
#   Magnesium
            Hfo_wOH + Mg+2 = Hfo_wOMg+ + H+
            log_k -4.6
#   Manganese
            Hfo_sOH + Mn+2 = Hfo_sOMn+ + H+
            log_k  -0.4                     # table 10.5

            Hfo_wOH + Mn+2 = Hfo_wOMn+ + H+
            log_k -3.5                  # table 10.5
# Iron
#           Hfo_sOH + Fe+2 = Hfo_sOFe+ + H+
#           log_k   0.7     # LFER using table 10.5

#           Hfo_wOH + Fe+2 = Hfo_wOFe+ + H+
#           log_k -2.5      # LFER using table 10.5

# Iron, strong site: Appelo, Van der Weiden, Tournassat & Charlet, subm.
            Hfo_sOH + Fe+2 = Hfo_sOFe+ + H+
            log_k   -0.95
# Iron, weak site: Liger et al., GCA 63, 2939, re-optimized for D&M
            Hfo_wOH + Fe+2 = Hfo_wOFe+ + H+
            log_k -2.98

            Hfo_wOH + Fe+2 + H2O = Hfo_wOFeOH + 2H+
            log_k -11.55

#################################################
#               ANIONS                          #
#################################################
#
#   Anions from table 10.6
#
#
#   Anions from table 10.7
#
#   Borate
            Hfo_wOH + B(OH)3 = Hfo_wH2BO3 + H2O
            log_k   0.62
#
#   Anions from table 10.8
#
#   Sulfate
            Hfo_wOH + SO4-2 + H+ = Hfo_wSO4- + H2O
            log_k   7.78

            Hfo_wOH + SO4-2 = Hfo_wOHSO4-2
            log_k   0.79
#
# Carbonate: Van Geen et al., 1994 reoptimized for HFO
# 0.15 g HFO/L has 0.344 mM sites == 2 g of Van Geen's Goethite/L
#
#           Hfo_wOH + CO3-2 + H+ = Hfo_wCO3- + H2O
#           log_k   12.56
```

```
#
#           Hfo_wOH + CO3-2 + 2H+= Hfo_wHCO3 + H2O
#           log_k   20.62


END
MEAN GAM
CaCl2
CaSO4
CaCO3
Ca(OH)2
MgCl2
MgSO4
MgCO3
Mg(OH)2
NaCl
Na2SO4
NaHCO3
Na2CO3
NaOH
KCl
K2SO4
KHCO3
K2CO3
KOH
HCl
H2SO4
HBr

END

# For the reaction aA + bB = cC + dD,
#   with delta_v = c*Vm(C) + d*Vm(D) - a*Vm(A) - b*Vm(B),
# PHREEQC adds the pressure term to log_k: -= delta_v * (P - 1) / (2.3RT).
#   Vm(A) is volume of A, cm3/mol, P is pressure, atm, R is the gas constant, T is Kelvin.
# Gas-pressures and fugacity coefficients are calculated with Peng-Robinson's EOS.
#   Binary interaction coefficients from Soreide and Whitson, 1992, FPE 77, 217 are
#    hard-coded in calc_PR():
#    kij    CH4    CO2    H2S    N2
#    H2O    0.49   0.19   0.19   0.49
# ================================================================================================
# The molar volumes of solids are entered with
#                       -Vm vm cm3/mol
#    vm is the molar volume, cm3/mol (default), but dm3/mol and m3/mol are permitted.
# Data for minerals' vm (= MW (g/mol) / rho (g/cm3)) are defined using rho from
#   Deer, Howie and Zussman, The rock-forming minerals, Longman.
#                         --------------------
# Temperature- and pressure-dependent volumina of aqueous species are calculated with a Redlich-
#   type equation (cf. Redlich and Meyer, Chem. Rev. 64, 221), from parameters entered with
#                       -Vm a1 a2 a3 a4 W a0 i1 i2 i3 i4
# The volume (cm3/mol) is
#    Vm(T, pb, I) = 41.84 * (a1 * 0.1 + a2 * 100 / (2600 + pb)  + a3 / (T - 228) +
#                            a4 * 1e4 / (2600 + pb) / (T - 228) - W * QBrn)
#                 + z^2 / 2 * Av * f(I^0.5)
#                 + (i1 + i2 / (T - 228) + i3 * (T - 228)) * I^i4
#   Volumina at I = 0 are obtained using supcrt92 formulas (Johnson et al., 1992, CG 18, 899).
#   41.84 transforms cal/bar/mol into cm3/mol.
#   pb is pressure in bar.
#   W * QBrn is the Born volume, calculated from Wref and the pressure dependence of the
#     dielectric constant of water (f(P, T), see below).
#   z is charge of the solute species.
#   Av is the Debye-Hueckel limiting slope.
#   a0 is the ion-size parameter in the extended Debye-Hueckel paramter:
#     f(I^0.5) = I^0.5) / (1 + a0 * DH_B * I^0.5),
#     a0 = -gamma x for cations, = 0 for anions.
# Av (P, T) is calculated using the dielectric constant of water from Bradley and Pitzer, 1979, JPC 83, 1599,
#   and the compressibility of pure water.
# The density of pure water at water saturation pressure is calculated with eqn 2.6 from
#   Wagner and Pruss, 2002, J. Phys. Chem. Ref. Data 31, 387. At higher P,T with polynomials
#   interpolated from IAPWS table 3 (2007).
```

```
#
# Data for species' parameters, commented with '# supcrt modified', were fitted from data
#   compiled by Laliberte, 2009, J. Chem. Eng. Data 54, 1725, + additions, see Appelo, Parkhurst and Post (in prep.)
# H+ has the reference volume of 0 at all P, T and I.
# For Cl-, parameters were obtained from densities of HCl solutions up to 176 oC, 1 - 280 atm.
# The numbers for cations were extracted from the densities of cation-Cl-solutions.
# Other anions and OH- then follow from the measured densities of cation-anion solutions.
# Water dissociation was fitted from Bandura and Lvov, 2006, J. Phys. Chem. Ref. Data, 35, 15, 0-200 oC, 1-2000 atm.
#                       --------------------
# If -Vm is not defined, the a-f values from -Millero a b c d e f (if available) will be used for calculating
#   Vm(t, I) = a + b * t + c * t^2 + z^2 / 2 * Av * I^0.5 + (d + e * t + f * t^2) * I
#   t is temperature in oC.
#
# redox-uncoupled gases have been added for H2 (Hdg), O2 (Oxg), CH4 (Mtg), N2 (Ntg),
#   H2S (H2Sg, species HSg-, etc.).
#
# ============================================================================================================
# It remains the responsibility of the user to check the calculated results, for example with
#   measured solubilities as a function of (P, T).
```

## B.2 EXAMPLE PHREEQC INPUT FILE FOR pH BUFFER SOLUTIONS

```
TITLE      Tris Buffer solutions (ionic strength 6 m)
#Part of a series of L-SPW based solutions to cover a large range of ionic strengths

SELECTED_OUTPUT
   -file               12xLSPWBuffersAsMade20131203.csv
   -reset                          false
   -solution                 true
   -ionic_strength      true
   -percent_error       true
   -pH                             true
   -totals             Na K Ca Mg Cl S(6) Tris
   -saturation_indices   halite gypsum

END

PITZER
-macinnes             false

SOLUTION_SPREAD
   -pe      11
   -units   mol/kgw
 Number     Na           K          Ca          Mg          Cl              S(6)         Tris         pH
                                                                                                    charge
      1     2.64240 0.59453 0.62866 0.26424 5.0775349 0.00110       0.0600     7.00000
      2     2.64240 0.59453 0.62866 0.26424 5.0755069 0.00110       0.0600     7.00000
      3     2.64240 0.59453 0.62866 0.26424 5.0725195 0.00110       0.0600     7.00000
      4     2.64240 0.59453 0.62866 0.26424 5.0695803 0.00110       0.0601     7.00000
      5     2.64240 0.59453 0.62866 0.26424 5.0655326 0.00110       0.0600     7.00000
      6     2.64240 0.59453 0.62866 0.26424 5.0585272 0.00110       0.0600     7.00000
      7     2.64240 0.59453 0.62866 0.26424 5.0505570 0.00110       0.0600     7.00000

Save Solution 1-7
END

Solution 8 Just 1.2x's LSPW (no Tris)
   -pe      11
   -units   mol/L
   -pH       7 charge
   -density  1.17505
Na          2.40000
K           0.54000
Ca          0.5710
Mg          0.24000
Cl          4.56000
```

```
S(6)        0.00100
Save Solution 8
END


USE solution 1
EQUILIBRIUM_PHASES 1
   CO2(g)    -3.4 10
END

USE solution 2
EQUILIBRIUM_PHASES 2
   CO2(g)    -3.4 10
END

USE solution 3
EQUILIBRIUM_PHASES 3
   CO2(g)    -3.4 10
END

USE solution 4
EQUILIBRIUM_PHASES 4
   CO2(g)    -3.4 10
END

USE solution 5
EQUILIBRIUM_PHASES 5
   CO2(g)    -3.4 10
END

USE solution 6
EQUILIBRIUM_PHASES 6
   CO2(g)    -3.4 10
END

USE solution 7
EQUILIBRIUM_PHASES 7
   CO2(g)    -3.4 10
END

USE solution 8
EQUILIBRIUM_PHASES 8
   CO2(g)    -3.4 10
```

## B.3 EXAMPLE PHREEQC OUTPUT FILE FOR pH BUFFER SOLUTIONS

```
  Input file: D:\NWMO\pH measurement\PRpKa\PHREEQC\12xLSPWBuffersAsMade20131203.pqi
 Output file: D:\NWMO\pH measurement\PRpKa\PHREEQC\12xLSPWBuffersAsMade20131203.pqo
Database file: C:\Program Files\USGS\Phreeqc Interactive 3.0.0-7430\database\pitzerUNB.dat

------------------
Reading data base.
------------------

        SOLUTION_MASTER_SPECIES
        SOLUTION_SPECIES
        PHASES
        PITZER
        EXCHANGE_MASTER_SPECIES
        EXCHANGE_SPECIES
        SURFACE_MASTER_SPECIES
        SURFACE_SPECIES
        END
-------------------------------------
Reading input data for simulation 1.
-------------------------------------
```

```
        DATABASE C:\Program Files\USGS\Phreeqc Interactive 3.0.0-7430\database\pitzerUNB.dat
        TITLE      Tris Buffer solutions (ionic strength 6 m)
        SELECTED_OUTPUT
           file               12xLSPWBuffersAsMade20131203.csv
           reset                          false
           solution                       true
           ionic_strength                 true
           percent_error                  true
           ph                             true
           totals                         Na K Ca Mg Cl S(6) Tris
           saturation_indices             halite gypsum
        END
-----
TITLE
-----

        Tris Buffer solutions (ionic strength 6 m)

------------------
End of simulation.
------------------
------------------------------------
Reading input data for simulation 2.
------------------------------------

        PITZER
        macinnes false
        SOLUTION_SPREAD
           pe      11
           units   mol/kgw
         Number        Na         K          Ca         Mg          Cl         S(6)       Tris        pH
                                                                                                     charge
             1       2.64240   0.59453   0.62866   0.26424   5.0775349  0.00110  0.0600  7.00000
             2       2.64240   0.59453   0.62866   0.26424   5.0755069  0.00110  0.0600  7.00000
             3       2.64240   0.59453   0.62866   0.26424   5.0725195  0.00110  0.0600  7.00000
             4       2.64240   0.59453   0.62866   0.26424   5.0695803  0.00110  0.0601  7.00000
             5       2.64240   0.59453   0.62866   0.26424   5.0655326  0.00110  0.0600  7.00000
             6       2.64240   0.59453   0.62866   0.26424   5.0585272  0.00110  0.0600  7.00000
             7       2.64240   0.59453   0.62866   0.26424   5.0505570  0.00110  0.0600  7.00000
        Save Solution 1-7
        END
-------------------------------------------
Beginning of initial solution calculations.
-------------------------------------------

Initial solution 1.

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Ca                6.287e-001  6.287e-001
        Cl                5.078e+000  5.078e+000
        K                 5.945e-001  5.945e-001
        Mg                2.642e-001  2.642e-001
        Na                2.642e+000  2.642e+000
        S(6)              1.100e-003  1.100e-003
        Tris              6.000e-002  6.000e-002

----------------------------Description of solution----------------------------

                                pH  =   7.087      Charge balance
                                pe  =  11.000
     Specific Conductance (uS/cm, 25 oC) = 511867
                      Density (g/cm3)  =   1.18218
                           Volume (L)  =   1.10231
                    Activity of water  =   0.808
                       Ionic strength  =  5.974e+000
                    Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.995e-003
```

Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 25.00
Electrical balance (eq) = 7.034e-016
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 0.00
Iterations = 12
Gamma iterations = 5
Osmotic coefficient = 1.27364
Density of water = 0.99704
Total H = 1.110695e+002
Total O = 5.551063e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 3.968e-007 | 9.957e-008 | -6.401 | -7.002 | -0.600 | 3.81 |
| H+ | 3.290e-008 | 8.180e-008 | -7.483 | -7.087 | 0.396 | 0.00 |
| H2O | 5.551e+001 | 8.084e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.118e-001 | -0.202 | -0.506 | -0.305 | -14.28 |
| Cl | 5.078e+000 | | | | | |
| Cl- | 5.078e+000 | 5.850e+000 | 0.706 | 0.767 | 0.062 | 20.09 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.470e-001 | -0.226 | -0.607 | -0.381 | 12.11 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.642e-001 | 1.983e-001 | -0.578 | -0.703 | -0.125 | -17.78 |
| MgOH+ | 8.228e-006 | 3.042e-006 | -5.085 | -5.517 | -0.432 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.016e+000 | 0.422 | 0.304 | -0.118 | 1.41 |
| S(6) | 1.100e-003 | | | | | |
| SO4-2 | 1.100e-003 | 2.412e-005 | -2.959 | -4.618 | -1.659 | 26.83 |
| HSO4- | 2.131e-010 | 1.880e-010 | -9.671 | -9.726 | -0.055 | 42.04 |
| Tris | 6.000e-002 | | | | | |
| (Tris)H+ | 5.701e-002 | 2.430e-002 | -1.244 | -1.614 | -0.370 | (0) |
| Tris | 2.987e-003 | 2.528e-003 | -2.525 | -2.597 | -0.072 | (0) |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.90 | -5.12 | -4.22 | CaSO4 |
| Arcanite | -4.06 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.18 | 0.28 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.35 | -9.70 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -3.83 | -14.71 | -10.88 | Mg(OH)2 |
| Carnallite | -3.89 | 0.44 | 4.33 | KMgCl3:6H2O |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.89 | -9.13 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 | CaSO4:2H2O |
| H2O(g) | -1.60 | -0.09 | 1.50 | H2O |
| Halite | -0.50 | 1.07 | 1.57 | NaCl |
| Hexahydrite | -4.24 | -5.87 | -1.63 | MgSO4:6H2O |
| Kainite | -5.24 | -5.44 | -0.19 | KMgClSO4:3H2O |
| Kieserite | -5.29 | -5.41 | -0.12 | MgSO4:H2O |
| Labile_S | -7.65 | -13.33 | -5.67 | Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.80 | -5.69 | -0.89 | MgSO4:4H2O |
| Leonite | -7.54 | -11.52 | -3.98 | K2Mg(SO4)2:4H2O |
| Mirabilite | -3.72 | -4.93 | -1.21 | Na2SO4:10H2O |
| Misenite | -68.90 | -79.71 | -10.81 | K8H6(SO4)7 |
| Pentahydrite | -4.50 | -5.78 | -1.28 | MgSO4:5H2O |
| Polyhalite | -7.84 | -21.58 | -13.74 | K2MgCa2(SO4)4:2H2O |
| Portlandite | -9.32 | -14.51 | -5.19 | Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 | K2Mg(SO4)2:6H2O |
| Sylvite | -0.74 | 0.16 | 0.90 | KCl |
| Syngenite | -3.60 | -11.05 | -7.45 | K2Ca(SO4)2:H2O |

Initial solution 2.

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.076e+000 | 5.076e+000 |
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S(6) | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

pH = 7.327 Charge balance
pe = 11.000
Specific Conductance (uS/cm, 25 oC) = 511605
Density (g/cm3) = 1.18216
Volume (L) = 1.10227
Activity of water = 0.808
Ionic strength = 5.972e+000
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 5.023e-003
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 25.00
Electrical balance (eq) = -5.523e-014
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
Iterations = 11
Gamma iterations = 5
Osmotic coefficient = 1.27350
Density of water = 0.99704
Total H = 1.110674e+002
Total O = 5.551063e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 6.897e-007 | 1.731e-007 | -6.161 | -6.762 | -0.600 | 3.81 |
| H+ | 1.893e-008 | 4.705e-008 | -7.723 | -7.327 | 0.395 | 0.00 |
| H2O | 5.551e+001 | 8.085e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.113e-001 | -0.202 | -0.507 | -0.305 | -14.29 |
| Cl | 5.076e+000 | | | | | |
| Cl- | 5.076e+000 | 5.848e+000 | 0.705 | 0.767 | 0.062 | 20.09 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.470e-001 | -0.226 | -0.607 | -0.381 | 12.11 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.642e-001 | 1.980e-001 | -0.578 | -0.703 | -0.125 | -17.79 |
| MgOH+ | 1.428e-005 | 5.283e-006 | -4.845 | -5.277 | -0.432 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.016e+000 | 0.422 | 0.304 | -0.118 | 1.41 |
| S(6) | 1.100e-003 | | | | | |
| SO4-2 | 1.100e-003 | 2.413e-005 | -2.959 | -4.618 | -1.659 | 26.83 |
| HSO4- | 1.226e-010 | 1.081e-010 | -9.912 | -9.966 | -0.054 | 42.04 |
| Tris | 6.000e-002 | | | | | |
| (Tris)H+ | 5.499e-002 | 2.344e-002 | -1.260 | -1.630 | -0.370 | (0) |
| Tris | 5.008e-003 | 4.240e-003 | -2.300 | -2.373 | -0.072 | (0) |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Anhydrite | -0.90 | -5.12 | -4.22 CaSO4 |
| Arcanite | -4.06 | -5.83 | -1.78 K2SO4 |
| Bischofite | -4.18 | 0.28 | 4.46 MgCl2:6H2O |
| Bloedite | -7.35 | -9.70 | -2.35 Na2Mg(SO4)2:4H2O |
| Brucite | -3.35 | -14.23 | -10.88 Mg(OH)2 |
| Carnallite | -3.89 | 0.44 | 4.33 KMgCl3:6H2O |
| Epsomite | -4.09 | -5.97 | -1.88 MgSO4:7H2O |
| Glaserite | -6.95 | -10.75 | -3.80 NaK3(SO4)2 |
| Glauberite | -3.89 | -9.13 | -5.25 Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 CaSO4:2H2O |
| H2O(g) | -1.60 | -0.09 | 1.50 H2O |
| Halite | -0.50 | 1.07 | 1.57 NaCl |
| Hexahydrite | -4.24 | -5.87 | -1.63 MgSO4:6H2O |
| Kainite | -5.25 | -5.44 | -0.19 KMgClSO4:3H2O |
| Kieserite | -5.29 | -5.41 | -0.12 MgSO4:H2O |
| Labile_S | -7.65 | -13.33 | -5.67 Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.80 | -5.69 | -0.89 MgSO4:4H2O |
| Leonite | -7.54 | -11.52 | -3.98 K2Mg(SO4)2:4H2O |
| Mirabilite | -3.72 | -4.93 | -1.21 Na2SO4:10H2O |
| Misenite | -70.34 | -81.15 | -10.81 K8H6(SO4)7 |
| Pentahydrite | -4.50 | -5.78 | -1.28 MgSO4:5H2O |
| Polyhalite | -7.84 | -21.59 | -13.74 K2MgCa2(SO4)4:2H2O |
| Portlandite | -8.84 | -14.03 | -5.19 Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 K2Mg(SO4)2:6H2O |
| Sylvite | -0.74 | 0.16 | 0.90 KCl |
| Syngenite | -3.60 | -11.05 | -7.45 K2Ca(SO4)2:H2O |

Initial solution 3.

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.073e+000 | 5.073e+000 |
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S(6) | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

pH = 7.554 Charge balance
pe = 11.000
Specific Conductance (uS/cm, 25 oC) = 511221
Density (g/cm3) = 1.18213
Volume (L) = 1.10220
Activity of water = 0.809
Ionic strength = 5.969e+000
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 8.011e-003
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 25.00
Electrical balance (eq) = -1.444e-013
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
Iterations = 12
Gamma iterations = 5
Osmotic coefficient = 1.27330
Density of water = 0.99704
Total H = 1.110645e+002
Total O = 5.551064e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | Gamma | cm3/mol |
|---|---|---|---|---|---|---|

```
   OH-          1.162e-006  2.919e-007    -5.935    -6.535    -0.600      3.81
   H+           1.124e-008  2.791e-008    -7.949    -7.554     0.395      0.00
   H2O          5.551e+001  8.086e-001     1.744    -0.092     0.000     18.07
Ca          6.287e-001
   Ca+2         6.287e-001  3.105e-001    -0.202    -0.508    -0.306    -14.29
Cl          5.073e+000
   Cl-          5.073e+000  5.844e+000     0.705     0.767     0.062     20.09
K           5.945e-001
   K+           5.945e-001  2.470e-001    -0.226    -0.607    -0.381     12.11
Mg          2.642e-001
   Mg+2         2.642e-001  1.977e-001    -0.578    -0.704    -0.126    -17.79
   MgOH+        2.403e-005  8.892e-006    -4.619    -5.051    -0.432      (0)
Na          2.642e+000
   Na+          2.642e+000  2.015e+000     0.422     0.304    -0.118      1.41
S(6)        1.100e-003
   SO4-2        1.100e-003  2.413e-005    -2.959    -4.617    -1.659     26.83
   HSO4-        7.270e-011  6.416e-011   -10.138   -10.193    -0.054     42.04
Tris        6.000e-002
   (Tris)H+     5.201e-002  2.217e-002    -1.284    -1.654    -0.370      (0)
   Tris         7.985e-003  6.761e-003    -2.098    -2.170    -0.072      (0)

-------------------------------Saturation indices--------------------------------

              Phase               SI   log IAP   log K(298 K,   1 atm)

              Anhydrite        -0.90     -5.13   -4.22  CaSO4
              Arcanite         -4.06     -5.83   -1.78  K2SO4
              Bischofite       -4.18      0.28    4.46  MgCl2:6H2O
              Bloedite         -7.35     -9.70   -2.35  Na2Mg(SO4)2:4H2O
              Brucite          -2.89    -13.77  -10.88  Mg(OH)2
              Carnallite       -3.89      0.44    4.33  KMgCl3:6H2O
              Epsomite         -4.09     -5.97   -1.88  MgSO4:7H2O
              Glaserite        -6.95    -10.75   -3.80  NaK3(SO4)2
              Glauberite       -3.89     -9.13   -5.25  Na2Ca(SO4)2
              Gypsum           -0.73     -5.31   -4.58  CaSO4:2H2O
              H2O(g)           -1.60     -0.09    1.50  H2O
              Halite           -0.50      1.07    1.57  NaCl
              Hexahydrite      -4.24     -5.88   -1.63  MgSO4:6H2O
              Kainite          -5.25     -5.44   -0.19  KMgClSO4:3H2O
              Kieserite        -5.29     -5.41   -0.12  MgSO4:H2O
              Labile_S         -7.66    -13.33   -5.67  Na4Ca(SO4)3:2H2O
              Leonhardite      -4.80     -5.69   -0.89  MgSO4:4H2O
              Leonite          -7.54    -11.52   -3.98  K2Mg(SO4)2:4H2O
              Mirabilite       -3.72     -4.93   -1.21  Na2SO4:10H2O
              Misenite        -71.70    -82.51  -10.81  K8H6(SO4)7
              Pentahydrite     -4.50     -5.78   -1.28  MgSO4:5H2O
              Polyhalite       -7.84    -21.59  -13.74  K2MgCa2(SO4)4:2H2O
              Portlandite      -8.39    -13.58   -5.19  Ca(OH)2
              Schoenite        -7.38    -11.71   -4.33  K2Mg(SO4)2:6H2O
              Sylvite          -0.74      0.16    0.90  KCl
              Syngenite        -3.60    -11.05   -7.45  K2Ca(SO4)2:H2O


Initial solution 4.

-------------------------------Solution composition--------------------------------

              Elements           Molality       Moles

              Ca                6.287e-001  6.287e-001
              Cl                5.070e+000  5.070e+000
              K                 5.945e-001  5.945e-001
              Mg                2.642e-001  2.642e-001
              Na                2.642e+000  2.642e+000
              S(6)              1.100e-003  1.100e-003
              Tris              6.010e-002  6.010e-002

-----------------------------Description of solution----------------------------
```

pH = 7.719 Charge balance
pe = 11.000
Specific Conductance (uS/cm, 25 oC) = 510842
Density (g/cm3) = 1.18211
Volume (L) = 1.10214
Activity of water = 0.809
Ionic strength = 5.966e+000
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 1.105e-002
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 25.00
Electrical balance (eq) = -2.426e-013
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
Iterations = 13
Gamma iterations = 5
Osmotic coefficient = 1.27310
Density of water = 0.99704
Total H = 1.110616e+002
Total O = 5.551065e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 1.698e-006 | 4.267e-007 | -5.770 | -6.370 | -0.600 | 3.80 |
| H+ | 7.696e-009 | 1.909e-008 | -8.114 | -7.719 | 0.395 | 0.00 |
| H2O | 5.551e+001 | 8.086e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.097e-001 | -0.202 | -0.509 | -0.307 | -14.29 |
| Cl | 5.070e+000 | | | | | |
| Cl- | 5.070e+000 | 5.841e+000 | 0.705 | 0.766 | 0.062 | 20.09 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.470e-001 | -0.226 | -0.607 | -0.381 | 12.11 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.642e-001 | 1.973e-001 | -0.578 | -0.705 | -0.127 | -17.79 |
| MgOH+ | 3.504e-005 | 1.297e-005 | -4.455 | -4.887 | -0.432 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.015e+000 | 0.422 | 0.304 | -0.118 | 1.41 |
| S(6) | 1.100e-003 | | | | | |
| SO4-2 | 1.100e-003 | 2.414e-005 | -2.959 | -4.617 | -1.659 | 26.83 |
| HSO4- | 4.974e-011 | 4.391e-011 | -10.303 | -10.357 | -0.054 | 42.04 |
| Tris | 6.010e-002 | | | | | |
| (Tris)H+ | 4.909e-002 | 2.092e-002 | -1.309 | -1.679 | -0.370 | (0) |
| Tris | 1.101e-002 | 9.324e-003 | -1.958 | -2.030 | -0.072 | (0) |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.90 | -5.13 | -4.22 | CaSO4 |
| Arcanite | -4.06 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.18 | 0.27 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.35 | -9.70 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -2.56 | -13.44 | -10.88 | Mg(OH)2 |
| Carnallite | -3.90 | 0.43 | 4.33 | KMgCl3:6H2O |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.89 | -9.14 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 | CaSO4:2H2O |
| H2O(g) | -1.60 | -0.09 | 1.50 | H2O |
| Halite | -0.50 | 1.07 | 1.57 | NaCl |
| Hexahydrite | -4.24 | -5.88 | -1.63 | MgSO4:6H2O |
| Kainite | -5.25 | -5.44 | -0.19 | KMgClSO4:3H2O |
| Kieserite | -5.29 | -5.41 | -0.12 | MgSO4:H2O |
| Labile_S | -7.66 | -13.33 | -5.67 | Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.80 | -5.69 | -0.89 | MgSO4:4H2O |
| Leonite | -7.54 | -11.52 | -3.98 | K2Mg(SO4)2:4H2O |

| | | | |
|---|---|---|---|
| Mirabilite | -3.72 | -4.93 | -1.21 Na2SO4:10H2O |
| Misenite | -72.69 | -83.49 | -10.81 K8H6(SO4)7 |
| Pentahydrite | -4.50 | -5.78 | -1.28 MgSO4:5H2O |
| Polyhalite | -7.85 | -21.59 | -13.74 K2MgCa2(SO4)4:2H2O |
| Portlandite | -8.06 | -13.25 | -5.19 Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 K2Mg(SO4)2:6H2O |
| Sylvite | -0.74 | 0.16 | 0.90 KCl |
| Syngenite | -3.60 | -11.05 | -7.45 K2Ca(SO4)2:H2O |

Initial solution 5.

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.066e+000 | 5.066e+000 |
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S(6) | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

pH = 7.889 Charge balance
pe = 11.000
Specific Conductance (uS/cm, 25 oC) = 510323
Density (g/cm3) = 1.18206
Volume (L) = 1.10205
Activity of water = 0.809
Ionic strength = 5.962e+000
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 1.500e-002
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 25.00
Electrical balance (eq) = -3.915e-013
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
Iterations = 14
Gamma iterations = 5
Osmotic coefficient = 1.27283
Density of water = 0.99704
Total H = 1.110575e+002
Total O = 5.551067e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 2.508e-006 | 6.309e-007 | -5.601 | -6.200 | -0.599 | 3.80 |
| H+ | 5.211e-009 | 1.292e-008 | -8.283 | -7.889 | 0.394 | 0.00 |
| H2O | 5.551e+001 | 8.088e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.087e-001 | -0.202 | -0.511 | -0.309 | -14.29 |
| Cl | 5.066e+000 | | | | | |
| Cl- | 5.066e+000 | 5.836e+000 | 0.705 | 0.766 | 0.062 | 20.09 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.471e-001 | -0.226 | -0.607 | -0.381 | 12.11 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.642e-001 | 1.968e-001 | -0.578 | -0.706 | -0.128 | -17.79 |
| MgOH+ | 5.165e-005 | 1.913e-005 | -4.287 | -4.718 | -0.431 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.014e+000 | 0.422 | 0.304 | -0.118 | 1.41 |
| S(6) | 1.100e-003 | | | | | |
| SO4-2 | 1.100e-003 | 2.415e-005 | -2.959 | -4.617 | -1.658 | 26.82 |
| HSO4- | 3.364e-011 | 2.972e-011 | -10.473 | -10.527 | -0.054 | 42.04 |

Tris 6.000e-002
(Tris)H+ 4.506e-002 1.920e-002 -1.346 -1.717 -0.371 (0)
Tris 1.494e-002 1.265e-002 -1.826 -1.898 -0.072 (0)

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.90 | -5.13 | -4.22 | CaSO4 |
| Arcanite | -4.06 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.18 | 0.27 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.35 | -9.70 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -2.23 | -13.11 | -10.88 | Mg(OH)2 |
| Carnallite | -3.90 | 0.43 | 4.33 | KMgCl3:6H2O |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.89 | -9.14 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 | CaSO4:2H2O |
| H2O(g) | -1.60 | -0.09 | 1.50 | H2O |
| Halite | -0.50 | 1.07 | 1.57 | NaCl |
| Hexahydrite | -4.24 | -5.88 | -1.63 | MgSO4:6H2O |
| Kainite | -5.25 | -5.44 | -0.19 | KMgClSO4:3H2O |
| Kieserite | -5.29 | -5.42 | -0.12 | MgSO4:H2O |
| Labile_S | -7.66 | -13.33 | -5.67 | Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.80 | -5.69 | -0.89 | MgSO4:4H2O |
| Leonite | -7.54 | -11.52 | -3.98 | K2Mg(SO4)2:4H2O |
| Mirabilite | -3.72 | -4.93 | -1.21 | Na2SO4:10H2O |
| Misenite | -73.70 | -84.51 | -10.81 | K8H6(SO4)7 |
| Pentahydrite | -4.50 | -5.78 | -1.28 | MgSO4:5H2O |
| Polyhalite | -7.85 | -21.59 | -13.74 | K2MgCa2(SO4)4:2H2O |
| Portlandite | -7.72 | -12.91 | -5.19 | Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 | K2Mg(SO4)2:6H2O |
| Sylvite | -0.74 | 0.16 | 0.90 | KCl |
| Syngenite | -3.60 | -11.05 | -7.45 | K2Ca(SO4)2:H2O |

Initial solution 6.

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.059e+000 | 5.059e+000 |
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S(6) | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

pH = 8.128 Charge balance
pe = 11.000
Specific Conductance (uS/cm, 25 oC) = 509425
Density (g/cm3) = 1.18200
Volume (L) = 1.10189
Activity of water = 0.809
Ionic strength = 5.955e+000
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 2.200e-002
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 25.00
Electrical balance (eq) = -7.137e-013
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
Iterations = 15
Gamma iterations = 5
Osmotic coefficient = 1.27236
Density of water = 0.99704

Total H = 1.110506e+002
Total O = 5.551071e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 4.347e-006 | 1.095e-006 | -5.362 | -5.961 | -0.599 | 3.79 |
| H+ | 3.009e-009 | 7.446e-009 | -8.522 | -8.128 | 0.393 | 0.00 |
| H2O | 5.551e+001 | 8.090e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.069e-001 | -0.202 | -0.513 | -0.311 | -14.29 |
| Cl | 5.059e+000 | | | | | |
| Cl- | 5.059e+000 | 5.828e+000 | 0.704 | 0.766 | 0.062 | 20.09 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.471e-001 | -0.226 | -0.607 | -0.381 | 12.11 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.642e-001 | 1.960e-001 | -0.578 | -0.708 | -0.130 | -17.79 |
| MgOH+ | 8.911e-005 | 3.306e-005 | -4.050 | -4.481 | -0.431 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.013e+000 | 0.422 | 0.304 | -0.118 | 1.40 |
| S(6) | 1.100e-003 | | | | | |
| SO4-2 | 1.100e-003 | 2.417e-005 | -2.959 | -4.617 | -1.658 | 26.81 |
| HSO4- | 1.938e-011 | 1.714e-011 | -10.713 | -10.766 | -0.053 | 42.04 |
| Tris | 6.000e-002 | | | | | |
| (Tris)H+ | 3.809e-002 | 1.623e-002 | -1.419 | -1.790 | -0.371 | (0) |
| Tris | 2.191e-002 | 1.855e-002 | -1.659 | -1.732 | -0.072 | (0) |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.90 | -5.13 | -4.22 | CaSO4 |
| Arcanite | -4.05 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.18 | 0.27 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.35 | -9.70 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -1.75 | -12.63 | -10.88 | Mg(OH)2 |
| Carnallite | -3.90 | 0.43 | 4.33 | KMgCl3:6H2O |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.89 | -9.14 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 | CaSO4:2H2O |
| H2O(g) | -1.59 | -0.09 | 1.50 | H2O |
| Halite | -0.50 | 1.07 | 1.57 | NaCl |
| Hexahydrite | -4.24 | -5.88 | -1.63 | MgSO4:6H2O |
| Kainite | -5.25 | -5.44 | -0.19 | KMgClSO4:3H2O |
| Kieserite | -5.29 | -5.42 | -0.12 | MgSO4:H2O |
| Labile_S | -7.66 | -13.33 | -5.67 | Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.81 | -5.69 | -0.89 | MgSO4:4H2O |
| Leonite | -7.54 | -11.52 | -3.98 | K2Mg(SO4)2:4H2O |
| Mirabilite | -3.72 | -4.93 | -1.21 | Na2SO4:10H2O |
| Misenite | -75.14 | -85.94 | -10.81 | K8H6(SO4)7 |
| Pentahydrite | -4.50 | -5.78 | -1.28 | MgSO4:5H2O |
| Polyhalite | -7.86 | -21.60 | -13.74 | K2MgCa2(SO4)4:2H2O |
| Portlandite | -7.24 | -12.43 | -5.19 | Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 | K2Mg(SO4)2:6H2O |
| Sylvite | -0.74 | 0.16 | 0.90 | KCl |
| Syngenite | -3.60 | -11.05 | -7.45 | K2Ca(SO4)2:H2O |

Initial solution 7.

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.051e+000 | 5.051e+000 |

| | | |
|---|---|---|
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S(6) | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

pH = 8.363 Charge balance
pe = 11.000
Specific Conductance (uS/cm, 25 oC) = 508405
Density (g/cm3) = 1.18193
Volume (L) = 1.10171
Activity of water = 0.809
Ionic strength = 5.947e+000
Mass of water (kg) = 1.000e+000
Total alkalinity (eq/kg) = 2.997e-002
Total carbon (mol/kg) = 0.000e+000
Total CO2 (mol/kg) = 0.000e+000
Temperature (deg C) = 25.00
Electrical balance (eq) = -1.229e-012
Percent error, 100*(Cat-|An|)/(Cat+|An|) = -0.00
Iterations = 16
Gamma iterations = 5
Osmotic coefficient = 1.27181
Density of water = 0.99704
Total H = 1.110428e+002
Total O = 5.551078e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 7.456e-006 | 1.880e-006 | -5.128 | -5.726 | -0.598 | 3.78 |
| H+ | 1.756e-009 | 4.336e-009 | -8.756 | -8.363 | 0.393 | 0.00 |
| H2O | 5.551e+001 | 8.092e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.048e-001 | -0.202 | -0.516 | -0.314 | -14.30 |
| Cl | 5.051e+000 | | | | | |
| Cl- | 5.051e+000 | 5.819e+000 | 0.703 | 0.765 | 0.061 | 20.09 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.472e-001 | -0.226 | -0.607 | -0.381 | 12.10 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.641e-001 | 1.950e-001 | -0.578 | -0.710 | -0.132 | -17.80 |
| MgOH+ | 1.521e-004 | 5.650e-005 | -3.818 | -4.248 | -0.430 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.012e+000 | 0.422 | 0.304 | -0.118 | 1.40 |
| S(6) | 1.100e-003 | | | | | |
| SO4-2 | 1.100e-003 | 2.419e-005 | -2.959 | -4.616 | -1.658 | 26.80 |
| HSO4- | 1.128e-011 | 9.990e-012 | -10.948 | -11.000 | -0.053 | 42.04 |
| Tris | 6.000e-002 | | | | | |
| (Tris)H+ | 3.019e-002 | 1.286e-002 | -1.520 | -1.891 | -0.371 | (0) |
| Tris | 2.981e-002 | 2.524e-002 | -1.526 | -1.598 | -0.072 | (0) |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.91 | -5.13 | -4.22 | CaSO4 |
| Arcanite | -4.05 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.19 | 0.27 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.36 | -9.70 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -1.28 | -12.16 | -10.88 | Mg(OH)2 |
| Carnallite | -3.90 | 0.43 | 4.33 | KMgCl3:6H2O |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.90 | -9.14 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.74 | -5.32 | -4.58 | CaSO4:2H2O |

```
H2O(g)          -1.59     -0.09    1.50  H2O
Halite          -0.50      1.07    1.57  NaCl
Hexahydrite     -4.24     -5.88   -1.63  MgSO4:6H2O
Kainite         -5.25     -5.44   -0.19  KMgClSO4:3H2O
Kieserite       -5.30     -5.42   -0.12  MgSO4:H2O
Labile_S        -7.66    -13.33   -5.67  Na4Ca(SO4)3:2H2O
Leonhardite     -4.81     -5.69   -0.89  MgSO4:4H2O
Leonite         -7.55    -11.52   -3.98  K2Mg(SO4)2:4H2O
Mirabilite      -3.72     -4.93   -1.21  Na2SO4:10H2O
Misenite        -76.54    -87.35  -10.81  K8H6(SO4)7
Pentahydrite    -4.50     -5.79   -1.28  MgSO4:5H2O
Polyhalite      -7.86    -21.61  -13.74  K2MgCa2(SO4)4:2H2O
Portlandite     -6.78    -11.97   -5.19  Ca(OH)2
Schoenite       -7.38    -11.71   -4.33  K2Mg(SO4)2:6H2O
Sylvite         -0.74      0.16    0.90  KCl
Syngenite       -3.61    -11.05   -7.45  K2Ca(SO4)2:H2O


------------------
End of simulation.
------------------

------------------------------------
Reading input data for simulation 3.
------------------------------------

        Solution 8 Just 1.2x's LSPW (no Tris)
           pe      11
           units   mol/L
           ph       7 charge
           density  1.17505
        Na          2.40000
        K           0.54000
        Ca          0.5710
        Mg          0.24000
        Cl          4.56000
        S(6)        0.00100
        Save Solution 8
        END
-----------------------------------------------
Beginning of initial solution calculations.
-----------------------------------------------

Initial solution 8.      Just 1.2x's LSPW (no Tris)

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Ca              6.287e-001  6.287e-001
        Cl              5.020e+000  5.020e+000
        K               5.945e-001  5.945e-001
        Mg              2.642e-001  2.642e-001
        Na              2.642e+000  2.642e+000
        S(6)            1.101e-003  1.101e-003

----------------------------Description of solution----------------------------

                                pH  =   5.889      Charge balance
                                pe  =  11.000
     Specific Conductance (uS/cm, 25 oC) = 505299
                     Density (g/cm3)  =   1.17504
                         Volume (L)  =   1.10105
                    Activity of water  =   0.811
                       Ionic strength  =  5.917e+000
                   Mass of water (kg)  =  1.000e+000
                Total alkalinity (eq/kg)  =  7.689e-016
                  Total carbon (mol/kg)  =  0.000e+000
                    Total CO2 (mol/kg)  =  0.000e+000
                   Temperature (deg C)  =  25.00
```

Electrical balance (eq) = 7.859e-014
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 0.00
Iterations = 12
Gamma iterations = 5
Osmotic coefficient = 1.27274
Density of water = 0.99704
Total H = 1.110124e+002
Total O = 5.551062e+001

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| H+ | 5.261e-007 | 1.290e-006 | -6.279 | -5.889 | 0.389 | 0.00 |
| OH- | 2.497e-008 | 6.333e-009 | -7.603 | -8.198 | -0.596 | 3.75 |
| H2O | 5.551e+001 | 8.107e-001 | 1.744 | -0.091 | 0.000 | 18.07 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.056e-001 | -0.202 | -0.515 | -0.313 | -14.31 |
| Cl | 5.020e+000 | | | | | |
| Cl- | 5.020e+000 | 5.785e+000 | 0.701 | 0.762 | 0.062 | 20.08 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.465e-001 | -0.226 | -0.608 | -0.382 | 12.09 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.642e-001 | 1.930e-001 | -0.578 | -0.714 | -0.136 | -17.81 |
| MgOH+ | 5.045e-007 | 1.884e-007 | -6.297 | -6.725 | -0.428 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.001e+000 | 0.422 | 0.301 | -0.121 | 1.39 |
| S(6) | 1.101e-003 | | | | | |
| SO4-2 | 1.101e-003 | 2.429e-005 | -2.958 | -4.615 | -1.656 | 26.78 |
| HSO4- | 3.354e-009 | 2.985e-009 | -8.474 | -8.525 | -0.051 | 42.03 |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.90 | -5.13 | -4.22 | CaSO4 |
| Arcanite | -4.05 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.19 | 0.26 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.36 | -9.71 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -6.23 | -17.11 | -10.88 | Mg(OH)2 |
| Carnallite | -3.91 | 0.42 | 4.33 | KMgCl3:6H2O |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.90 | -9.14 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 | CaSO4:2H2O |
| H2O(g) | -1.59 | -0.09 | 1.50 | H2O |
| Halite | -0.51 | 1.06 | 1.57 | NaCl |
| Hexahydrite | -4.24 | -5.88 | -1.63 | MgSO4:6H2O |
| Kainite | -5.26 | -5.45 | -0.19 | KMgClSO4:3H2O |
| Kieserite | -5.30 | -5.42 | -0.12 | MgSO4:H2O |
| Labile_S | -7.66 | -13.34 | -5.67 | Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.81 | -5.69 | -0.89 | MgSO4:4H2O |
| Leonite | -7.55 | -11.52 | -3.98 | K2Mg(SO4)2:4H2O |
| Mirabilite | -3.71 | -4.92 | -1.21 | Na2SO4:10H2O |
| Misenite | -61.70 | -72.50 | -10.81 | K8H6(SO4)7 |
| Pentahydrite | -4.50 | -5.78 | -1.28 | MgSO4:5H2O |
| Polyhalite | -7.86 | -21.60 | -13.74 | K2MgCa2(SO4)4:2H2O |
| Portlandite | -11.72 | -16.91 | -5.19 | Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 | K2Mg(SO4)2:6H2O |
| Sylvite | -0.75 | 0.15 | 0.90 | KCl |
| Syngenite | -3.60 | -11.05 | -7.45 | K2Ca(SO4)2:H2O |

---
End of simulation.
---

---

Reading input data for simulation 4.
---

```
USE solution 1
EQUILIBRIUM_PHASES 1
   CO2(g)    -3.4 10
END
```

---
Beginning of batch-reaction calculations.
---

Reaction step 1.

Using solution 1.
Using pure phase assemblage 1.

----------Phase assemblage----------

| Phase | SI | log IAP | log K(T, P) | Moles in assemblage: Initial | Final | Delta |
|---|---|---|---|---|---|---|
| CO2(g) | -3.40 | -4.86 | -1.46 | 1.000e+001 | 1.000e+001 | -8.234e-005 |

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| C | 8.234e-005 | 8.234e-005 |
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.078e+000 | 5.078e+000 |
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

```
                            pH  =   7.074      Charge balance
                            pe  =  11.000      Adjusted to redox equilibrium
      Specific Conductance (uS/cm, 25 oC) = 511871
                   Density (g/cm3)  =   1.18218
                       Volume (L)  =   1.10232
                  Activity of water  =   0.808
                    Ionic strength  =  5.974e+000
                 Mass of water (kg)  =  1.000e+000
              Total alkalinity (eq/kg)  =  2.995e-003
                 Total CO2 (mol/kg)  =  8.234e-005
                Temperature (deg C)  =  25.00
              Electrical balance (eq)  = -5.591e-015
Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                       Iterations  =  16
                  Gamma iterations  =   4
                Osmotic coefficient  =   1.27364
                  Density of water  =   0.99704
                        Total H  = 1.110695e+002
                        Total O  = 5.551079e+001
```

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 3.850e-007 | 9.661e-008 | -6.415 | -7.015 | -0.600 | 3.81 |
| H+ | 3.391e-008 | 8.430e-008 | -7.470 | -7.074 | 0.396 | 0.00 |
| H2O | 5.551e+001 | 8.084e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| C(4) | 8.234e-005 | | | | | |
| HCO3- | 6.737e-005 | 6.027e-005 | -4.172 | -4.220 | -0.048 | 37.58 |
| CO2 | 6.287e-006 | 1.380e-005 | -5.202 | -4.860 | 0.341 | 30.26 |

```
  MgCO3         5.501e-006  5.501e-006    -5.260    -5.260     0.000    -17.09
  CO3-2         3.183e-006  3.274e-008    -5.497    -7.485    -1.988      8.69
Ca          6.287e-001
  Ca+2          6.287e-001  3.118e-001    -0.202    -0.506    -0.304    -14.28
Cl          5.078e+000
  Cl-           5.078e+000  5.850e+000     0.706     0.767     0.062     20.09
K           5.945e-001
  K+            5.945e-001  2.470e-001    -0.226    -0.607    -0.381     12.11
Mg          2.642e-001
  Mg+2          2.642e-001  1.983e-001    -0.578    -0.703    -0.125    -17.78
  MgOH+         7.984e-006  2.952e-006    -5.098    -5.530    -0.432     (0)
  MgCO3         5.501e-006  5.501e-006    -5.260    -5.260     0.000    -17.09
Na          2.642e+000
  Na+           2.642e+000  2.016e+000     0.422     0.304    -0.118      1.41
S(6)        1.100e-003
  SO4-2         1.100e-003  2.412e-005    -2.959    -4.618    -1.659     26.83
  HSO4-         2.197e-010  1.937e-010    -9.658    -9.713    -0.055     42.04
Tris        6.000e-002
  (Tris)H+      5.710e-002  2.434e-002    -1.243    -1.614    -0.370     (0)
  Tris          2.902e-003  2.457e-003    -2.537    -2.610    -0.072     (0)

-------------------------------Saturation indices--------------------------------

             Phase              SI   log IAP   log K(298 K,   1 atm)

             Anhydrite       -0.90     -5.12   -4.22  CaSO4
             Aragonite        0.23     -7.99   -8.22  CaCO3
             Arcanite        -4.06     -5.83   -1.78  K2SO4
             Bischofite      -4.18      0.28    4.46  MgCl2:6H2O
             Bloedite        -7.35     -9.70   -2.35  Na2Mg(SO4)2:4H2O
             Brucite         -3.85    -14.73  -10.88  Mg(OH)2
             Burkeite       -14.12    -14.89   -0.77  Na6CO3(SO4)2
             Calcite          0.42     -7.99   -8.41  CaCO3
             Carnallite      -3.89      0.44    4.33  KMgCl3:6H2O
             CO2(g)          -3.40     -4.86   -1.46  CO2              Pressure   0.0 atm, phi 1.000
             Dolomite         0.90    -16.18  -17.08  CaMg(CO3)2
             Epsomite        -4.09     -5.97   -1.88  MgSO4:7H2O
             Gaylussite      -5.91    -15.33   -9.42  CaNa2(CO3)2:5H2O
             Glaserite       -6.95    -10.75   -3.80  NaK3(SO4)2
             Glauberite      -3.89     -9.13   -5.25  Na2Ca(SO4)2
             Gypsum          -0.73     -5.31   -4.58  CaSO4:2H2O
             H2O(g)          -1.60     -0.09    1.50  H2O
             Halite          -0.50      1.07    1.57  NaCl
             Hexahydrite     -4.24     -5.87   -1.63  MgSO4:6H2O
             Kainite         -5.24     -5.44   -0.19  KMgClSO4:3H2O
             Kalicinite      -5.11    -15.17  -10.06  KHCO3
             Kieserite       -5.29     -5.41   -0.12  MgSO4:H2O
             Labile_S        -7.65    -13.33   -5.67  Na4Ca(SO4)3:2H2O
             Leonhardite     -4.80     -5.69   -0.89  MgSO4:4H2O
             Leonite         -7.54    -11.52   -3.98  K2Mg(SO4)2:4H2O
             Magnesite       -0.35     -8.19   -7.83  MgCO3
             Mirabilite      -3.72     -4.93   -1.21  Na2SO4:10H2O
             Misenite       -68.82    -79.63  -10.81  K8H6(SO4)7
             Nahcolite       -3.51    -14.25  -10.74  NaHCO3
             Natron          -6.97     -7.80   -0.82  Na2CO3:10H2O
             Nesquehonite    -3.30     -8.46   -5.17  MgCO3:3H2O
             Pentahydrite    -4.50     -5.78   -1.28  MgSO4:5H2O
             Pirssonite      -5.82    -15.05   -9.23  Na2Ca(CO3)2:2H2O
             Polyhalite      -7.84    -21.58  -13.74  K2MgCa2(SO4)4:2H2O
             Portlandite     -9.35    -14.54   -5.19  Ca(OH)2
             Schoenite       -7.38    -11.71   -4.33  K2Mg(SO4)2:6H2O
             Sylvite         -0.74      0.16    0.90  KCl
             Syngenite       -3.60    -11.05   -7.45  K2Ca(SO4)2:H2O
             Trona           -9.93    -21.32  -11.38  Na3H(CO3)2:2H2O


------------------
End of simulation.
------------------
```

```
------------------------------------
Reading input data for simulation 5.
------------------------------------

        USE solution 2
        EQUILIBRIUM_PHASES 2
           CO2(g)    -3.4 10
        END
----------------------------------------
Beginning of batch-reaction calculations.
----------------------------------------

Reaction step 1.

Using solution 2.
Using pure phase assemblage 2.

-------------------------------Phase assemblage--------------------------------

                                                Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)          -3.40    -4.86     -1.46   1.000e+001  1.000e+001 -1.485e-004

------------------------------Solution composition------------------------------

        Elements          Molality       Moles

        C                1.485e-004  1.485e-004
        Ca               6.287e-001  6.287e-001
        Cl               5.076e+000  5.076e+000
        K                5.945e-001  5.945e-001
        Mg               2.642e-001  2.642e-001
        Na               2.642e+000  2.642e+000
        S                1.100e-003  1.100e-003
        Tris             6.000e-002  6.000e-002

-----------------------------Description of solution-----------------------------

                                pH  =   7.311      Charge balance
                                pe  =  11.000      Adjusted to redox equilibrium
      Specific Conductance (uS/cm, 25 oC) = 511613
                         Density (g/cm3)  =   1.18216
                             Volume (L)  =   1.10228
                       Activity of water  =   0.808
                          Ionic strength  =  5.972e+000
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  5.023e-003
                      Total CO2 (mol/kg)  =  1.485e-004
                    Temperature (deg C)  =  25.00
                  Electrical balance (eq)  = -9.226e-011
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                             Iterations  =  17
                        Gamma iterations  =  5
                     Osmotic coefficient  =  1.27350
                       Density of water  =  0.99704
                             Total H  = 1.110674e+002
                             Total O  = 5.551093e+001

-----------------------------Distribution of species-----------------------------

                                            Unscaled   Unscaled
                                  Unscaled    log        log         log
  Species         Molality    Activity  Molality  Activity     Gamma   cm3/mol

  OH-           6.646e-007  1.668e-007    -6.177    -6.778    -0.600      3.81
  H+            1.965e-008  4.882e-008    -7.707    -7.311     0.395      0.00
  H2O           5.551e+001  8.085e-001     1.744    -0.092     0.000     18.07
C(4)         1.485e-004
  HCO3-         1.163e-004  1.041e-004    -3.934    -3.983    -0.048     37.57
```

```
  MgCO3         1.638e-005  1.638e-005    -4.786    -4.786     0.000    -17.09
  CO3-2         9.484e-006  9.761e-008    -5.023    -7.010    -1.987      8.69
  CO2           6.287e-006  1.380e-005    -5.202    -4.860     0.341     30.26
Ca          6.287e-001
  Ca+2          6.287e-001  3.113e-001    -0.202    -0.507    -0.305    -14.29
Cl          5.076e+000
  Cl-           5.076e+000  5.848e+000     0.705     0.767     0.062     20.09
K           5.945e-001
  K+            5.945e-001  2.470e-001    -0.226    -0.607    -0.381     12.11
Mg          2.642e-001
  Mg+2          2.642e-001  1.980e-001    -0.578    -0.703    -0.125    -17.79
  MgCO3         1.638e-005  1.638e-005    -4.786    -4.786     0.000    -17.09
  MgOH+         1.376e-005  5.091e-006    -4.861    -5.293    -0.432     (0)
Na          2.642e+000
  Na+           2.642e+000  2.016e+000     0.422     0.304    -0.118      1.41
S(6)        1.100e-003
  SO4-2         1.100e-003  2.413e-005    -2.959    -4.618    -1.659     26.83
  HSO4-         1.272e-010  1.122e-010    -9.895    -9.950    -0.054     42.04
Tris        6.000e-002
  (Tris)H+      5.516e-002  2.351e-002    -1.258    -1.629    -0.370     (0)
  Tris          4.841e-003  4.098e-003    -2.315    -2.387    -0.072     (0)

-------------------------------Saturation indices-------------------------------

          Phase              SI   log IAP   log K(298 K,   1 atm)

          Anhydrite       -0.90    -5.12   -4.22  CaSO4
          Aragonite        0.70    -7.52   -8.22  CaCO3
          Arcanite        -4.06    -5.83   -1.78  K2SO4
          Bischofite      -4.18     0.28    4.46  MgCl2:6H2O
          Bloedite        -7.35    -9.70   -2.35  Na2Mg(SO4)2:4H2O
          Brucite         -3.38   -14.26  -10.88  Mg(OH)2
          Burkeite       -13.65   -14.42   -0.77  Na6CO3(SO4)2
          Calcite          0.89    -7.52   -8.41  CaCO3
          Carnallite      -3.89     0.44    4.33  KMgCl3:6H2O
          CO2(g)          -3.40    -4.86   -1.46  CO2              Pressure   0.0 atm, phi 1.000
          Dolomite         1.85   -15.23  -17.08  CaMg(CO3)2
          Epsomite        -4.09    -5.97   -1.88  MgSO4:7H2O
          Gaylussite      -4.96   -14.38   -9.42  CaNa2(CO3)2:5H2O
          Glaserite       -6.95   -10.75   -3.80  NaK3(SO4)2
          Glauberite      -3.89    -9.13   -5.25  Na2Ca(SO4)2
          Gypsum          -0.73    -5.31   -4.58  CaSO4:2H2O
          H2O(g)          -1.60    -0.09    1.50  H2O
          Halite          -0.50     1.07    1.57  NaCl
          Hexahydrite     -4.24    -5.87   -1.63  MgSO4:6H2O
          Kainite         -5.25    -5.44   -0.19  KMgClSO4:3H2O
          Kalicinite      -4.87   -14.93  -10.06  KHCO3
          Kieserite       -5.29    -5.41   -0.12  MgSO4:H2O
          Labile_S        -7.65   -13.33   -5.67  Na4Ca(SO4)3:2H2O
          Leonhardite     -4.80    -5.69   -0.89  MgSO4:4H2O
          Leonite         -7.54   -11.52   -3.98  K2Mg(SO4)2:4H2O
          Magnesite        0.12    -7.71   -7.83  MgCO3
          Mirabilite      -3.72    -4.93   -1.21  Na2SO4:10H2O
          Misenite       -70.24   -81.05  -10.81  K8H6(SO4)7
          Nahcolite       -3.28   -14.02  -10.74  NaHCO3
          Natron          -6.50    -7.32   -0.82  Na2CO3:10H2O
          Nesquehonite    -2.82    -7.99   -5.17  MgCO3:3H2O
          Pentahydrite    -4.50    -5.78   -1.28  MgSO4:5H2O
          Pirssonite      -4.87   -14.10   -9.23  Na2Ca(CO3)2:2H2O
          Polyhalite      -7.84   -21.59  -13.74  K2MgCa2(SO4)4:2H2O
          Portlandite     -8.87   -14.06   -5.19  Ca(OH)2
          Schoenite       -7.38   -11.71   -4.33  K2Mg(SO4)2:6H2O
          Sylvite         -0.74     0.16    0.90  KCl
          Syngenite       -3.60   -11.05   -7.45  K2Ca(SO4)2:H2O
          Trona           -9.22   -20.60  -11.38  Na3H(CO3)2:2H2O


-----------------
End of simulation.
-----------------
```

```
------------------------------------
Reading input data for simulation 6.
------------------------------------

        USE solution 3
        EQUILIBRIUM_PHASES 3
          CO2(g)    -3.4 10
        END
----------------------------------------
Beginning of batch-reaction calculations.
----------------------------------------


Reaction step 1.
Using solution 3.
Using pure phase assemblage 3.

--------------------------------Phase assemblage--------------------------------

                                                Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)          -3.40    -4.86     -1.46   1.000e+001  1.000e+001 -2.715e-004

-------------------------------Solution composition-------------------------------

        Elements           Molality       Moles

        C                2.715e-004  2.715e-004
        Ca               6.287e-001  6.287e-001
        Cl               5.073e+000  5.073e+000
        K                5.945e-001  5.945e-001
        Mg               2.642e-001  2.642e-001
        Na               2.642e+000  2.642e+000
        S                1.100e-003  1.100e-003
        Tris             6.000e-002  6.000e-002

-----------------------------Description of solution-----------------------------

                                pH  =   7.533      Charge balance
                                pe  =  11.000      Adjusted to redox equilibrium
     Specific Conductance (uS/cm, 25 oC) = 511233
                      Density (g/cm3)  =   1.18214
                          Volume (L)  =   1.10222
                     Activity of water  =   0.809
                       Ionic strength  =  5.969e+000
                    Mass of water (kg)  =  1.000e+000
                Total alkalinity (eq/kg)  =  8.011e-003
                    Total CO2 (mol/kg)  =  2.715e-004
                   Temperature (deg C)  =  25.00
                 Electrical balance (eq)  = -2.200e-010
Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                         Iterations  =  17
                    Gamma iterations  =  5
                  Osmotic coefficient  =  1.27329
                    Density of water  =  0.99704
                           Total H  = 1.110645e+002
                           Total O  = 5.551118e+001

-----------------------------Distribution of species-----------------------------

                                          Unscaled   Unscaled
                                 Unscaled    log        log        log
  Species         Molality      Activity  Molality   Activity    Gamma   cm3/mol

  OH-           1.106e-006  2.779e-007    -5.956     -6.556     -0.600      3.81
  H+            1.181e-008  2.932e-008    -7.928     -7.533      0.395      0.00
  H2O           5.551e+001  8.086e-001     1.744     -0.092      0.000     18.07
```

```
C(4)         2.715e-004
  HCO3-          1.936e-004  1.733e-004    -3.713    -3.761    -0.048     37.57
  MgCO3          4.534e-005  4.534e-005    -4.344    -4.344     0.000    -17.09
  CO3-2          2.627e-005  2.707e-007    -4.580    -6.568    -1.987      8.68
  CO2            6.287e-006  1.380e-005    -5.202    -4.860     0.341     30.26
Ca           6.287e-001
  Ca+2           6.287e-001  3.106e-001    -0.202    -0.508    -0.306    -14.29
Cl           5.073e+000
  Cl-            5.073e+000  5.844e+000     0.705     0.767     0.062     20.09
K            5.945e-001
  K+             5.945e-001  2.470e-001    -0.226    -0.607    -0.381     12.11
Mg           2.642e-001
  Mg+2           2.642e-001  1.977e-001    -0.578    -0.704    -0.126    -17.79
  MgCO3          4.534e-005  4.534e-005    -4.344    -4.344     0.000    -17.09
  MgOH+          2.287e-005  8.462e-006    -4.641    -5.073    -0.432      (0)
Na           2.642e+000
  Na+            2.642e+000  2.015e+000     0.422     0.304    -0.118      1.41
S(6)         1.100e-003
  SO4-2          1.100e-003  2.413e-005    -2.959    -4.617    -1.659     26.83
  HSO4-          7.638e-011  6.741e-011   -10.117   -10.171    -0.054     42.04
Tris         6.000e-002
  (Tris)H+       5.235e-002  2.231e-002    -1.281    -1.652    -0.370      (0)
  Tris           7.650e-003  6.476e-003    -2.116    -2.189    -0.072      (0)

-----------------------------Saturation indices-------------------------------

             Phase              SI   log IAP   log K(298 K,   1 atm)

             Anhydrite        -0.90    -5.13   -4.22  CaSO4
             Aragonite         1.14    -7.08   -8.22  CaCO3
             Arcanite         -4.06    -5.83   -1.78  K2SO4
             Bischofite       -4.18     0.28    4.46  MgCl2:6H2O
             Bloedite         -7.35    -9.70   -2.35  Na2Mg(SO4)2:4H2O
             Brucite          -2.94   -13.82  -10.88  Mg(OH)2
             Burkeite        -13.20   -13.98   -0.77  Na6CO3(SO4)2
             Calcite          1.33    -7.08   -8.41  CaCO3
             Carnallite       -3.89     0.44    4.33  KMgCl3:6H2O
             CO2(g)           -3.40    -4.86   -1.46  CO2              Pressure   0.0 atm, phi 1.000
             Dolomite          2.74   -14.35  -17.08  CaMg(CO3)2
             Epsomite         -4.09    -5.97   -1.88  MgSO4:7H2O
             Gaylussite       -4.07   -13.50   -9.42  CaNa2(CO3)2:5H2O
             Glaserite        -6.95   -10.75   -3.80  NaK3(SO4)2
             Glauberite       -3.89    -9.13   -5.25  Na2Ca(SO4)2
             Gypsum           -0.73    -5.31   -4.58  CaSO4:2H2O
             H2O(g)           -1.60    -0.09    1.50  H2O
             Halite           -0.50     1.07    1.57  NaCl
             Hexahydrite      -4.24    -5.88   -1.63  MgSO4:6H2O
             Kainite          -5.25    -5.44   -0.19  KMgClSO4:3H2O
             Kalicinite       -4.65   -14.71  -10.06  KHCO3
             Kieserite        -5.29    -5.41   -0.12  MgSO4:H2O
             Labile_S         -7.66   -13.33   -5.67  Na4Ca(SO4)3:2H2O
             Leonhardite      -4.80    -5.69   -0.89  MgSO4:4H2O
             Leonite          -7.54   -11.52   -3.98  K2Mg(SO4)2:4H2O
             Magnesite         0.56    -7.27   -7.83  MgCO3
             Mirabilite       -3.72    -4.93   -1.21  Na2SO4:10H2O
             Misenite        -71.57   -82.38  -10.81  K8H6(SO4)7
             Nahcolite        -3.05   -13.80  -10.74  NaHCO3
             Natron           -6.06    -6.88   -0.82  Na2CO3:10H2O
             Nesquehonite     -2.38    -7.55   -5.17  MgCO3:3H2O
             Pentahydrite     -4.50    -5.78   -1.28  MgSO4:5H2O
             Pirssonite       -3.98   -13.22   -9.23  Na2Ca(CO3)2:2H2O
             Polyhalite       -7.84   -21.59  -13.74  K2MgCa2(SO4)4:2H2O
             Portlandite      -8.43   -13.62   -5.19  Ca(OH)2
             Schoenite        -7.38   -11.71   -4.33  K2Mg(SO4)2:6H2O
             Sylvite          -0.74     0.16    0.90  KCl
             Syngenite        -3.60   -11.05   -7.45  K2Ca(SO4)2:H2O
             Trona            -8.56   -19.94  -11.38  Na3H(CO3)2:2H2O


------------------
```

End of simulation.
---

---
Reading input data for simulation 7.
---

```
USE solution 4
EQUILIBRIUM_PHASES 4
   CO2(g)    -3.4 10
END
```

---
Beginning of batch-reaction calculations.
---

Reaction step 1.

Using solution 4.
Using pure phase assemblage 4.

----------Phase assemblage----------

| Phase | SI | log IAP | log K(T, P) | Moles in assemblage: Initial | Final | Delta |
|---|---|---|---|---|---|---|
| CO2(g) | -3.40 | -4.86 | -1.46 | 1.000e+001 | 1.000e+001 | -4.329e-004 |

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| C | 4.329e-004 | 4.329e-004 |
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.070e+000 | 5.070e+000 |
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S | 1.100e-003 | 1.100e-003 |
| Tris | 6.010e-002 | 6.010e-002 |

----------Description of solution----------

```
                            pH  =   7.691      Charge balance
                            pe  =  11.000      Adjusted to redox equilibrium
      Specific Conductance (uS/cm, 25 oC) = 510860
                   Density (g/cm3)  =   1.18213
                       Volume (L)  =   1.10216
                  Activity of water  =   0.809
                     Ionic strength  =  5.966e+000
                 Mass of water (kg)  =  1.000e+000
              Total alkalinity (eq/kg)  =  1.105e-002
                 Total CO2 (mol/kg)  =  4.329e-004
                Temperature (deg C)  =  25.00
             Electrical balance (eq)  = -3.834e-010
Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                       Iterations  =  18
                  Gamma iterations  =   5
                Osmotic coefficient  =   1.27308
                  Density of water  =   0.99704
                         Total H  = 1.110616e+002
                         Total O  = 5.551152e+001
```

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 1.591e-006 | 3.998e-007 | -5.798 | -6.398 | -0.600 | 3.80 |
| H+ | 8.212e-009 | 2.038e-008 | -8.086 | -7.691 | 0.395 | 0.00 |

```
  H2O          5.551e+001  8.086e-001     1.744    -0.092     0.000     18.07
C(4)         4.329e-004
  HCO3-        2.786e-004  2.494e-004    -3.555    -3.603    -0.048     37.56
  MgCO3        9.370e-005  9.370e-005    -4.028    -4.028     0.000    -17.09
  CO3-2        5.434e-005  5.605e-007    -4.265    -6.251    -1.987      8.68
  CO2          6.286e-006  1.380e-005    -5.202    -4.860     0.341     30.26
Ca           6.287e-001
  Ca+2         6.287e-001  3.099e-001    -0.202    -0.509    -0.307    -14.29
Cl           5.070e+000
  Cl-          5.070e+000  5.841e+000     0.705     0.766     0.061     20.09
K            5.945e-001
  K+           5.945e-001  2.470e-001    -0.226    -0.607    -0.381     12.11
Mg           2.642e-001
  Mg+2         2.641e-001  1.973e-001    -0.578    -0.705    -0.127    -17.79
  MgCO3        9.370e-005  9.370e-005    -4.028    -4.028     0.000    -17.09
  MgOH+        3.283e-005  1.215e-005    -4.484    -4.915    -0.432     (0)
Na           2.642e+000
  Na+          2.642e+000  2.015e+000     0.422     0.304    -0.118      1.41
S(6)         1.100e-003
  SO4-2        1.100e-003  2.414e-005    -2.959    -4.617    -1.659     26.83
  HSO4-        5.308e-011  4.686e-011   -10.275   -10.329    -0.054     42.04
Tris         6.010e-002
  (Tris)H+     4.966e-002  2.116e-002    -1.304    -1.674    -0.370     (0)
  Tris         1.044e-002  8.839e-003    -1.981    -2.054    -0.072     (0)

-------------------------------Saturation indices--------------------------------

          Phase              SI   log IAP   log K(298 K,   1 atm)

          Anhydrite       -0.90     -5.13   -4.22  CaSO4
          Aragonite        1.46     -6.76   -8.22  CaCO3
          Arcanite        -4.06     -5.83   -1.78  K2SO4
          Bischofite      -4.18      0.27    4.46  MgCl2:6H2O
          Bloedite        -7.35     -9.70   -2.35  Na2Mg(SO4)2:4H2O
          Brucite         -2.62    -13.50  -10.88  Mg(OH)2
          Burkeite       -12.89    -13.66   -0.77  Na6CO3(SO4)2
          Calcite          1.65     -6.76   -8.41  CaCO3
          Carnallite      -3.90      0.43    4.33  KMgCl3:6H2O
          CO2(g)          -3.40     -4.86   -1.46  CO2              Pressure   0.0 atm, phi 1.000
          Dolomite         3.37    -13.72  -17.08  CaMg(CO3)2
          Epsomite        -4.09     -5.97   -1.88  MgSO4:7H2O
          Gaylussite      -3.44    -12.86   -9.42  CaNa2(CO3)2:5H2O
          Glaserite       -6.95    -10.75   -3.80  NaK3(SO4)2
          Glauberite      -3.89     -9.13   -5.25  Na2Ca(SO4)2
          Gypsum          -0.73     -5.31   -4.58  CaSO4:2H2O
          H2O(g)          -1.60     -0.09    1.50  H2O
          Halite          -0.50      1.07    1.57  NaCl
          Hexahydrite     -4.24     -5.88   -1.63  MgSO4:6H2O
          Kainite         -5.25     -5.44   -0.19  KMgClSO4:3H2O
          Kalicinite      -4.49    -14.55  -10.06  KHCO3
          Kieserite       -5.29     -5.41   -0.12  MgSO4:H2O
          Labile_S        -7.66    -13.33   -5.67  Na4Ca(SO4)3:2H2O
          Leonhardite     -4.80     -5.69   -0.89  MgSO4:4H2O
          Leonite         -7.54    -11.52   -3.98  K2Mg(SO4)2:4H2O
          Magnesite        0.88     -6.96   -7.83  MgCO3
          Mirabilite      -3.72     -4.93   -1.21  Na2SO4:10H2O
          Misenite       -72.52    -83.32  -10.81  K8H6(SO4)7
          Nahcolite       -2.90    -13.64  -10.74  NaHCO3
          Natron          -5.74     -6.57   -0.82  Na2CO3:10H2O
          Nesquehonite    -2.07     -7.23   -5.17  MgCO3:3H2O
          Pentahydrite    -4.50     -5.78   -1.28  MgSO4:5H2O
          Pirssonite      -3.35    -12.59   -9.23  Na2Ca(CO3)2:2H2O
          Polyhalite      -7.85    -21.59  -13.74  K2MgCa2(SO4)4:2H2O
          Portlandite     -8.12    -13.31   -5.19  Ca(OH)2
          Schoenite       -7.38    -11.71   -4.33  K2Mg(SO4)2:6H2O
          Sylvite         -0.74      0.16    0.90  KCl
          Syngenite       -3.60    -11.05   -7.45  K2Ca(SO4)2:H2O
          Trona           -8.08    -19.47  -11.38  Na3H(CO3)2:2H2O
```

---
End of simulation.
---

---
Reading input data for simulation 8.
---

```
USE solution 5
EQUILIBRIUM_PHASES 5
   CO2(g)    -3.4 10
END
```

---
Beginning of batch-reaction calculations.
---

Reaction step 1.

Using solution 5.
Using pure phase assemblage 5.

----------Phase assemblage----------

| Phase | SI | log IAP | log K(T, P) | Moles in assemblage: Initial | Final | Delta |
|---|---|---|---|---|---|---|
| CO2(g) | -3.40 | -4.86 | -1.46 | 1.000e+001 | 9.999e+000 | -7.130e-004 |

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| C | 7.130e-004 | 7.130e-004 |
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.066e+000 | 5.066e+000 |
| K | 5.945e-001 | 5.945e-001 |
| Mg | 2.642e-001 | 2.642e-001 |
| Na | 2.642e+000 | 2.642e+000 |
| S | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

```
                            pH  =   7.849      Charge balance
                            pe  =  11.000      Adjusted to redox equilibrium
      Specific Conductance (uS/cm, 25 oC) = 510349
                  Density (g/cm3)  =   1.18209
                      Volume (L)  =   1.10208
                 Activity of water  =   0.809
                    Ionic strength  =  5.962e+000
                 Mass of water (kg)  =  1.000e+000
              Total alkalinity (eq/kg)  =  1.500e-002
                 Total CO2 (mol/kg)  =  7.130e-004
                Temperature (deg C)  =  25.00
              Electrical balance (eq)  = -5.752e-010
Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                      Iterations  =  18
                  Gamma iterations  =   5
                Osmotic coefficient  =   1.27279
                  Density of water  =   0.99704
                        Total H  = 1.110575e+002
                        Total O  = 5.551210e+001
```

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | log Activity | log Gamma | Unscaled cm3/mol |
|---|---|---|---|---|---|---|
| OH- | 2.288e-006 | 5.755e-007 | -5.641 | -6.240 | -0.599 | 3.80 |

```
  H+            5.713e-009  1.416e-008    -8.243    -7.849     0.394      0.00
  H2O           5.551e+001  8.088e-001     1.744    -0.092     0.000     18.07
C(4)          7.130e-004
  HCO3-         4.008e-004  3.590e-004    -3.397    -3.445    -0.048     37.55
  MgCO3         1.935e-004  1.935e-004    -3.713    -3.713     0.000    -17.09
  CO3-2         1.124e-004  1.161e-006    -3.949    -5.935    -1.986      8.67
  CO2           6.286e-006  1.380e-005    -5.202    -4.860     0.341     30.26
Ca            6.287e-001
  Ca+2          6.287e-001  3.089e-001    -0.202    -0.510    -0.309    -14.29
Cl            5.066e+000
  Cl-           5.066e+000  5.836e+000     0.705     0.766     0.061     20.09
K             5.945e-001
  K+            5.945e-001  2.471e-001    -0.226    -0.607    -0.381     12.11
Mg            2.642e-001
  Mg+2          2.640e-001  1.967e-001    -0.578    -0.706    -0.128    -17.79
  MgCO3         1.935e-004  1.935e-004    -3.713    -3.713     0.000    -17.09
  MgOH+         4.708e-005  1.744e-005    -4.327    -4.758    -0.431     (0)
Na            2.642e+000
  Na+           2.642e+000  2.014e+000     0.422     0.304    -0.118      1.41
S(6)          1.100e-003
  SO4-2         1.100e-003  2.415e-005    -2.959    -4.617    -1.659     26.82
  HSO4-         3.688e-011  3.257e-011   -10.433   -10.487    -0.054     42.04
Tris          6.000e-002
  (Tris)H+      4.607e-002  1.963e-002    -1.337    -1.707    -0.371     (0)
  Tris          1.394e-002  1.180e-002    -1.856    -1.928    -0.072     (0)

-----------------------------Saturation indices-------------------------------

          Phase              SI   log IAP   log K(298 K,   1 atm)

          Anhydrite        -0.90     -5.13   -4.22  CaSO4
          Aragonite         1.77     -6.45   -8.22  CaCO3
          Arcanite         -4.06     -5.83   -1.78  K2SO4
          Bischofite       -4.18      0.27    4.46  MgCl2:6H2O
          Bloedite         -7.35     -9.70   -2.35  Na2Mg(SO4)2:4H2O
          Brucite          -2.31    -13.19  -10.88  Mg(OH)2
          Burkeite        -12.57    -13.34   -0.77  Na6CO3(SO4)2
          Calcite           1.96     -6.45   -8.41  CaCO3
          Carnallite       -3.90      0.43    4.33  KMgCl3:6H2O
          CO2(g)           -3.40     -4.86   -1.46  CO2              Pressure   0.0 atm, phi 1.000
          Dolomite          4.00    -13.09  -17.08  CaMg(CO3)2
          Epsomite         -4.09     -5.97   -1.88  MgSO4:7H2O
          Gaylussite       -2.81    -12.23   -9.42  CaNa2(CO3)2:5H2O
          Glaserite        -6.95    -10.75   -3.80  NaK3(SO4)2
          Glauberite       -3.89     -9.14   -5.25  Na2Ca(SO4)2
          Gypsum           -0.73     -5.31   -4.58  CaSO4:2H2O
          H2O(g)           -1.60     -0.09    1.50  H2O
          Halite           -0.50      1.07    1.57  NaCl
          Hexahydrite      -4.24     -5.88   -1.63  MgSO4:6H2O
          Kainite          -5.25     -5.44   -0.19  KMgClSO4:3H2O
          Kalicinite       -4.33    -14.39  -10.06  KHCO3
          Kieserite        -5.29     -5.42   -0.12  MgSO4:H2O
          Labile_S         -7.66    -13.33   -5.67  Na4Ca(SO4)3:2H2O
          Leonhardite      -4.81     -5.69   -0.89  MgSO4:4H2O
          Leonite          -7.54    -11.52   -3.98  K2Mg(SO4)2:4H2O
          Magnesite         1.19     -6.64   -7.83  MgCO3
          Mirabilite       -3.72     -4.93   -1.21  Na2SO4:10H2O
          Misenite        -73.46    -84.27  -10.81  K8H6(SO4)7
          Nahcolite        -2.74    -13.48  -10.74  NaHCO3
          Natron           -5.42     -6.25   -0.82  Na2CO3:10H2O
          Nesquehonite     -1.75     -6.92   -5.17  MgCO3:3H2O
          Pentahydrite     -4.50     -5.78   -1.28  MgSO4:5H2O
          Pirssonite       -2.72    -11.96   -9.23  Na2Ca(CO3)2:2H2O
          Polyhalite       -7.85    -21.59  -13.74  K2MgCa2(SO4)4:2H2O
          Portlandite      -7.80    -12.99   -5.19  Ca(OH)2
          Schoenite        -7.38    -11.71   -4.33  K2Mg(SO4)2:6H2O
          Sylvite          -0.74      0.16    0.90  KCl
          Syngenite        -3.60    -11.05   -7.45  K2Ca(SO4)2:H2O
          Trona            -7.61    -18.99  -11.38  Na3H(CO3)2:2H2O
```

```
----------
End of simulation.
----------

------------------------------------
Reading input data for simulation 9.
------------------------------------

        USE solution 6
        EQUILIBRIUM_PHASES 6
          CO2(g)    -3.4 10
        END
----------------------------------------
Beginning of batch-reaction calculations.
----------------------------------------

Reaction step 1.

Using solution 6.
Using pure phase assemblage 6.

-------------------------------Phase assemblage--------------------------------

                                                    Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)          -3.40    -4.86     -1.46   1.000e+001  9.999e+000 -1.447e-003

-----------------------------Solution composition------------------------------

        Elements          Molality       Moles

        C                1.447e-003  1.447e-003
        Ca               6.287e-001  6.287e-001
        Cl               5.059e+000  5.059e+000
        K                5.945e-001  5.945e-001
        Mg               2.642e-001  2.642e-001
        Na               2.642e+000  2.642e+000
        S                1.100e-003  1.100e-003
        Tris             6.000e-002  6.000e-002

----------------------------Description of solution----------------------------

                                pH  =   8.057      Charge balance
                                pe  =  11.000      Adjusted to redox equilibrium
      Specific Conductance (uS/cm, 25 oC) = 509468
                         Density (g/cm3)  =   1.18206
                             Volume (L)  =   1.10195
                       Activity of water  =   0.809
                          Ionic strength  =  5.956e+000
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  2.200e-002
                     Total CO2 (mol/kg)  =  1.447e-003
                    Temperature (deg C)  =  25.00
                  Electrical balance (eq)  = -3.454e-010
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =  -0.00
                          Iterations  =  19
                     Gamma iterations  =   5
                    Osmotic coefficient  =   1.27224
                      Density of water  =   0.99704
                            Total H  = 1.110506e+002
                            Total O  = 5.551361e+001

-------------------------------Distribution of species-------------------------------

                                                Unscaled   Unscaled
                                      Unscaled    log        log         log
  Species          Molality    Activity  Molality  Activity     Gamma    cm3/mol
```

| | | | | | | |
|---|---|---|---|---|---|---|
| OH- | 3.691e-006 | 9.294e-007 | -5.433 | -6.032 | -0.599 | 3.79 |
| H+ | 3.544e-009 | 8.769e-009 | -8.450 | -8.057 | 0.393 | 0.00 |
| H2O | 5.551e+001 | 8.089e-001 | 1.744 | -0.092 | 0.000 | 18.07 |
| C(4) | 1.447e-003 | | | | | |
| HCO3- | 6.469e-004 | 5.798e-004 | -3.189 | -3.237 | -0.048 | 37.54 |
| MgCO3 | 5.020e-004 | 5.020e-004 | -3.299 | -3.299 | 0.000 | -17.09 |
| CO3-2 | 2.924e-004 | 3.028e-006 | -3.534 | -5.519 | -1.985 | 8.66 |
| CO2 | 6.287e-006 | 1.380e-005 | -5.202 | -4.860 | 0.341 | 30.26 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.073e-001 | -0.202 | -0.512 | -0.311 | -14.29 |
| Cl | 5.059e+000 | | | | | |
| Cl- | 5.059e+000 | 5.826e+000 | 0.704 | 0.765 | 0.061 | 20.09 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.471e-001 | -0.226 | -0.607 | -0.381 | 12.11 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.637e-001 | 1.956e-001 | -0.579 | -0.709 | -0.130 | -17.79 |
| MgCO3 | 5.020e-004 | 5.020e-004 | -3.299 | -3.299 | 0.000 | -17.09 |
| MgOH+ | 7.555e-005 | 2.802e-005 | -4.122 | -4.553 | -0.431 | (0) |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.013e+000 | 0.422 | 0.304 | -0.118 | 1.40 |
| S(6) | 1.100e-003 | | | | | |
| SO4-2 | 1.100e-003 | 2.416e-005 | -2.959 | -4.617 | -1.658 | 26.81 |
| HSO4- | 2.284e-011 | 2.018e-011 | -10.641 | -10.695 | -0.054 | 42.04 |
| Tris | 6.000e-002 | | | | | |
| (Tris)H+ | 4.031e-002 | 1.717e-002 | -1.395 | -1.765 | -0.371 | (0) |
| Tris | 1.969e-002 | 1.667e-002 | -1.706 | -1.778 | -0.072 | (0) |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.90 | -5.13 | -4.22 | CaSO4 |
| Aragonite | 2.19 | -6.03 | -8.22 | CaCO3 |
| Arcanite | -4.05 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.19 | 0.27 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.36 | -9.70 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -1.89 | -12.77 | -10.88 | Mg(OH)2 |
| Burkeite | -12.16 | -12.93 | -0.77 | Na6CO3(SO4)2 |
| Calcite | 2.37 | -6.03 | -8.41 | CaCO3 |
| Carnallite | -3.90 | 0.43 | 4.33 | KMgCl3:6H2O |
| CO2(g) | -3.40 | -4.86 | -1.46 | CO2 Pressure 0.0 atm, phi 1.000 |
| Dolomite | 4.82 | -12.26 | -17.08 | CaMg(CO3)2 |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Gaylussite | -1.98 | -11.40 | -9.42 | CaNa2(CO3)2:5H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.89 | -9.14 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 | CaSO4:2H2O |
| H2O(g) | -1.59 | -0.09 | 1.50 | H2O |
| Halite | -0.50 | 1.07 | 1.57 | NaCl |
| Hexahydrite | -4.24 | -5.88 | -1.63 | MgSO4:6H2O |
| Kainite | -5.25 | -5.44 | -0.19 | KMgClSO4:3H2O |
| Kalicinite | -4.12 | -14.18 | -10.06 | KHCO3 |
| Kieserite | -5.29 | -5.42 | -0.12 | MgSO4:H2O |
| Labile_S | -7.66 | -13.33 | -5.67 | Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.81 | -5.69 | -0.89 | MgSO4:4H2O |
| Leonite | -7.55 | -11.52 | -3.98 | K2Mg(SO4)2:4H2O |
| Magnesite | 1.61 | -6.23 | -7.83 | MgCO3 |
| Mirabilite | -3.72 | -4.93 | -1.21 | Na2SO4:10H2O |
| Misenite | -74.71 | -85.52 | -10.81 | K8H6(SO4)7 |
| Nahcolite | -2.53 | -13.27 | -10.74 | NaHCO3 |
| Natron | -5.01 | -5.83 | -0.82 | Na2CO3:10H2O |
| Nesquehonite | -1.34 | -6.50 | -5.17 | MgCO3:3H2O |
| Pentahydrite | -4.50 | -5.79 | -1.28 | MgSO4:5H2O |
| Pirssonite | -1.89 | -11.13 | -9.23 | Na2Ca(CO3)2:2H2O |
| Polyhalite | -7.86 | -21.60 | -13.74 | K2MgCa2(SO4)4:2H2O |
| Portlandite | -7.39 | -12.58 | -5.19 | Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 | K2Mg(SO4)2:6H2O |
| Sylvite | -0.74 | 0.16 | 0.90 | KCl |
| Syngenite | -3.60 | -11.05 | -7.45 | K2Ca(SO4)2:H2O |
| Trona | -6.98 | -18.37 | -11.38 | Na3H(CO3)2:2H2O |

---
End of simulation.
---

---
Reading input data for simulation 10.
---

```
USE solution 7
EQUILIBRIUM_PHASES 7
   CO2(g)    -3.4 10
END
```

---
Beginning of batch-reaction calculations.
---

Reaction step 1.

Using solution 7.
Using pure phase assemblage 7.

----------Phase assemblage----------

| Phase | SI | log IAP | log K(T, P) | Moles in assemblage: Initial | Final | Delta |
|---|---|---|---|---|---|---|
| CO2(g) | -3.40 | -4.86 | -1.46 | 1.000e+001 | 9.997e+000 | -2.747e-003 |

----------Solution composition----------

| Elements | Molality | Moles |
|---|---|---|
| C | 2.747e-003 | 2.747e-003 |
| Ca | 6.287e-001 | 6.287e-001 |
| Cl | 5.051e+000 | 5.051e+000 |
| K | 5.946e-001 | 5.945e-001 |
| Mg | 2.643e-001 | 2.642e-001 |
| Na | 2.643e+000 | 2.642e+000 |
| S | 1.100e-003 | 1.100e-003 |
| Tris | 6.000e-002 | 6.000e-002 |

----------Description of solution----------

```
                                pH  =   8.232      Charge balance
                                pe  =  11.000      Adjusted to redox equilibrium
      Specific Conductance (uS/cm, 25 oC) = 508471
                          Density (g/cm3)  =   1.18204
                              Volume (L)  =   1.10182
                         Activity of water  =   0.809
                           Ionic strength  =  5.949e+000
                        Mass of water (kg)  =  1.000e+000
                  Total alkalinity (eq/kg)  =  2.997e-002
                      Total CO2 (mol/kg)  =  2.747e-003
                     Temperature (deg C)  =  25.00
                   Electrical balance (eq)  =  2.213e-009
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                           Iterations  =  20
                         Gamma iterations  =   5
                      Osmotic coefficient  =   1.27153
                        Density of water  =   0.99704
                              Total H  = 1.110428e+002
                              Total O  = 5.551627e+001
```

----------Distribution of species----------

| Species | Molality | Unscaled Activity | Unscaled log Molality | Unscaled log Activity | log Gamma | cm3/mol |
|---|---|---|---|---|---|---|

```
   OH-          5.521e-006  1.392e-006    -5.258    -5.856    -0.598      3.78
   H+           2.372e-009  5.855e-009    -8.625    -8.232     0.393      0.00
   H2O          5.551e+001  8.092e-001     1.744    -0.092     0.000     18.07
C(4)        2.747e-003
   MgCO3        1.118e-003  1.118e-003    -2.952    -2.952     0.000    -17.09
   HCO3-        9.685e-004  8.686e-004    -3.014    -3.061    -0.047     37.52
   CO3-2        6.540e-004  6.792e-006    -3.184    -5.168    -1.984      8.65
   CO2          6.288e-006  1.380e-005    -5.202    -4.860     0.341     30.26
Ca          6.287e-001
   Ca+2         6.287e-001  3.056e-001    -0.202    -0.515    -0.313    -14.29
Cl          5.051e+000
   Cl-          5.051e+000  5.815e+000     0.703     0.765     0.061     20.09
K           5.946e-001
   K+           5.946e-001  2.472e-001    -0.226    -0.607    -0.381     12.10
Mg          2.643e-001
   Mg+2         2.630e-001  1.942e-001    -0.580    -0.712    -0.132    -17.80
   MgCO3        1.118e-003  1.118e-003    -2.952    -2.952     0.000    -17.09
   MgOH+        1.122e-004  4.167e-005    -3.950    -4.380    -0.430      (0)
Na          2.643e+000
   Na+          2.643e+000  2.012e+000     0.422     0.304    -0.118      1.40
S(6)        1.100e-003
   SO4-2        1.100e-003  2.417e-005    -2.959    -4.617    -1.658     26.81
   HSO4-        1.525e-011  1.348e-011   -10.817   -10.870    -0.054     42.04
Tris        6.000e-002
   (Tris)H+     3.466e-002  1.476e-002    -1.460    -1.831    -0.371      (0)
   Tris         2.534e-002  2.146e-002    -1.596    -1.668    -0.072      (0)

-------------------------------Saturation indices--------------------------------

            Phase              SI   log IAP   log K(298 K,   1 atm)

            Anhydrite        -0.91     -5.13   -4.22  CaSO4
            Aragonite         2.54     -5.68   -8.22  CaCO3
            Arcanite         -4.05     -5.83   -1.78  K2SO4
            Bischofite       -4.19      0.27    4.46  MgCl2:6H2O
            Bloedite         -7.36     -9.71   -2.35  Na2Mg(SO4)2:4H2O
            Brucite          -1.54    -12.42  -10.88  Mg(OH)2
            Burkeite        -11.81    -12.58   -0.77  Na6CO3(SO4)2
            Calcite          2.72      -5.68   -8.41  CaCO3
            Carnallite       -3.91      0.42    4.33  KMgCl3:6H2O
            CO2(g)           -3.40     -4.86   -1.46  CO2              Pressure   0.0 atm, phi 1.000
            Dolomite          5.52    -11.56  -17.08  CaMg(CO3)2
            Epsomite         -4.09     -5.97   -1.88  MgSO4:7H2O
            Gaylussite       -1.28    -10.70   -9.42  CaNa2(CO3)2:5H2O
            Glaserite        -6.95    -10.75   -3.80  NaK3(SO4)2
            Glauberite       -3.90     -9.14   -5.25  Na2Ca(SO4)2
            Gypsum           -0.73     -5.32   -4.58  CaSO4:2H2O
            H2O(g)           -1.59     -0.09    1.50  H2O
            Halite          -0.50      1.07     1.57  NaCl
            Hexahydrite      -4.25     -5.88   -1.63  MgSO4:6H2O
            Kainite          -5.25     -5.45   -0.19  KMgClSO4:3H2O
            Kalicinite       -3.95    -14.01  -10.06  KHCO3
            Kieserite        -5.30     -5.42   -0.12  MgSO4:H2O
            Labile_S         -7.66    -13.33   -5.67  Na4Ca(SO4)3:2H2O
            Leonhardite      -4.81     -5.70   -0.89  MgSO4:4H2O
            Leonite          -7.55    -11.53   -3.98  K2Mg(SO4)2:4H2O
            Magnesite         1.95     -5.88   -7.83  MgCO3
            Mirabilite       -3.72     -4.93   -1.21  Na2SO4:10H2O
            Misenite        -75.76    -86.57  -10.81  K8H6(SO4)7
            Nahcolite        -2.35    -13.10  -10.74  NaHCO3
            Natron           -4.66     -5.48   -0.82  Na2CO3:10H2O
            Nesquehonite     -0.99     -6.16   -5.17  MgCO3:3H2O
            Pentahydrite     -4.50     -5.79   -1.28  MgSO4:5H2O
            Pirssonite       -1.19    -10.43   -9.23  Na2Ca(CO3)2:2H2O
            Polyhalite       -7.86    -21.61  -13.74  K2MgCa2(SO4)4:2H2O
            Portlandite      -7.04    -12.23   -5.19  Ca(OH)2
            Schoenite        -7.38    -11.71   -4.33  K2Mg(SO4)2:6H2O
            Sylvite         -0.74      0.16    0.90  KCl
            Syngenite        -3.61    -11.05   -7.45  K2Ca(SO4)2:H2O
```

```
        Trona           -6.46    -17.84  -11.38  Na3H(CO3)2:2H2O


-----------------
End of simulation.
-----------------

------------------------------------
Reading input data for simulation 11.
------------------------------------

        USE solution 8
        EQUILIBRIUM_PHASES 8
           CO2(g)    -3.4 10
        END
----------------------------------------
Beginning of batch-reaction calculations.
----------------------------------------

Reaction step 1.

Using solution 8.      Just 1.2x's LSPW (no Tris)
Using pure phase assemblage 8.

-------------------------------Phase assemblage--------------------------------

                                        Moles in assemblage
Phase               SI  log IAP  log K(T, P)   Initial       Final       Delta

CO2(g)          -3.40    -4.86     -1.46   1.000e+001  1.000e+001 -7.723e-006

-------------------------------Solution composition--------------------------------

        Elements          Molality       Moles

        C                7.723e-006  7.723e-006
        Ca                6.287e-001  6.287e-001
        Cl               5.020e+000  5.020e+000
        K                5.945e-001  5.945e-001
        Mg                2.642e-001  2.642e-001
        Na                2.642e+000  2.642e+000
        S                1.101e-003  1.101e-003

----------------------------Description of solution----------------------------

                                pH  =   5.404      Charge balance
                                pe  =  11.000      Adjusted to redox equilibrium
     Specific Conductance (uS/cm, 25 oC) = 505300
                         Density (g/cm3)  =   1.17504
                             Volume (L)  =   1.10105
                        Activity of water  =   0.811
                          Ionic strength  =  5.917e+000
                       Mass of water (kg)  =  1.000e+000
                 Total alkalinity (eq/kg)  =  1.696e-014
                     Total CO2 (mol/kg)  =  7.723e-006
                    Temperature (deg C)  =  25.00
                  Electrical balance (eq)  =  1.808e-014
Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.00
                           Iterations  =  15
                       Gamma iterations  =   4
                    Osmotic coefficient  =   1.27274
                      Density of water  =   0.99704
                            Total H  = 1.110124e+002
                            Total O  = 5.551064e+001

----------------------------Distribution of species----------------------------

                                              Unscaled   Unscaled
                                  Unscaled    log        log        log
  Species          Molality    Activity  Molality  Activity     Gamma   cm3/mol
```

| | | | | | | |
|---|---|---|---|---|---|---|
| H+ | 1.607e-006 | 3.940e-006 | -5.794 | -5.404 | 0.389 | 0.00 |
| OH- | 8.174e-009 | 2.073e-009 | -8.088 | -8.683 | -0.596 | 3.75 |
| H2O | 5.551e+001 | 8.107e-001 | 1.744 | -0.091 | 0.000 | 18.07 |
| C(4) | 7.723e-006 | | | | | |
| CO2 | 6.283e-006 | 1.380e-005 | -5.202 | -4.860 | 0.342 | 30.26 |
| HCO3- | 1.436e-006 | 1.293e-006 | -5.843 | -5.888 | -0.046 | 37.47 |
| MgCO3 | 2.458e-009 | 2.458e-009 | -8.609 | -8.609 | 0.000 | -17.09 |
| CO3-2 | 1.430e-009 | 1.503e-011 | -8.845 | -10.823 | -1.978 | 8.61 |
| Ca | 6.287e-001 | | | | | |
| Ca+2 | 6.287e-001 | 3.056e-001 | -0.202 | -0.515 | -0.313 | -14.31 |
| Cl | 5.020e+000 | | | | | |
| Cl- | 5.020e+000 | 5.785e+000 | 0.701 | 0.762 | 0.062 | 20.08 |
| K | 5.945e-001 | | | | | |
| K+ | 5.945e-001 | 2.465e-001 | -0.226 | -0.608 | -0.382 | 12.09 |
| Mg | 2.642e-001 | | | | | |
| Mg+2 | 2.642e-001 | 1.930e-001 | -0.578 | -0.714 | -0.136 | -17.81 |
| MgOH+ | 1.652e-007 | 6.166e-008 | -6.782 | -7.210 | -0.428 | (0) |
| MgCO3 | 2.458e-009 | 2.458e-009 | -8.609 | -8.609 | 0.000 | -17.09 |
| Na | 2.642e+000 | | | | | |
| Na+ | 2.642e+000 | 2.001e+000 | 0.422 | 0.301 | -0.121 | 1.39 |
| S(6) | 1.101e-003 | | | | | |
| SO4-2 | 1.101e-003 | 2.429e-005 | -2.958 | -4.615 | -1.656 | 26.78 |
| HSO4- | 1.025e-008 | 9.117e-009 | -7.989 | -8.040 | -0.051 | 42.03 |

----------Saturation indices----------

| Phase | SI | log IAP | log K(298 K, 1 atm) | |
|---|---|---|---|---|
| Anhydrite | -0.90 | -5.13 | -4.22 | CaSO4 |
| Aragonite | -3.12 | -11.34 | -8.22 | CaCO3 |
| Arcanite | -4.05 | -5.83 | -1.78 | K2SO4 |
| Bischofite | -4.19 | 0.26 | 4.46 | MgCl2:6H2O |
| Bloedite | -7.36 | -9.71 | -2.35 | Na2Mg(SO4)2:4H2O |
| Brucite | -7.20 | -18.08 | -10.88 | Mg(OH)2 |
| Burkeite | -17.47 | -18.24 | -0.77 | Na6CO3(SO4)2 |
| Calcite | -2.93 | -11.34 | -8.41 | CaCO3 |
| Carnallite | -3.91 | 0.42 | 4.33 | KMgCl3:6H2O |
| CO2(g) | -3.40 | -4.86 | -1.46 | CO2 Pressure 0.0 atm, phi 1.000 |
| Dolomite | -5.79 | -22.88 | -17.08 | CaMg(CO3)2 |
| Epsomite | -4.09 | -5.97 | -1.88 | MgSO4:7H2O |
| Gaylussite | -12.59 | -22.01 | -9.42 | CaNa2(CO3)2:5H2O |
| Glaserite | -6.95 | -10.75 | -3.80 | NaK3(SO4)2 |
| Glauberite | -3.90 | -9.14 | -5.25 | Na2Ca(SO4)2 |
| Gypsum | -0.73 | -5.31 | -4.58 | CaSO4:2H2O |
| H2O(g) | -1.59 | -0.09 | 1.50 | H2O |
| Halite | -0.51 | 1.06 | 1.57 | NaCl |
| Hexahydrite | -4.24 | -5.88 | -1.63 | MgSO4:6H2O |
| Kainite | -5.26 | -5.45 | -0.19 | KMgClSO4:3H2O |
| Kalicinite | -6.78 | -16.84 | -10.06 | KHCO3 |
| Kieserite | -5.30 | -5.42 | -0.12 | MgSO4:H2O |
| Labile_S | -7.66 | -13.34 | -5.67 | Na4Ca(SO4)3:2H2O |
| Leonhardite | -4.81 | -5.69 | -0.89 | MgSO4:4H2O |
| Leonite | -7.55 | -11.52 | -3.98 | K2Mg(SO4)2:4H2O |
| Magnesite | -3.70 | -11.54 | -7.83 | MgCO3 |
| Mirabilite | -3.71 | -4.92 | -1.21 | Na2SO4:10H2O |
| Misenite | -58.79 | -69.59 | -10.81 | K8H6(SO4)7 |
| Nahcolite | -5.18 | -15.93 | -10.74 | NaHCO3 |
| Natron | -10.31 | -11.13 | -0.82 | Na2CO3:10H2O |
| Nesquehonite | -6.64 | -11.81 | -5.17 | MgCO3:3H2O |
| Pentahydrite | -4.50 | -5.78 | -1.28 | MgSO4:5H2O |
| Pirssonite | -12.51 | -21.74 | -9.23 | Na2Ca(CO3)2:2H2O |
| Polyhalite | -7.86 | -21.60 | -13.74 | K2MgCa2(SO4)4:2H2O |
| Portlandite | -12.69 | -17.88 | -5.19 | Ca(OH)2 |
| Schoenite | -7.38 | -11.71 | -4.33 | K2Mg(SO4)2:6H2O |
| Sylvite | -0.75 | 0.15 | 0.90 | KCl |
| Syngenite | -3.60 | -11.05 | -7.45 | K2Ca(SO4)2:H2O |
| Trona | -14.95 | -26.33 | -11.38 | Na3H(CO3)2:2H2O |

---
End of simulation.
---

---
Reading input data for simulation 12.
---

---
End of Run after 0.348 Seconds.
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## B.4 pH BUFFER SOLUTIONS

### Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NaCl solutions for molar absorptivity coefficient (ε) determinations | | | | | | | | | | | | |
| no $CO_2$ | 0.05 | 3.22 | 0.05 | 0.050 | - | - | - | 0.050 | - | - | -4.35 | - |
| log $PCO_2$ = -3.4 | 0.05m | 3.22 | 0.05 | 0.050 | - | - | - | 0.050 | - | - | -4.35 | - |
| no $CO_2$ | 0.05m | 11.11 | 0.12 | 0.101 | - | - | - | 0.050 | - | - | -4.11 | - |
| log $PCO_2$ = -3.4 | 0.05m | 9.61 | 0.11 | 0.101 | - | - | - | 0.050 | - | - | -4.10 | - |
| no $CO_2$ | 1.0m | 3.10 | 1.01 | 1.005 | - | - | - | 1.005 | - | - | -1.93 | - |
| log $PCO_2$ = -3.4 | 1.0m | 3.10 | 1.01 | 1.005 | - | - | - | 1.005 | - | - | -1.93 | - |
| no $CO_2$ | 1.0m | 10.87 | 1.07 | 1.050 | - | - | - | 1.000 | - | - | -1.92 | - |
| log $PCO_2$ = -3.4 | 1.0m | 9.38 | 1.06 | 1.050 | - | - | - | 1.000 | - | - | -1.92 | - |
| no $CO_2$ | 5.0m | 2.66 | 5.04 | 5.041 | - | - | - | 5.041 | - | - | -0.28 | - |
| log $PCO_2$ = -3.4 | 5.0m | 2.66 | 5.04 | 5.041 | - | - | - | 5.041 | - | - | -0.28 | - |
| no $CO_2$ | 5.0m | 10.69 | 5.07 | 5.046 | - | - | - | 4.996 | - | - | -0.29 | - |
| log $PCO_2$ = -3.4 | 5.0m | 9.19 | 5.06 | 5.047 | - | - | - | 4.997 | - | - | -0.29 | - |
| Buffer solutions containing only Tris/TrisHCl buffer (Just Tris) | | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.10 | 0.05 | - | - | - | - | 0.046 | - | 0.0500 | - | - |
| no $CO_2$ | 2 | 7.29 | 0.04 | - | - | - | - | 0.044 | - | 0.0500 | - | - |
| no $CO_2$ | 3 | 7.43 | 0.04 | - | - | - | - | 0.042 | - | 0.0500 | - | - |
| no $CO_2$ | 4 | 7.43 | 0.04 | - | - | - | - | 0.042 | - | 0.0500 | - | - |
| no $CO_2$ | 5 | 7.65 | 0.04 | - | - | - | - | 0.038 | - | 0.0500 | - | - |
| no $CO_2$ | 6 | 7.86 | 0.03 | - | - | - | - | 0.033 | - | 0.0500 | - | - |
| no $CO_2$ | 7 | 8.04 | 0.03 | - | - | - | - | 0.028 | - | 0.0500 | - | - |
| log $PCO_2$ = -3.4 | 1 | 7.09 | 0.05 | - | - | - | - | 0.046 | - | 0.0500 | - | - |
| log $PCO_2$ = -3.4 | 2 | 7.28 | 0.04 | - | - | - | - | 0.044 | - | 0.0500 | - | - |
| log $PCO_2$ = -3.4 | 3 | 7.42 | 0.04 | - | - | - | - | 0.042 | - | 0.0500 | - | - |
| log $PCO_2$ = -3.4 | 4 | 7.42 | 0.04 | - | - | - | - | 0.042 | - | 0.0500 | - | - |
| log $PCO_2$ = -3.4 | 5 | 7.63 | 0.04 | - | - | - | - | 0.038 | - | 0.0500 | - | - |
| log $PCO_2$ = -3.4 | 6 | 7.84 | 0.03 | - | - | - | - | 0.033 | - | 0.0500 | - | - |
| log $PCO_2$ = -3.4 | 7 | 8.01 | 0.03 | - | - | - | - | 0.028 | - | 0.0500 | - | - |
| NaCl buffer solutions for pH and pka measurements | | | | | | | | | | | | |
| | 0.1 m NaCl | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.15 | 0.10 | 0.045 | - | - | - | 0.100 | - | 0.0600 | -4.14 | - |
| no $CO_2$ | 2 | 7.49 | 0.10 | 0.050 | - | - | - | 0.100 | - | 0.0601 | -4.09 | - |
| no $CO_2$ | 3 | 7.71 | 0.10 | 0.055 | - | - | - | 0.100 | - | 0.0599 | -4.05 | - |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| no $CO_2$ | 4 | 7.95 | 0.10 | 0.062 | - | - | - | 0.100 | - | 0.0599 | -4.00 | - |
| no $CO_2$ | 5 | 8.13 | 0.10 | 0.068 | - | - | - | 0.100 | - | 0.0600 | -3.96 | - |
| no $CO_2$ | 6 | 8.33 | 0.10 | 0.075 | - | - | - | 0.100 | - | 0.0598 | -3.91 | - |
| no $CO_2$ | 7 | 8.49 | 0.10 | 0.080 | - | - | - | 0.100 | - | 0.0599 | -3.89 | - |
| no $CO_2$ | 8 | 8.89 | 0.10 | 0.090 | - | - | - | 0.100 | - | 0.0598 | -3.83 | - |
| log $PCO_2$ = -3.4 | 1 | 7.13 | 0.10 | 0.045 | - | - | - | 0.100 | - | 0.0600 | -4.14 | - |
| log $PCO_2$ = -3.4 | 2 | 7.47 | 0.10 | 0.050 | - | - | - | 0.100 | - | 0.0601 | -4.09 | - |
| log $PCO_2$ = -3.4 | 3 | 7.70 | 0.10 | 0.055 | - | - | - | 0.100 | - | 0.0599 | -4.05 | - |
| log $PCO_2$ = -3.4 | 4 | 7.93 | 0.10 | 0.062 | - | - | - | 0.100 | - | 0.0599 | -4.00 | - |
| log $PCO_2$ = -3.4 | 5 | 8.10 | 0.10 | 0.068 | - | - | - | 0.100 | - | 0.0600 | -3.96 | - |
| log $PCO_2$ = -3.4 | 6 | 8.29 | 0.10 | 0.075 | - | - | - | 0.100 | - | 0.0598 | -3.92 | - |
| log $PCO_2$ = -3.4 | 7 | 8.42 | 0.10 | 0.080 | - | - | - | 0.100 | - | 0.0599 | -3.89 | - |
| log $PCO_2$ = -3.4 | 8 | 8.69 | 0.10 | 0.090 | - | - | - | 0.100 | - | 0.0598 | -3.84 | - |
| | 1.0 m NaCl | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.04 | 1.02 | 0.962 | - | - | - | 1.019 | - | 0.0600 | -1.95 | - |
| no $CO_2$ | 2a | 7.29 | 1.02 | 0.965 | - | - | - | 1.020 | - | 0.0599 | -1.95 | - |
| no $CO_2$ | 2b | 7.28 | 1.02 | 0.967 | - | - | - | 1.022 | - | 0.0600 | -1.95 | - |
| no $CO_2$ | 3 | 7.51 | 1.03 | 0.975 | - | - | - | 1.027 | - | 0.0600 | -1.94 | - |
| no $CO_2$ | 4 | 7.85 | 1.03 | 0.982 | - | - | - | 1.027 | - | 0.0600 | -1.94 | - |
| no $CO_2$ | 5 | 8.02 | 1.03 | 0.988 | - | - | - | 1.028 | - | 0.0599 | -1.93 | - |
| no $CO_2$ | 6 | 8.18 | 1.03 | 0.995 | - | - | - | 1.030 | - | 0.0599 | -1.93 | - |
| log $PCO_2$ = -3.4 | 1 | 7.03 | 1.02 | 0.962 | - | - | - | 1.019 | - | 0.0600 | -1.95 | - |
| log $PCO_2$ = -3.4 | 2a | 7.27 | 1.02 | 0.965 | - | - | - | 1.020 | - | 0.0599 | -1.95 | - |
| log $PCO_2$ = -3.4 | 2b | 7.26 | 1.02 | 0.967 | - | - | - | 1.022 | - | 0.0600 | -1.95 | - |
| log $PCO_2$ = -3.4 | 3 | 7.49 | 1.03 | 0.975 | - | - | - | 1.027 | - | 0.0600 | -1.94 | - |
| log $PCO_2$ = -3.4 | 4 | 7.82 | 1.03 | 0.982 | - | - | - | 1.027 | - | 0.0600 | -1.94 | - |
| log $PCO_2$ = -3.4 | 5 | 7.99 | 1.03 | 0.988 | - | - | - | 1.028 | - | 0.0599 | -1.93 | - |
| log $PCO_2$ = -3.4 | 6 | 8.13 | 1.03 | 0.995 | - | - | - | 1.030 | - | 0.0599 | -1.93 | - |
| | 1.0 m NaCl | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.86 | 0.99 | 0.936 | - | - | - | 0.994 | - | 0.0600 | -1.97 | - |
| no $CO_2$ | 2 | 7.18 | 1.00 | 0.944 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| no $CO_2$ | 3 | 7.44 | 1.00 | 0.947 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| no $CO_2$ | 4 | 7.62 | 1.00 | 0.950 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| no $CO_2$ | 5 | 7.84 | 1.00 | 0.955 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| no $CO_2$ | 6 | 8.02 | 1.00 | 0.960 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| log $PCO_2$ = -3.4 | 1 | 6.84 | 0.99 | 0.936 | - | - | - | 0.994 | - | 0.0600 | -1.97 | - |
| log $PCO_2$ = -3.4 | 2 | 7.16 | 1.00 | 0.944 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| log $PCO_2$ = -3.4 | 3 | 7.42 | 1.00 | 0.947 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| log $PCO_2$ = -3.4 | 4 | 7.60 | 1.00 | 0.950 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| log $PCO_2$ = -3.4 | 5 | 7.81 | 1.00 | 0.955 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| log $PCO_2$ = -3.4 | 6 | 7.98 | 1.00 | 0.960 | - | - | - | 1.000 | - | 0.0600 | -1.96 | - |
| | 5.0 m NaCl | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.87 | 5.00 | 4.942 | - | - | - | 5.000 | - | 0.0595 | -0.30 | - |
| no $CO_2$ | 2 | 7.18 | 5.00 | 4.942 | - | - | - | 4.999 | - | 0.0600 | -0.30 | - |
| no $CO_2$ | 3 | 7.41 | 5.00 | 4.944 | - | - | - | 4.999 | - | 0.0600 | -0.30 | - |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| no $CO_2$ | 4 | 7.64 | 5.00 | 4.948 | - | - | - | 5.000 | - | 0.0600 | -0.30 | - |
| no $CO_2$ | 5 | 7.98 | 5.00 | 4.953 | - | - | - | 4.998 | - | 0.0600 | -0.30 | - |
| no $CO_2$ | 6 | 8.16 | 5.00 | 4.959 | - | - | - | 4.999 | - | 0.0600 | -0.30 | - |
| log $PCO_2$ = -3.4 | 1 | 6.84 | 5.00 | 4.942 | - | - | - | 5.000 | - | 0.0595 | -0.30 | - |
| log $PCO_2$ = -3.4 | 2 | 7.15 | 5.00 | 4.942 | - | - | - | 4.999 | - | 0.0600 | -0.30 | - |
| log $PCO_2$ = -3.4 | 3 | 7.38 | 5.00 | 4.944 | - | - | - | 4.999 | - | 0.0600 | -0.30 | - |
| log $PCO_2$ = -3.4 | 4 | 7.61 | 5.00 | 4.948 | - | - | - | 5.000 | - | 0.0600 | -0.30 | - |
| log $PCO_2$ = -3.4 | 5 | 7.93 | 5.00 | 4.953 | - | - | - | 4.998 | - | 0.0600 | -0.30 | - |
| log $PCO_2$ = -3.4 | 6 | 8.09 | 5.00 | 4.959 | - | - | - | 4.999 | - | 0.0600 | -0.30 | - |
| L-SPW series buffer solutions for pH and pka measurements | | | | | | | | | | | | |
| | 1.57x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.94 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.520 | 0.0011 | 0.052 | -0.11 | -0.50 |
| no $CO_2$ | 2 | 7.12 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.520 | 0.0011 | 0.053 | -0.11 | -0.50 |
| no $CO_2$ | 3 | 7.26 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.519 | 0.0011 | 0.053 | -0.11 | -0.50 |
| no $CO_2$ | 4 | 7.45 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.517 | 0.0011 | 0.053 | -0.11 | -0.50 |
| no $CO_2$ | 5 | 7.65 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.514 | 0.0011 | 0.053 | -0.11 | -0.50 |
| no $CO_2$ | 6 | 7.94 | 7.66 | 3.405 | 0.766 | 0.810 | 0.341 | 6.508 | 0.0011 | 0.053 | -0.11 | -0.51 |
| no $CO_2$ | 7 | 8.45 | 7.65 | 3.405 | 0.766 | 0.810 | 0.341 | 6.493 | 0.0011 | 0.053 | -0.11 | -0.51 |
| log $PCO_2$ = -3.4 | 1 | 6.92 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.520 | 0.0011 | 0.052 | -0.11 | -0.50 |
| log $PCO_2$ = -3.4 | 2 | 7.11 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.520 | 0.0011 | 0.053 | -0.11 | -0.50 |
| log $PCO_2$ = -3.4 | 3 | 7.24 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.519 | 0.0011 | 0.053 | -0.11 | -0.50 |
| log $PCO_2$ = -3.4 | 4 | 7.42 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.517 | 0.0011 | 0.053 | -0.11 | -0.50 |
| log $PCO_2$ = -3.4 | 5 | 7.62 | 7.67 | 3.405 | 0.766 | 0.810 | 0.341 | 6.514 | 0.0011 | 0.053 | -0.11 | -0.50 |
| log $PCO_2$ = -3.4 | 6 | 7.87 | 7.66 | 3.405 | 0.766 | 0.810 | 0.341 | 6.508 | 0.0011 | 0.053 | -0.11 | -0.51 |
| log $PCO_2$ = -3.4 | 7 | 8.22 | 7.65 | 3.405 | 0.766 | 0.810 | 0.341 | 6.493 | 0.0011 | 0.053 | -0.11 | -0.51 |
| no $CO_2$ | HCl 1 | 2.74 | 6.51 | 2.908 | 0.654 | 0.691 | 0.291 | 5.524 | 0.0010 | - | -0.37 | -0.69 |
| | 1.45x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | unbuffered | 5.70 | 7.03 | 3.143 | 0.707 | 0.746 | 0.314 | 5.969 | 0.0011 | 0.000 | -0.25 | -0.58 |
| no $CO_2$ | unbuffered | 5.62 | 7.03 | 3.143 | 0.707 | 0.746 | 0.314 | 5.969 | 0.0011 | 0.000 | -0.25 | -0.59 |
| no $CO_2$ | 3 | 7.08 | 7.09 | 3.143 | 0.707 | 0.746 | 0.314 | 6.026 | 0.0011 | 0.060 | -0.24 | -0.58 |
| no $CO_2$ | 4 | 7.31 | 7.09 | 3.143 | 0.707 | 0.746 | 0.314 | 6.024 | 0.0011 | 0.060 | -0.24 | -0.58 |
| no $CO_2$ | 5 | 7.48 | 7.09 | 3.143 | 0.707 | 0.746 | 0.314 | 6.022 | 0.0011 | 0.060 | -0.24 | -0.58 |
| no $CO_2$ | 6 | 7.60 | 7.08 | 3.143 | 0.707 | 0.746 | 0.314 | 6.020 | 0.0011 | 0.060 | -0.24 | -0.58 |
| no $CO_2$ | 7 | 7.87 | 7.08 | 3.143 | 0.707 | 0.746 | 0.314 | 6.014 | 0.0011 | 0.060 | -0.24 | -0.58 |
| no $CO_2$ | 8 | 8.05 | 7.07 | 3.143 | 0.707 | 0.746 | 0.314 | 6.009 | 0.0011 | 0.060 | -0.24 | -0.59 |
| no $CO_2$ | 9 | 8.35 | 7.06 | 3.143 | 0.707 | 0.746 | 0.314 | 5.999 | 0.0011 | 0.060 | -0.24 | -0.59 |
| log $PCO_2$ = -3.4 | 3 | 7.06 | 7.09 | 3.143 | 0.707 | 0.746 | 0.314 | 6.026 | 0.0011 | 0.060 | -0.24 | -0.58 |
| log $PCO_2$ = -3.4 | 4 | 7.30 | 7.09 | 3.143 | 0.707 | 0.746 | 0.314 | 6.024 | 0.0011 | 0.060 | -0.24 | -0.58 |
| log $PCO_2$ = -3.4 | 5 | 7.46 | 7.09 | 3.143 | 0.707 | 0.746 | 0.314 | 6.022 | 0.0011 | 0.060 | -0.24 | -0.58 |
| log $PCO_2$ = -3.4 | 6 | 7.58 | 7.08 | 3.143 | 0.707 | 0.746 | 0.314 | 6.020 | 0.0011 | 0.060 | -0.24 | -0.58 |
| log $PCO_2$ = -3.4 | 7 | 7.83 | 7.08 | 3.143 | 0.707 | 0.746 | 0.314 | 6.014 | 0.0011 | 0.060 | -0.24 | -0.58 |
| log $PCO_2$ = -3.4 | 8 | 7.98 | 7.07 | 3.143 | 0.707 | 0.746 | 0.314 | 6.009 | 0.0011 | 0.060 | -0.24 | -0.59 |
| log $PCO_2$ = -3.4 | 9 | 8.19 | 7.06 | 3.143 | 0.707 | 0.746 | 0.314 | 6.000 | 0.0011 | 0.060 | -0.24 | -0.59 |
| no $CO_2$ | HCl 1 | 2.64 | 7.26 | 3.244 | 0.730 | 0.771 | 0.324 | 6.162 | 0.0011 | - | -0.20 | -0.58 |
| | 1.34x's L-SPW | | | | | | | | | | | |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| no $CO_2$ | 1 | 6.90 | 6.53 | 2.890 | 0.650 | 0.687 | 0.289 | 5.548 | 0.0011 | 0.060 | -0.37 | -0.65 |
| no $CO_2$ | 2 | 7.32 | 6.53 | 2.890 | 0.650 | 0.687 | 0.289 | 5.546 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | 3a | 7.55 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.542 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | 3b | 7.55 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.543 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | 3c | 7.55 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.543 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | 4 | 7.71 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.539 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | 5 | 7.99 | 6.51 | 2.890 | 0.650 | 0.687 | 0.289 | 5.532 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | 6 | 8.36 | 6.50 | 2.890 | 0.650 | 0.687 | 0.289 | 5.520 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | 7 | 8.71 | 6.49 | 2.890 | 0.650 | 0.687 | 0.289 | 5.509 | 0.0011 | 0.060 | -0.37 | -0.67 |
| no $CO_2$ | unbuffered | 5.78 | 6.47 | 2.890 | 0.650 | 0.687 | 0.289 | 5.491 | 0.0011 | 0.000 | -0.38 | -0.66 |
| log $PCO_2$ = -3.4 | 1 | 6.89 | 6.53 | 2.890 | 0.650 | 0.687 | 0.289 | 5.549 | 0.0011 | 0.060 | -0.37 | -0.65 |
| log $PCO_2$ = -3.4 | 2 | 7.31 | 6.53 | 2.890 | 0.650 | 0.687 | 0.289 | 5.546 | 0.0011 | 0.060 | -0.37 | -0.66 |
| log $PCO_2$ = -3.4 | 3a | 7.53 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.543 | 0.0011 | 0.060 | -0.37 | -0.66 |
| log $PCO_2$ = -3.4 | 3b | 7.52 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.543 | 0.0011 | 0.060 | -0.37 | -0.66 |
| log $PCO_2$ = -3.4 | 3c | 7.52 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.543 | 0.0011 | 0.060 | -0.37 | -0.66 |
| log $PCO_2$ = -3.4 | 4 | 7.68 | 6.52 | 2.890 | 0.650 | 0.687 | 0.289 | 5.540 | 0.0011 | 0.060 | -0.37 | -0.66 |
| log $PCO_2$ = -3.4 | 5 | 7.94 | 6.51 | 2.890 | 0.650 | 0.687 | 0.289 | 5.533 | 0.0011 | 0.060 | -0.37 | -0.66 |
| log $PCO_2$ = -3.4 | 6 | 8.22 | 6.50 | 2.890 | 0.650 | 0.687 | 0.289 | 5.521 | 0.0011 | 0.060 | -0.37 | -0.66 |
| log $PCO_2$ = -3.4 | 7 | 8.40 | 6.49 | 2.890 | 0.650 | 0.687 | 0.289 | 5.509 | 0.0011 | 0.060 | -0.37 | -0.66 |
| no $CO_2$ | HCl 1a | 1.42 | 6.48 | 2.887 | 0.650 | 0.687 | 0.289 | 5.499 | 0.0011 | 0.000 | -0.37 | -0.70 |
| no $CO_2$ | HCl 1a | 1.41 | 6.48 | 2.887 | 0.650 | 0.687 | 0.289 | 5.499 | 0.0011 | 0.000 | -0.37 | -0.70 |
| | 1.22x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.09 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.078 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 2 | 7.33 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.076 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 3 | 7.55 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.073 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 4 | 7.72 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.070 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 5 | 7.89 | 5.96 | 2.642 | 0.595 | 0.629 | 0.264 | 5.066 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 6 | 8.13 | 5.95 | 2.642 | 0.595 | 0.629 | 0.264 | 5.059 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 7 | 8.36 | 5.95 | 2.642 | 0.595 | 0.629 | 0.264 | 5.051 | 0.0011 | 0.060 | -0.50 | -0.74 |
| no $CO_2$ | unbuffered | 5.89 | 5.92 | 2.642 | 0.595 | 0.629 | 0.264 | 5.021 | 0.0011 | 0.000 | -0.51 | -0.73 |
| log $PCO_2$ = -3.4 | 1 | 7.07 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.078 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 2 | 7.31 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.076 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 3 | 7.53 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.073 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 4 | 7.69 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.070 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 5 | 7.85 | 5.96 | 2.642 | 0.595 | 0.629 | 0.264 | 5.066 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 6 | 8.06 | 5.96 | 2.643 | 0.595 | 0.629 | 0.264 | 5.059 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 7 | 8.23 | 5.95 | 2.643 | 0.595 | 0.629 | 0.264 | 5.051 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | unbuffered | 5.40 | 5.92 | 2.642 | 0.595 | 0.629 | 0.264 | 5.021 | 0.0011 | 0.000 | -0.51 | -0.73 |
| | 1.22x's L-SPWb | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.09 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.078 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 2 | 7.33 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.076 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 3 | 7.55 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.073 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 4 | 7.72 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.070 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 5 | 7.89 | 5.96 | 2.642 | 0.595 | 0.629 | 0.264 | 5.066 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 6 | 8.13 | 5.95 | 2.642 | 0.595 | 0.629 | 0.264 | 5.059 | 0.0011 | 0.060 | -0.50 | -0.73 |
| no $CO_2$ | 7 | 8.36 | 5.95 | 2.642 | 0.595 | 0.629 | 0.264 | 5.051 | 0.0011 | 0.060 | -0.50 | -0.74 |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| no $CO_2$ | unbuffered | 5.89 | 5.92 | 2.642 | 0.595 | 0.629 | 0.264 | 5.021 | 0.0011 | 0.000 | -0.51 | -0.73 |
| log $PCO_2$ = -3.4 | 1 | 7.08 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.078 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 2 | 7.31 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.076 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 3 | 7.53 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.073 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 4 | 7.69 | 5.97 | 2.642 | 0.595 | 0.629 | 0.264 | 5.070 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 5 | 7.85 | 5.96 | 2.642 | 0.595 | 0.629 | 0.264 | 5.066 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 6 | 8.06 | 5.96 | 2.643 | 0.595 | 0.629 | 0.264 | 5.059 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | 7 | 8.23 | 5.95 | 2.643 | 0.595 | 0.629 | 0.264 | 5.051 | 0.0011 | 0.060 | -0.50 | -0.73 |
| log $PCO_2$ = -3.4 | unbuffered | 5.40 | 5.92 | 2.642 | 0.595 | 0.629 | 0.264 | 5.021 | 0.0011 | 0.000 | -0.51 | -0.73 |
| | L-SPW2 | (less $CaSO_4$ than LSPW) | | | | | | | | | | |
| no $CO_2$ | 1 | 6.92 | 4.90 | 2.163 | 0.487 | 0.515 | 0.216 | 4.167 | 0.0011 | 0.060 | -0.77 | -0.87 |
| no $CO_2$ | 2 | 7.23 | 4.90 | 2.163 | 0.487 | 0.515 | 0.216 | 4.165 | 0.0011 | 0.060 | -0.77 | -0.87 |
| no $CO_2$ | 3 | 7.50 | 4.90 | 2.163 | 0.487 | 0.515 | 0.216 | 4.162 | 0.0011 | 0.060 | -0.77 | -0.87 |
| no $CO_2$ | 4 | 7.68 | 4.89 | 2.163 | 0.487 | 0.515 | 0.216 | 4.159 | 0.0011 | 0.060 | -0.77 | -0.87 |
| no $CO_2$ | 5 | 7.90 | 4.89 | 2.163 | 0.487 | 0.515 | 0.216 | 4.154 | 0.0011 | 0.060 | -0.77 | -0.87 |
| no $CO_2$ | 6 | 8.14 | 4.88 | 2.163 | 0.487 | 0.515 | 0.216 | 4.147 | 0.0011 | 0.060 | -0.77 | -0.87 |
| no $CO_2$ | 7 | 8.37 | 4.87 | 2.163 | 0.487 | 0.515 | 0.216 | 4.139 | 0.0011 | 0.060 | -0.77 | -0.87 |
| no $CO_2$ | unbuffered | 6.11 | 4.84 | 2.163 | 0.487 | 0.515 | 0.216 | 4.109 | 0.0011 | 0.000 | -0.78 | -0.87 |
| log $PCO_2$ = -3.4 | 1 | 6.90 | 4.90 | 2.163 | 0.487 | 0.515 | 0.216 | 4.167 | 0.0011 | 0.060 | -0.77 | -0.87 |
| log $PCO_2$ = -3.4 | 2 | 7.22 | 4.90 | 2.163 | 0.487 | 0.515 | 0.216 | 4.165 | 0.0011 | 0.060 | -0.77 | -0.87 |
| log $PCO_2$ = -3.4 | 3 | 7.48 | 4.90 | 2.163 | 0.487 | 0.515 | 0.216 | 4.162 | 0.0011 | 0.060 | -0.77 | -0.87 |
| log $PCO_2$ = -3.4 | 4 | 7.65 | 4.89 | 2.163 | 0.487 | 0.515 | 0.216 | 4.159 | 0.0011 | 0.060 | -0.77 | -0.87 |
| log $PCO_2$ = -3.4 | 5 | 7.86 | 4.89 | 2.163 | 0.487 | 0.515 | 0.216 | 4.154 | 0.0011 | 0.060 | -0.77 | -0.87 |
| log $PCO_2$ = -3.4 | 6 | 8.08 | 4.88 | 2.163 | 0.487 | 0.515 | 0.216 | 4.147 | 0.0011 | 0.060 | -0.77 | -0.87 |
| log $PCO_2$ = -3.4 | 7 | 8.26 | 4.88 | 2.163 | 0.487 | 0.515 | 0.216 | 4.139 | 0.0011 | 0.060 | -0.77 | -0.87 |
| log $PCO_2$ = -3.4 | unbuffered | 5.46 | 4.84 | 2.163 | 0.487 | 0.515 | 0.216 | 4.109 | 0.0011 | 0.000 | -0.78 | -0.87 |
| | L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1a | 6.92 | 4.95 | 2.163 | 0.487 | 0.525 | 0.216 | 4.188 | 0.0054 | 0.069 | -0.76 | -0.16 |
| no $CO_2$ | 1b | 6.91 | 4.88 | 2.098 | 0.492 | 0.525 | 0.216 | 4.119 | 0.0054 | 0.060 | -0.79 | -0.17 |
| no $CO_2$ | 2a | 7.33 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.185 | 0.0054 | 0.069 | -0.77 | -0.16 |
| no $CO_2$ | 2b | 7.33 | 4.88 | 2.107 | 0.487 | 0.524 | 0.216 | 4.119 | 0.0054 | 0.060 | -0.79 | -0.17 |
| no $CO_2$ | 3 | 7.56 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.181 | 0.0054 | 0.069 | -0.77 | -0.16 |
| no $CO_2$ | 4 | 7.68 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.179 | 0.0054 | 0.069 | -0.77 | -0.16 |
| no $CO_2$ | 4b | 7.68 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.179 | 0.0054 | 0.069 | -0.77 | -0.16 |
| no $CO_2$ | 5 | 8.07 | 4.93 | 2.163 | 0.487 | 0.525 | 0.216 | 4.168 | 0.0054 | 0.069 | -0.77 | -0.17 |
| no $CO_2$ | 6 | 8.37 | 4.91 | 2.163 | 0.487 | 0.525 | 0.216 | 4.156 | 0.0054 | 0.069 | -0.77 | -0.17 |
| no $CO_2$ | 7 | 8.67 | 4.90 | 2.163 | 0.487 | 0.525 | 0.216 | 4.145 | 0.0054 | 0.069 | -0.77 | -0.17 |
| no $CO_2$ | 8 | 9.06 | 4.89 | 2.163 | 0.487 | 0.525 | 0.216 | 4.133 | 0.0054 | 0.069 | -0.77 | -0.17 |
| log $PCO_2$ = -3.4 | 1a | 6.91 | 4.95 | 2.163 | 0.487 | 0.525 | 0.216 | 4.188 | 0.0054 | 0.069 | -0.76 | -0.16 |
| log $PCO_2$ = -3.4 | 1b | 6.90 | 4.88 | 2.098 | 0.492 | 0.525 | 0.216 | 4.119 | 0.0054 | 0.060 | -0.79 | -0.17 |
| log $PCO_2$ = -3.4 | 2a | 7.32 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.185 | 0.0054 | 0.069 | -0.77 | -0.16 |
| log $PCO_2$ = -3.4 | 2b | 7.32 | 4.88 | 2.107 | 0.487 | 0.524 | 0.216 | 4.119 | 0.0054 | 0.060 | -0.79 | -0.17 |
| log $PCO_2$ = -3.4 | 3 | 7.55 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.182 | 0.0054 | 0.069 | -0.77 | -0.16 |
| log $PCO_2$ = -3.4 | 4 | 7.66 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.179 | 0.0054 | 0.069 | -0.77 | -0.16 |
| log $PCO_2$ = -3.4 | 4b | 7.66 | 4.94 | 2.163 | 0.487 | 0.525 | 0.216 | 4.179 | 0.0054 | 0.069 | -0.77 | -0.16 |
| log $PCO_2$ = -3.4 | 5 | 8.03 | 4.93 | 2.163 | 0.487 | 0.525 | 0.216 | 4.168 | 0.0054 | 0.069 | -0.77 | -0.17 |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| log $PCO_2$ = -3.4 | 6 | 8.27 | 4.92 | 2.163 | 0.487 | 0.525 | 0.216 | 4.156 | 0.0054 | 0.069 | -0.77 | -0.17 |
| log $PCO_2$ = -3.4 | 7 | 8.45 | 4.91 | 2.163 | 0.487 | 0.525 | 0.216 | 4.145 | 0.0054 | 0.069 | -0.77 | -0.17 |
| log $PCO_2$ = -3.4 | 8 | 8.59 | 4.90 | 2.164 | 0.487 | 0.525 | 0.216 | 4.134 | 0.0054 | 0.069 | -0.77 | -0.17 |
| no $CO_2$ | HCl 1 | 3.43 | 4.78 | 2.120 | 0.477 | 0.515 | 0.212 | 4.040 | 0.0053 | - | -0.80 | -0.18 |
| no $CO_2$ | HCl 2 | 3.06 | 4.64 | 2.055 | 0.462 | 0.499 | 0.206 | 3.916 | 0.0051 | - | -0.84 | -0.21 |
| no $CO_2$ | HCl 3 | 1.61 | 4.89 | 2.161 | 0.486 | 0.524 | 0.216 | 4.131 | 0.0054 | 0.000 | -0.77 | -0.19 |
| | 0.73x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.91 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.075 | 0.0008 | 0.060 | -1.14 | -1.15 |
| no $CO_2$ | 2 | 7.23 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.073 | 0.0008 | 0.060 | -1.14 | -1.15 |
| no $CO_2$ | 3 | 7.50 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.070 | 0.0008 | 0.060 | -1.14 | -1.15 |
| no $CO_2$ | 4 | 7.68 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.067 | 0.0008 | 0.060 | -1.14 | -1.15 |
| no $CO_2$ | 5 | 7.90 | 3.60 | 1.588 | 0.357 | 0.378 | 0.159 | 3.062 | 0.0008 | 0.060 | -1.14 | -1.15 |
| no $CO_2$ | 6 | 8.14 | 3.59 | 1.588 | 0.357 | 0.378 | 0.159 | 3.055 | 0.0008 | 0.060 | -1.14 | -1.15 |
| no $CO_2$ | 7 | 8.38 | 3.59 | 1.588 | 0.357 | 0.378 | 0.159 | 3.047 | 0.0008 | 0.060 | -1.14 | -1.16 |
| no $CO_2$ | unbuffered | 6.36 | 3.56 | 1.588 | 0.357 | 0.378 | 0.159 | 3.017 | 0.0008 | 0.000 | -1.15 | -1.15 |
| log $PCO_2$ = -3.4 | 1 | 6.90 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.075 | 0.0008 | 0.060 | -1.14 | -1.15 |
| log $PCO_2$ = -3.4 | 2 | 7.22 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.073 | 0.0008 | 0.060 | -1.14 | -1.15 |
| log $PCO_2$ = -3.4 | 3 | 7.48 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.070 | 0.0008 | 0.060 | -1.14 | -1.15 |
| log $PCO_2$ = -3.4 | 4 | 7.66 | 3.61 | 1.588 | 0.357 | 0.378 | 0.159 | 3.067 | 0.0008 | 0.060 | -1.14 | -1.15 |
| log $PCO_2$ = -3.4 | 5 | 7.87 | 3.60 | 1.588 | 0.357 | 0.378 | 0.159 | 3.062 | 0.0008 | 0.060 | -1.14 | -1.15 |
| log $PCO_2$ = -3.4 | 6 | 8.09 | 3.60 | 1.588 | 0.357 | 0.378 | 0.159 | 3.055 | 0.0008 | 0.060 | -1.14 | -1.15 |
| log $PCO_2$ = -3.4 | 7 | 8.28 | 3.59 | 1.588 | 0.357 | 0.378 | 0.159 | 3.047 | 0.0008 | 0.060 | -1.14 | -1.16 |
| log $PCO_2$ = -3.4 | unbuffered | 5.51 | 3.56 | 1.588 | 0.357 | 0.378 | 0.159 | 3.017 | 0.0008 | 0.000 | -1.15 | -1.15 |
| | 0.48x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.90 | 2.38 | 1.038 | 0.234 | 0.247 | 0.104 | 2.030 | 0.0005 | 0.060 | -1.58 | -1.46 |
| no $CO_2$ | 2 | 7.22 | 2.38 | 1.038 | 0.234 | 0.247 | 0.104 | 2.028 | 0.0005 | 0.060 | -1.58 | -1.46 |
| no $CO_2$ | 3 | 7.41 | 2.38 | 1.038 | 0.234 | 0.247 | 0.104 | 2.026 | 0.0005 | 0.060 | -1.58 | -1.46 |
| no $CO_2$ | 4 | 7.67 | 2.37 | 1.038 | 0.234 | 0.247 | 0.104 | 2.022 | 0.0005 | 0.060 | -1.58 | -1.46 |
| no $CO_2$ | 5 | 7.89 | 2.37 | 1.038 | 0.234 | 0.247 | 0.104 | 2.017 | 0.0005 | 0.060 | -1.58 | -1.46 |
| no $CO_2$ | 6 | 8.07 | 2.36 | 1.038 | 0.234 | 0.247 | 0.104 | 2.012 | 0.0005 | 0.060 | -1.59 | -1.46 |
| no $CO_2$ | 7 | 8.37 | 2.35 | 1.038 | 0.234 | 0.247 | 0.104 | 2.002 | 0.0005 | 0.060 | -1.59 | -1.46 |
| no $CO_2$ | unbuffered | 6.58 | 2.32 | 1.038 | 0.234 | 0.247 | 0.104 | 1.972 | 0.0005 | 0.000 | -1.60 | -1.45 |
| log $PCO_2$ = -3.4 | 1 | 6.89 | 2.38 | 1.038 | 0.234 | 0.247 | 0.104 | 2.030 | 0.0005 | 0.060 | -1.58 | -1.46 |
| log $PCO_2$ = -3.4 | 2 | 7.21 | 2.38 | 1.038 | 0.234 | 0.247 | 0.104 | 2.028 | 0.0005 | 0.060 | -1.58 | -1.46 |
| log $PCO_2$ = -3.4 | 3 | 7.39 | 2.38 | 1.038 | 0.234 | 0.247 | 0.104 | 2.026 | 0.0005 | 0.060 | -1.58 | -1.46 |
| log $PCO_2$ = -3.4 | 4 | 7.65 | 2.37 | 1.038 | 0.234 | 0.247 | 0.104 | 2.022 | 0.0005 | 0.060 | -1.58 | -1.46 |
| log $PCO_2$ = -3.4 | 5 | 7.86 | 2.37 | 1.038 | 0.234 | 0.247 | 0.104 | 2.017 | 0.0005 | 0.060 | -1.58 | -1.46 |
| log $PCO_2$ = -3.4 | 6 | 8.03 | 2.37 | 1.038 | 0.234 | 0.247 | 0.104 | 2.012 | 0.0005 | 0.060 | -1.59 | -1.46 |
| log $PCO_2$ = -3.4 | 7 | 8.29 | 2.36 | 1.038 | 0.234 | 0.247 | 0.104 | 2.002 | 0.0005 | 0.060 | -1.59 | -1.46 |
| log $PCO_2$ = -3.4 | unbuffered | 5.56 | 2.32 | 1.038 | 0.234 | 0.247 | 0.104 | 1.972 | 0.0005 | 0.000 | -1.60 | -1.45 |
| | 0.24x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.87 | 1.20 | 0.510 | 0.115 | 0.121 | 0.051 | 1.026 | 0.0003 | 0.060 | -2.22 | -1.87 |
| no $CO_2$ | 2 | 7.19 | 1.20 | 0.510 | 0.115 | 0.121 | 0.051 | 1.024 | 0.0003 | 0.060 | -2.22 | -1.87 |
| no $CO_2$ | 3 | 7.38 | 1.20 | 0.510 | 0.115 | 0.121 | 0.051 | 1.022 | 0.0003 | 0.060 | -2.22 | -1.87 |
| no $CO_2$ | 4a | 7.52 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.020 | 0.0003 | 0.060 | -2.22 | -1.87 |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| no $CO_2$ | 4b | 7.52 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.020 | 0.0003 | 0.060 | -2.22 | -1.87 |
| no $CO_2$ | 4c | 7.52 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.020 | 0.0003 | 0.060 | -2.22 | -1.87 |
| no $CO_2$ | 5 | 7.73 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.016 | 0.0003 | 0.060 | -2.22 | -1.87 |
| no $CO_2$ | 6 | 8.03 | 1.18 | 0.510 | 0.115 | 0.121 | 0.051 | 1.008 | 0.0003 | 0.060 | -2.23 | -1.87 |
| no $CO_2$ | unbuffered | 6.77 | 1.14 | 0.510 | 0.115 | 0.121 | 0.051 | 0.968 | 0.0003 | 0.000 | -2.24 | -1.85 |
| log $PCO_2$ = -3.4 | 1 | 6.85 | 1.20 | 0.510 | 0.115 | 0.121 | 0.051 | 1.026 | 0.0003 | 0.060 | -2.22 | -1.87 |
| log $PCO_2$ = -3.4 | 2 | 7.18 | 1.20 | 0.510 | 0.115 | 0.121 | 0.051 | 1.024 | 0.0003 | 0.060 | -2.22 | -1.87 |
| log $PCO_2$ = -3.4 | 3 | 7.36 | 1.20 | 0.510 | 0.115 | 0.121 | 0.051 | 1.022 | 0.0003 | 0.060 | -2.22 | -1.87 |
| log $PCO_2$ = -3.4 | 4a | 7.50 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.020 | 0.0003 | 0.060 | -2.22 | -1.87 |
| log $PCO_2$ = -3.4 | 4b | 7.51 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.020 | 0.0003 | 0.060 | -2.22 | -1.87 |
| log $PCO_2$ = -3.4 | 4c | 7.50 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.020 | 0.0003 | 0.060 | -2.22 | -1.87 |
| log $PCO_2$ = -3.4 | 5 | 7.71 | 1.19 | 0.510 | 0.115 | 0.121 | 0.051 | 1.016 | 0.0003 | 0.060 | -2.22 | -1.87 |
| log $PCO_2$ = -3.4 | 6 | 8.00 | 1.18 | 0.510 | 0.115 | 0.121 | 0.051 | 1.008 | 0.0003 | 0.060 | -2.23 | -1.87 |
| log $PCO_2$ = -3.4 | unbuffered | 5.59 | 1.14 | 0.510 | 0.115 | 0.121 | 0.051 | 0.968 | 0.0003 | 0.000 | -2.24 | -1.85 |
| | 0.09x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1a | 6.89 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.432 | 0.0001 | 0.050 | -2.96 | -2.34 |
| no $CO_2$ | 1b | 6.90 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.432 | 0.0001 | 0.050 | -2.96 | -2.34 |
| no $CO_2$ | 2 | 7.21 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.429 | 0.0001 | 0.050 | -2.97 | -2.34 |
| no $CO_2$ | 3 | 7.41 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.427 | 0.0001 | 0.050 | -2.97 | -2.34 |
| no $CO_2$ | 4 | 7.56 | 0.49 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.425 | 0.0001 | 0.050 | -2.97 | -2.33 |
| no $CO_2$ | 5 | 7.78 | 0.49 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.422 | 0.0001 | 0.050 | -2.97 | -2.33 |
| no $CO_2$ | 6 | 8.10 | 0.48 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.413 | 0.0001 | 0.050 | -2.98 | -2.33 |
| no $CO_2$ | unbuffered | 6.87 | 0.45 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.383 | 0.0001 | 0.000 | -3.01 | -2.30 |
| log $PCO_2$ = -3.4 | 1a | 6.87 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.432 | 0.0001 | 0.050 | -2.96 | -2.34 |
| log $PCO_2$ = -3.4 | 1b | 6.88 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.432 | 0.0001 | 0.050 | -2.96 | -2.34 |
| log $PCO_2$ = -3.4 | 2 | 7.20 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.429 | 0.0001 | 0.050 | -2.97 | -2.34 |
| log $PCO_2$ = -3.4 | 3 | 7.39 | 0.50 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.427 | 0.0001 | 0.050 | -2.97 | -2.34 |
| log $PCO_2$ = -3.4 | 4 | 7.54 | 0.49 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.425 | 0.0001 | 0.050 | -2.97 | -2.33 |
| log $PCO_2$ = -3.4 | 5 | 7.75 | 0.49 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.422 | 0.0001 | 0.050 | -2.97 | -2.33 |
| log $PCO_2$ = -3.4 | 6 | 8.06 | 0.48 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.413 | 0.0001 | 0.050 | -2.98 | -2.33 |
| log $PCO_2$ = -3.4 | unbuffered | 5.60 | 0.45 | 0.202 | 0.0454 | 0.0480 | 0.0202 | 0.383 | 0.0001 | 0.000 | -3.01 | -2.30 |
| | 0.01x's L-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.81 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.086 | 0.0001 | 0.050 | -4.55 | -2.69 |
| no $CO_2$ | 2 | 7.13 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.084 | 0.0001 | 0.050 | -4.56 | -2.69 |
| no $CO_2$ | 3 | 7.32 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.082 | 0.0001 | 0.050 | -4.57 | -2.68 |
| no $CO_2$ | 4 | 7.47 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.080 | 0.0001 | 0.050 | -4.58 | -2.67 |
| no $CO_2$ | 5 | 7.68 | 0.08 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.076 | 0.0001 | 0.050 | -4.59 | -2.66 |
| no $CO_2$ | 6 | 7.68 | 0.08 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.076 | 0.0001 | 0.050 | -4.59 | -2.66 |
| no $CO_2$ | 7 | 8.00 | 0.07 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.068 | 0.0001 | 0.049 | -4.64 | -2.63 |
| no $CO_2$ | unbuffered | 6.97 | 0.05 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.038 | 0.0001 | 0.000 | -4.85 | -2.49 |
| log $PCO_2$ = -3.4 | 1 | 6.80 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.086 | 0.0001 | 0.050 | -4.55 | -2.69 |
| log $PCO_2$ = -3.4 | 2 | 7.12 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.084 | 0.0001 | 0.050 | -4.56 | -2.69 |
| log $PCO_2$ = -3.4 | 3 | 7.30 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.082 | 0.0001 | 0.050 | -4.57 | -2.68 |
| log $PCO_2$ = -3.4 | 4 | 7.45 | 0.09 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.080 | 0.0001 | 0.050 | -4.58 | -2.68 |
| log $PCO_2$ = -3.4 | 5 | 7.66 | 0.08 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.076 | 0.0001 | 0.050 | -4.59 | -2.66 |
| log $PCO_2$ = -3.4 | 6 | 7.66 | 0.08 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.076 | 0.0001 | 0.050 | -4.59 | -2.66 |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| log $PCO_2$ = -3.4 | 7 | 7.97 | 0.08 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.068 | 0.0001 | 0.049 | -4.64 | -2.63 |
| log $PCO_2$ = -3.4 | unbuffered | 5.60 | 0.05 | 0.020 | 0.0045 | 0.0049 | 0.0020 | 0.038 | 0.0001 | 0.000 | -4.85 | -2.49 |
| S-SPW buffer solutions for pH and pka measurements | | | | | | | | | | | | |
| | S-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 6.97 | 8.22 | 2.702 | 0.563 | 1.352 | 0.282 | 6.588 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | 2 | 7.31 | 8.22 | 2.702 | 0.563 | 1.352 | 0.282 | 6.585 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | 3 | 7.50 | 8.22 | 2.702 | 0.563 | 1.352 | 0.282 | 6.582 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | 4a | 7.70 | 8.21 | 2.702 | 0.563 | 1.352 | 0.282 | 6.578 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | 4b | 7.70 | 8.21 | 2.702 | 0.563 | 1.352 | 0.282 | 6.578 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | 5 | 7.89 | 8.21 | 2.702 | 0.563 | 1.352 | 0.282 | 6.573 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | 6 | 8.05 | 8.20 | 2.702 | 0.563 | 1.352 | 0.282 | 6.568 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | 7 | 8.25 | 8.20 | 2.702 | 0.563 | 1.352 | 0.282 | 6.561 | 0.0011 | 0.060 | -0.14 | -0.33 |
| no $CO_2$ | unbuffered | 5.57 | 8.17 | 2.702 | 0.563 | 1.352 | 0.282 | 6.531 | 0.0011 | 0.000 | -0.15 | -0.33 |
| log $PCO_2$ = -3.4 | 1 | 6.97 | 8.22 | 2.702 | 0.563 | 1.352 | 0.282 | 6.588 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | 2 | 7.29 | 8.22 | 2.702 | 0.563 | 1.352 | 0.282 | 6.585 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | 3 | 7.49 | 8.22 | 2.702 | 0.563 | 1.352 | 0.282 | 6.582 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | 4 | 7.67 | 8.21 | 2.702 | 0.563 | 1.352 | 0.282 | 6.578 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | 5 | 7.67 | 8.22 | 2.702 | 0.563 | 1.352 | 0.282 | 6.578 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | 6 | 7.84 | 8.21 | 2.702 | 0.563 | 1.352 | 0.282 | 6.573 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | 7 | 7.98 | 8.21 | 2.703 | 0.563 | 1.352 | 0.282 | 6.568 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | 8 | 8.13 | 8.20 | 2.703 | 0.563 | 1.352 | 0.282 | 6.561 | 0.0011 | 0.060 | -0.14 | -0.33 |
| log $PCO_2$ = -3.4 | unbuffered | 5.38 | 8.17 | 2.702 | 0.563 | 1.352 | 0.282 | 6.531 | 0.0011 | 0.000 | -0.15 | -0.33 |
| no $CO_2$ | HCl 1 | 3.16 | 8.01 | 2.649 | 0.552 | 1.326 | 0.276 | 6.402 | 0.0011 | 0.000 | -0.18 | -0.36 |
| log $PCO_2$ = -3.4 | HCl 1 | 3.16 | 8.01 | 2.649 | 0.552 | 1.326 | 0.276 | 6.402 | 0.0011 | 0.000 | -0.18 | -0.36 |
| no $CO_2$ | HCl 2 | 2.88 | 7.85 | 2.598 | 0.541 | 1.300 | 0.271 | 6.278 | 0.0011 | 0.000 | -0.21 | -0.39 |
| log $PCO_2$ = -3.4 | HCl 2 | 2.88 | 7.85 | 2.598 | 0.541 | 1.300 | 0.271 | 6.28 | 0.0011 | 0.000 | -0.21 | -0.39 |
| | 0.81x's S-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.14 | 6.68 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.350 | 0.00091 | 0.060 | -0.48 | -0.60 |
| no $CO_2$ | 2 | 7.34 | 6.67 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.348 | 0.00091 | 0.060 | -0.48 | -0.60 |
| no $CO_2$ | 3 | 7.54 | 6.67 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.345 | 0.00091 | 0.060 | -0.48 | -0.60 |
| no $CO_2$ | 4 | 7.74 | 6.67 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.341 | 0.00091 | 0.060 | -0.48 | -0.60 |
| no $CO_2$ | 5 | 7.93 | 6.66 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.335 | 0.00091 | 0.060 | -0.48 | -0.60 |
| no $CO_2$ | unbuffered | 5.24 | 6.62 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.294 | 0.00091 | 0.000 | -0.49 | -0.60 |
| log $PCO_2$ = -3.4 | 1 | 7.14 | 6.68 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.350 | 0.00091 | 0.060 | -0.48 | -0.60 |
| log $PCO_2$ = -3.4 | 2 | 7.33 | 6.67 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.348 | 0.00091 | 0.060 | -0.48 | -0.60 |
| log $PCO_2$ = -3.4 | 3 | 7.52 | 6.67 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.345 | 0.00091 | 0.060 | -0.48 | -0.60 |
| log $PCO_2$ = -3.4 | 4 | 7.71 | 6.67 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.341 | 0.00091 | 0.060 | -0.48 | -0.60 |
| log $PCO_2$ = -3.4 | 5 | 7.89 | 6.66 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.336 | 0.00091 | 0.060 | -0.48 | -0.60 |
| log $PCO_2$ = -3.4 | unbuffered | 5.16 | 6.62 | 2.190 | 0.4563 | 1.0961 | 0.2282 | 5.294 | 0.00091 | 0.000 | -0.49 | -0.60 |
| | 0.60x's S-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.05 | 4.96 | 1.620 | 0.338 | 0.812 | 0.169 | 3.974 | 0.0007 | 0.060 | -0.90 | -0.92 |
| no $CO_2$ | 2 | 7.38 | 4.95 | 1.620 | 0.338 | 0.812 | 0.169 | 3.971 | 0.0007 | 0.060 | -0.90 | -0.92 |
| no $CO_2$ | 3 | 7.58 | 4.95 | 1.620 | 0.338 | 0.812 | 0.169 | 3.968 | 0.0007 | 0.060 | -0.90 | -0.92 |
| no $CO_2$ | 4 | 7.77 | 4.95 | 1.620 | 0.338 | 0.812 | 0.169 | 3.964 | 0.0007 | 0.060 | -0.90 | -0.93 |
| no $CO_2$ | 5a | 7.96 | 4.94 | 1.620 | 0.338 | 0.812 | 0.169 | 3.959 | 0.0007 | 0.060 | -0.90 | -0.93 |

## Table B.1: As-Made Buffer Solutions for pH and pK'a Measurements (Units are mol/kg water)

| Details | Solution | pH | mu | Na | K | Ca | Mg | Cl | $SO_4$ | Tris | si_ halite | si_ gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| no $CO_2$ | 5b | 7.96 | 4.94 | 1.620 | 0.338 | 0.812 | 0.169 | 3.959 | 0.0007 | 0.060 | -0.90 | -0.93 |
| no $CO_2$ | 6 | 8.18 | 4.93 | 1.620 | 0.338 | 0.812 | 0.169 | 3.952 | 0.0007 | 0.060 | -0.91 | -0.93 |
| no $CO_2$ | unbuffered | 6.19 | 4.90 | 1.620 | 0.338 | 0.812 | 0.169 | 3.917 | 0.0007 | 0.000 | -0.91 | -0.93 |
| log $PCO_2$ = -3.4 | 1 | 7.04 | 4.96 | 1.620 | 0.338 | 0.812 | 0.169 | 3.974 | 0.0007 | 0.060 | -0.90 | -0.92 |
| log $PCO_2$ = -3.4 | 2 | 7.36 | 4.95 | 1.620 | 0.338 | 0.812 | 0.169 | 3.971 | 0.0007 | 0.060 | -0.90 | -0.92 |
| log $PCO_2$ = -3.4 | 3 | 7.56 | 4.95 | 1.620 | 0.338 | 0.812 | 0.169 | 3.968 | 0.0007 | 0.060 | -0.90 | -0.92 |
| log $PCO_2$ = -3.4 | 4 | 7.75 | 4.95 | 1.620 | 0.338 | 0.812 | 0.169 | 3.964 | 0.0007 | 0.060 | -0.90 | -0.93 |
| log $PCO_2$ = -3.4 | 5a | 7.93 | 4.94 | 1.620 | 0.338 | 0.812 | 0.169 | 3.959 | 0.0007 | 0.060 | -0.90 | -0.93 |
| log $PCO_2$ = -3.4 | 5b | 7.93 | 4.94 | 1.620 | 0.338 | 0.812 | 0.169 | 3.960 | 0.0007 | 0.060 | -0.90 | -0.93 |
| log $PCO_2$ = -3.4 | 6 | 8.12 | 4.94 | 1.620 | 0.338 | 0.812 | 0.169 | 3.953 | 0.0007 | 0.060 | -0.91 | -0.93 |
| log $PCO_2$ = -3.4 | unbuffered | 5.56 | 4.90 | 1.620 | 0.338 | 0.812 | 0.169 | 3.917 | 0.0007 | 0.000 | -0.91 | -0.93 |
| | 0.36x's S-SPW | | | | | | | | | | | |
| | soln | pH | mu | Na | K | Ca | Mg | Cl | S(6) | Tris | si_halite | si_gypsum |
| no $CO_2$ | 1 | 7.15 | 2.96 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.367 | 0.00041 | 0.060 | -1.50 | -1.35 |
| no $CO_2$ | 2 | 7.44 | 2.95 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.364 | 0.00041 | 0.060 | -1.50 | -1.35 |
| no $CO_2$ | 3 | 7.63 | 2.95 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.360 | 0.00041 | 0.059 | -1.50 | -1.35 |
| no $CO_2$ | 4 | 7.82 | 2.95 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.357 | 0.00041 | 0.060 | -1.50 | -1.35 |
| no $CO_2$ | 5 | 7.99 | 2.94 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.352 | 0.00041 | 0.060 | -1.51 | -1.36 |
| no $CO_2$ | 6 | 8.22 | 2.94 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.345 | 0.00041 | 0.060 | -1.51 | -1.36 |
| no $CO_2$ | unbuffered | 7.12 | 2.90 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.310 | 0.00041 | 0.000 | -1.51 | -1.35 |
| log $PCO_2$ = -3.4 | 1 | 7.14 | 2.96 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.367 | 0.00041 | 0.060 | -1.50 | -1.35 |
| log $PCO_2$ = -3.4 | 2 | 7.42 | 2.95 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.364 | 0.00041 | 0.060 | -1.50 | -1.35 |
| log $PCO_2$ = -3.4 | 3 | 7.62 | 2.95 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.360 | 0.00041 | 0.059 | -1.50 | -1.35 |
| log $PCO_2$ = -3.4 | 4 | 7.79 | 2.95 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.357 | 0.00041 | 0.060 | -1.50 | -1.35 |
| log $PCO_2$ = -3.4 | 5 | 7.96 | 2.94 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.352 | 0.00041 | 0.060 | -1.51 | -1.36 |
| log $PCO_2$ = -3.4 | 6 | 8.17 | 2.94 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.345 | 0.00041 | 0.060 | -1.51 | -1.36 |
| log $PCO_2$ = -3.4 | unbuffered | 5.70 | 2.90 | 0.974 | 0.1591 | 0.4875 | 0.1015 | 2.310 | 0.00041 | 0.000 | -1.51 | -1.35 |
| | 0.03x's S-SPW | | | | | | | | | | | |
| no $CO_2$ | 1 | 7.04 | 0.28 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.231 | 0.00003 | 0.050 | -3.62 | -2.73 |
| no $CO_2$ | 2 | 7.38 | 0.27 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.228 | 0.00003 | 0.050 | -3.63 | -2.73 |
| no $CO_2$ | 3 | 7.58 | 0.27 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.225 | 0.00003 | 0.050 | -3.63 | -2.73 |
| no $CO_2$ | 4 | 7.79 | 0.27 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.221 | 0.00003 | 0.050 | -3.64 | -2.72 |
| no $CO_2$ | 5 | 7.99 | 0.26 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.216 | 0.00003 | 0.050 | -3.64 | -2.72 |
| no $CO_2$ | 6 | 8.24 | 0.25 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.209 | 0.00003 | 0.050 | -3.66 | -2.71 |
| no $CO_2$ | unbuffered | 7.05 | 0.23 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.184 | 0.00003 | 0.000 | -3.70 | -2.68 |
| log $PCO_2$ = -3.4 | 1 | 7.03 | 0.28 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.231 | 0.00003 | 0.050 | -3.62 | -2.73 |
| log $PCO_2$ = -3.4 | 2 | 7.36 | 0.27 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.228 | 0.00003 | 0.050 | -3.63 | -2.73 |
| log $PCO_2$ = -3.4 | 3 | 7.57 | 0.27 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.225 | 0.00003 | 0.050 | -3.63 | -2.73 |
| log $PCO_2$ = -3.4 | 4 | 7.76 | 0.27 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.221 | 0.00003 | 0.050 | -3.64 | -2.73 |
| log $PCO_2$ = -3.4 | 5 | 7.96 | 0.26 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.216 | 0.00003 | 0.050 | -3.64 | -2.72 |
| log $PCO_2$ = -3.4 | 6 | 8.19 | 0.26 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.209 | 0.00003 | 0.050 | -3.66 | -2.71 |
| log $PCO_2$ = -3.4 | unbuffered | 5.62 | 0.23 | 0.076 | 0.0158 | 0.0381 | 0.0079 | 0.184 | 0.00003 | 0.000 | -3.70 | -2.68 |

## B.5 POTENTIOMETRIC pH MEASUREMENTS

### Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| Just Tris | | Ross 815600 + Barnant 20 meter | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5a | 5b | 6 | ° C |
| | *I (mol/kg)* | *0.05* | *0.04* | *0.04* | *0.04* | *0.04* | *0.03* | *0.03* | |
| modelled pH, no $CO_2$ | | 7.10 | 7.29 | 7.43 | 7.43 | 7.65 | 7.86 | 8.04 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 7.09 | 7.28 | 7.42 | 7.42 | 7.63 | 7.84 | 8.01 | 25.00 |
| measured pH | 9-Jan-14 | 7.08 | 7.28 | 7.42 | 7.42 | 7.64 | 7.86 | 8.04 | 24.88 |
| measured pH | 10-Jan-14 | 7.08 | 7.28 | 7.42 | 7.42 | 7.64 | 7.86 | 8.04 | 24.48 |
| measured pH | 10-Jan-14 | 7.06 | 7.26 | 7.41 | 7.41 | 7.63 | 7.85 | 8.03 | 24.98 |
| measured pH | Mean | 7.07 | 7.27 | 7.42 | 7.42 | 7.64 | 7.86 | 8.04 | 24.78 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.26 |
| mV | 9-Jan-14 | -18 | -30 | -38 | -38 | -51 | -63 | -74 | |
| mV | 10-Jan-14 | -18 | -30 | -38 | -38 | -51 | -64 | -74 | |
| mV | 10-Jan-14 | -17 | -29 | -38 | -38 | -51 | -63 | -74 | |
| mV | Mean | -18 | -30 | -38 | -38 | -51 | -63 | -74 | |
| mV | σ | 1 | 1 | 0 | 0 | 0 | 1 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5a | 5b | 6 | |
| measured pH | 9-Jan-14 | 7.08 | 7.28 | 7.42 | 7.43 | 7.65 | 7.86 | 8.05 | |
| measured pH | 10-Jan-14 | 7.08 | 7.28 | 7.43 | 7.43 | 7.65 | 7.87 | 8.06 | |
| measured pH | 10-Jan-14 | 7.06 | 7.26 | 7.41 | 7.41 | 7.63 | 7.85 | 8.03 | |
| measured pH | Mean | 7.07 | 7.27 | 7.42 | 7.42 | 7.64 | 7.86 | 8.05 | |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | |
| mV | 9-Jan-14 | 1 | -10 | -18 | -18 | -31 | -44 | -54 | |
| mV | 10-Jan-14 | 1 | -10 | -18 | -18 | -31 | -44 | -55 | |
| mV | 10-Jan-14 | 2 | -9 | -18 | -18 | -31 | -43 | -54 | |
| mV | Mean | 1 | -10 | -18 | -18 | -31 | -44 | -54 | |
| mV | σ | 1 | 1 | 0 | 0 | 0 | 1 | 1 | |

| 0.1m NaCl | | Ross 815600 + Barnant 20 meter | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | ° C |
| | *I (mol/kg)* | *0.10* | *0.10* | *0.10* | *0.10* | *0.10* | *0.10* | *0.10* | *0.10* | |
| modelled pH, no $CO_2$ | | 7.15 | 7.49 | 7.71 | 7.95 | 8.13 | 8.33 | 8.49 | 8.89 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 7.13 | 7.48 | 7.69 | 7.93 | 8.10 | 8.29 | 8.42 | 8.69 | 25.00 |
| measured pH | 9-Sep-13 | 7.14 | 7.49 | 7.71 | 7.95 | 8.14 | 8.34 | 8.50 | 8.91 | 24.00 |
| measured pH | 11-Sep-13 | 7.12 | 7.47 | 7.70 | 7.94 | 8.13 | 8.33 | 8.49 | 8.90 | 24.80 |
| measured pH | 13-Sep-13 | 7.10 | 7.44 | 7.68 | 7.92 | 8.10 | 8.31 | 8.47 | - | 25.50 |
| measured pH | Mean | 7.12 | 7.47 | 7.70 | 7.94 | 8.12 | 8.33 | 8.49 | 8.91 | 24.77 |
| measured pH | σ | 0.02 | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 | 0.75 |
| mV | 9-Sep-13 | -13 | -33 | -46 | -60 | -70 | -83 | -92 | -115 | |
| mV | 11-Sep-13 | -13 | -33 | -46 | -60 | -70 | -83 | -92 | -115 | |
| mV | 13-Sep-13 | -11 | -32 | -44 | -59 | -69 | -81 | -91 | - | |
| mV | Mean | -12 | -33 | -45 | -60 | -70 | -82 | -92 | -115 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | |

| 1.0m NaCl | | Ross 815600 + Barnant 20 meter | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | ° C |
| | *I (mol/kg)* | *1.02* | *1.02* | *1.03* | *1.03* | *1.03* | *1.03* | |
| modelled pH, no $CO_2$ | | 7.04 | 7.28 | 7.51 | 7.85 | 8.02 | 8.18 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 7.03 | 7.26 | 7.49 | 7.82 | 7.99 | 8.13 | 25.00 |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| measured pH | 18-Sep-13 | 6.98 | 7.24 | 7.47 | 7.81 | 7.99 | 8.14 | 23.70 |
| measured pH | 24-Sep-13 | 6.94 | 7.19 | 7.42 | 7.77 | 7.95 | 8.11 | 25.10 |
| measured pH | 24-Sep-13 | 6.94 | 7.19 | 7.42 | 7.77 | 7.95 | 8.11 | 24.60 |
| measured pH | Mean | 6.95 | 7.21 | 7.44 | 7.78 | 7.96 | 8.12 | |
| measured pH | σ | 0.02 | 0.03 | 0.03 | 0.02 | 0.02 | 0.02 | |
| mV | 18-Sep-13 | -5 | -20 | -33 | -52 | -63 | -72 | |
| mV | 24-Sep-13 | -2 | -16 | -30 | -50 | -61 | -70 | |
| mV | 24-Sep-13 | -3 | -17 | -30 | -50 | -60 | -70 | |
| mV | Mean | -3 | -18 | -31 | -51 | -61 | -71 | |
| mV | σ | 2 | 2 | 2 | 1 | 2 | 1 | |
| | | | | | | | | |
| 1.0m NaCl | | Ross 815600 + Barnant 20 meter | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | ° C |
| | *I (mol/kg)* | *0.99* | *1.00* | *1.00* | *1.00* | *1.00* | *1.00* | |
| modelled pH, no $CO_2$ | | 6.86 | 7.18 | 7.44 | 7.62 | 7.84 | 8.02 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 6.84 | 7.16 | 7.42 | 7.60 | 7.81 | 7.98 | 25.00 |
| measured pH | 13-Jan-14 | 6.77 | 7.10 | 7.37 | 7.55 | 7.78 | 7.96 | 24.61 |
| measured pH | 13-Jan-14 | 6.76 | 7.08 | 7.36 | 7.54 | 7.77 | 7.95 | 24.69 |
| measured pH | 14-Jan-14 | 6.75 | 7.08 | 7.35 | 7.53 | 7.76 | 7.94 | 24.64 |
| measured pH | Mean | 6.76 | 7.09 | 7.36 | 7.54 | 7.77 | 7.95 | 24.65 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.04 |
| mV | 18-Sep-13 | 0 | -19 | -35 | -46 | -59 | -69 | |
| mV | 24-Sep-13 | 1 | -18 | -34 | -45 | -58 | -68 | |
| mV | 24-Sep-13 | 1 | -18 | -34 | -45 | -58 | -68 | |
| mV | Mean | 1 | -18 | -34 | -45 | -58 | -68 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | |
| measured pH | 13-Jan-14 | 6.84 | 7.16 | 7.42 | 7.60 | 7.81 | 7.98 | |
| measured pH | 13-Jan-14 | 6.76 | 7.09 | 7.36 | 7.54 | 7.76 | 7.94 | |
| measured pH | 14-Jan-14 | 6.75 | 7.07 | 7.35 | 7.53 | 7.76 | 7.93 | |
| measured pH | Mean | 6.73 | 7.07 | 7.34 | 7.52 | 7.75 | 7.93 | |
| measured pH | σ | 6.75 | 7.08 | 7.35 | 7.53 | 7.76 | 7.93 | |
| mV | 18-Sep-13 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | |
| mV | 24-Sep-13 | 19 | 0 | -15 | -25 | -39 | -49 | |
| mV | 24-Sep-13 | 20 | 1 | -14 | -25 | -38 | -48 | |
| mV | Mean | 20 | 1 | -14 | -27 | -38 | -48 | |
| mV | σ | 20 | 1 | -14 | -26 | -38 | -48 | |
| | | 1 | 1 | 1 | 1 | 1 | 1 | |
| | | | | | | | | |
| 5.0m NaCl | | Ross 815600 + Barnant 20 meter | | | | | | |
| | *I (mol/kg)* | *5.00* | *5.00* | *5.00* | *5.00* | *5.00* | *5.00* | ° C |
| modelled pH, no $CO_2$ | | 6.87 | 7.18 | 7.41 | 7.64 | 7.98 | 8.15 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 6.84 | 7.15 | 7.38 | 7.61 | 7.93 | 8.09 | 25.00 |
| measured pH | 27-Sep-13 | 6.63 | 6.94 | 7.18 | 7.42 | 7.76 | 7.94 | 25.55 |
| measured pH | 30-Sep-13 | 6.62 | 6.93 | 7.17 | 7.41 | 7.75 | 7.93 | 25.32 |
| measured pH | 1-Oct-13 | 6.63 | 6.94 | 7.18 | 7.41 | 7.76 | 7.94 | 25.20 |
| measured pH | Mean | 6.63 | 6.94 | 7.18 | 7.41 | 7.76 | 7.94 | 25.36 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.18 |
| mV | 27-Sep-13 | 15 | -3 | -17 | -31 | -51 | -61 | |
| mV | 30-Sep-13 | 16 | -3 | -17 | -30 | -50 | -61 | |
| mV | 1-Oct-13 | 15 | -3 | -17 | -31 | -50 | -61 | |
| mV | Mean | 15 | -3 | -17 | -31 | -50 | -61 | |
| mV | σ | 1 | 0 | 0 | 1 | 1 | 0 | |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | HCl 1 | HCl 2 | HCl 3 | 1a | 1b | 2a | 2b | 3 | 4 | 4b | 5 | 6 | 7 | 8 | ° C |
| | *I (mol/kg)* | *4.78* | *4.64* | *4.89* | *4.95* | *4.88* | *4.94* | *4.88* | *4.94* | *4.94* | *4.94* | *4.93* | *4.91* | *4.90* | *4.89* | |
| modelled pH, no $CO_2$ | | 3.43 | 3.06 | 1.61 | 6.92 | 6.91 | 7.33 | 7.33 | 7.56 | 7.68 | 7.68 | 8.07 | 8.37 | 8.67 | 9.06 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 3.43 | 3.06 | 1.61 | 6.91 | 6.90 | 7.32 | 7.32 | 7.55 | 7.66 | 7.66 | 8.03 | 8.27 | 8.45 | 8.59 | 25.00 |
| measured pH | 24-Oct-13 | - | - | - | 6.53 | 6.55 | 6.95 | 6.97 | 7.19 | 7.31 | - | 7.71 | 8.02 | 8.32 | 8.72 | 25.01 |
| measured pH | 25-Oct-13 | - | - | - | 6.50 | 6.52 | 6.93 | 6.94 | 7.16 | 7.29 | 7.25 | 7.69 | 8.00 | 8.30 | 8.70 | 24.60 |
| measured pH | 28-Oct-13 | - | - | - | 6.50 | 6.52 | 6.93 | 6.94 | 7.16 | 7.29 | 7.25 | 7.69 | 8.00 | 8.30 | 8.70 | 24.70 |
| measured pH | 30-Oct-13 | 3.13 | 2.66 | - | - | - | - | - | - | - | - | - | - | - | - | 25.18 |
| measured pH | 5-Nov-13 | 3.19 | 2.69 | - | 6.50 | 6.51 | 6.92 | 6.94 | 7.16 | 7.29 | 7.28 | 7.69 | 8.00 | 8.30 | 8.69 | 25.30 |
| measured pH | 8-Nov-13 | 3.19 | 2.68 | - | 6.50 | 6.52 | 6.93 | 6.95 | 7.17 | 7.29 | 7.29 | 7.69 | 8.00 | 8.31 | 8.71 | 25.05 |
| measured pH | 21-Nov-13 | 3.19 | 2.68 | - | 6.49 | 6.51 | 6.92 | 6.94 | 7.15 | 7.29 | 7.29 | 7.69 | 8.00 | 8.30 | 8.70 | 25.09 |
| measured pH | 2-Dec-13 | 3.21 | 2.69 | - | 6.50 | 6.52 | 6.93 | 6.95 | 7.16 | 7.29 | 7.29 | 7.70 | 8.01 | 8.31 | 8.71 | 24.90 |
| measured pH | 11-Dec-13 | 3.21 | 2.69 | - | 6.49 | 6.51 | 6.92 | 6.93 | 7.15 | 7.28 | 7.28 | 7.69 | 7.99 | 8.30 | 8.69 | 24.78 |
| measured pH | 23-Dec-13 | - | - | - | 6.48 | 6.50 | 6.91 | 6.93 | 7.14 | 7.28 | 7.27 | 7.68 | 7.99 | 8.29 | 8.68 | 25.00 |
| measured pH | 3-Feb-14 | - | - | 1.22 | - | - | - | - | - | - | - | - | - | - | - | 25.18 |
| measured pH | 4-Feb-14 | - | - | 1.23 | - | - | - | - | - | - | - | - | - | - | - | 24.96 |
| measured pH | 4-Feb-14 | - | - | 1.23 | - | - | - | - | - | - | - | - | - | - | - | 25.18 |
| measured pH | Mean | 3.19 | 2.68 | 1.23 | 6.50 | 6.52 | 6.93 | 6.94 | 7.16 | 7.29 | 7.28 | 7.69 | 8.00 | 8.30 | 8.70 | 24.96 |
| measured pH | σ | 0.03 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.13 |
| mV | 24-Oct-13 | - | - | - | 19 | 18 | -5 | -6 | -19 | -26 | | -49 | -67 | -84 | -107 | |
| mV | 25-Oct-13 | - | - | - | 21 | 20 | -4 | -5 | -17 | -25 | -24 | -48 | -66 | -84 | -107 | |
| mV | 28-Oct-13 | - | - | - | 21 | 20 | -4 | -5 | -17 | -25 | -24 | -48 | -66 | -84 | -107 | |
| mV | 30-Oct-13 | 217 | 244 | - | - | - | - | - | - | - | - | - | - | - | - | |
| mV | 5-Nov-13 | 213 | 242 | - | 20 | 20 | -4 | -5 | -18 | -25 | -25 | -49 | -67 | -84 | -107 | |
| mV | 8-Nov-13 | 213 | 242 | - | 20 | 19 | -5 | -6 | -18 | -26 | -25 | -49 | -67 | -85 | -108 | |
| mV | 21-Nov-13 | 211 | 241 | - | 19 | 18 | -5 | -7 | -19 | -27 | -27 | -50 | -68 | -86 | -109 | |
| mV | 2-Dec-13 | 210 | 240 | - | 19 | 18 | -6 | -7 | -19 | -27 | -27 | -51 | -68 | -86 | -109 | |
| mV | 11-Dec-13 | 209 | 239 | - | 19 | 18 | -7 | -7 | -20 | -28 | -28 | -51 | -69 | -87 | -109 | |
| mV | 23-Dec-13 | - | - | - | 18 | 17 | -7 | -8 | -20 | -28 | -28 | -52 | -70 | -87 | -110 | |
| mV | 3-Feb-14 | - | - | 321 | - | - | - | - | - | - | - | - | - | - | - | |
| mV | 4-Feb-14 | - | - | 320 | - | - | - | - | - | - | - | - | - | - | - | |
| mV | 4-Feb-14 | - | - | 321 | - | - | - | - | - | - | - | - | - | - | - | |
| mV | Mean | 212 | 241 | 321 | 20 | 19 | -5 | -6 | -19 | -26 | -26 | -50 | -68 | -85 | -108 | |
| mV | σ | 3 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 1 | 1 | 1 | 1 | |
| SureFlow 8165BNWP + Hanna HI 8014 meter | | | | | | | | | | | | | | | | |
| measured pH | 8-Nov-13 | 3.19 | 2.69 | - | 6.50 | 6.51 | 6.92 | 6.94 | 7.15 | 7.28 | 7.28 | 7.68 | 7.99 | 8.30 | 8.70 | 25.05 |
| mV | 8-Nov-13 | 231 | 260 | - | 39 | 38 | 14 | 13 | 1 | -5 | -4 | -28 | -46 | -64 | -87 | |
| SureFlow + Jenco Model 5005 meter | | | | | | | | | | | | | | | | |
| measured pH | 21-Nov-13 | 3.19 | - | | 6.49 | 6.51 | 6.92 | 6.94 | 7.15 | 7.28 | 7.28 | 7.68 | 7.99 | 8.30 | 8.69 | 24.79 |
| measured pH | 3-Feb-14 | - | - | 1.21 | - | - | - | - | - | - | - | - | - | - | - | 25.18 |
| measured pH | 4-Feb-14 | - | - | 1.23 | - | - | - | - | - | - | - | - | - | - | - | 24.96 |
| measured pH | 4-Feb-14 | - | - | 1.23 | - | - | - | - | - | - | - | - | - | - | - | 25.18 |
| mV | 21-Nov-13 | 231 | - | - | 38 | 37 | 14 | 12 | 0 | -7 | -6 | -30 | -48 | -66 | -88 | |
| mV | 3-Feb-14 | - | - | 339 | - | - | - | - | - | - | - | - | - | - | - | |
| mV | 4-Feb-14 | - | - | 339 | - | - | - | - | - | - | - | - | - | - | - | |
| mV | 4-Feb-14 | - | - | 340 | - | - | - | - | - | - | - | - | - | - | - | |

| 1.57x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | HCl | 1 | 2 | 3a | 3b | 4 | 5 | 6 | 7a | 7b | ° C |
| | *I (mol/kg)* | *7.26* | *7.67* | *7.67* | *7.67* | *7.67* | *7.67* | *7.67* | *7.66* | *7.65* | *7.65* | |
| modelled pH, no $CO_2$ | | 2.64 | 6.94 | 7.12 | 7.26 | 7.26 | 7.45 | 7.65 | 7.94 | 8.45 | 8.45 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 2.64 | 6.92 | 7.11 | 7.24 | 7.24 | 7.42 | 7.62 | 7.87 | 8.22 | 8.22 | 25.00 |
| measured pH | 13-Nov-13 | - | 6.4 | 6.58 | 6.72 | 6.72 | 6.91 | 7.12 | 7.41 | 7.94 | 7.94 | 25.07 |
| measured pH | 14-Nov-13 | - | 6.38 | 6.56 | 6.69 | 6.69 | 6.89 | 7.1 | 7.39 | 7.92 | 7.92 | 25.08 |
| measured pH | 15-Nov-13 | - | 6.36 | 6.55 | 6.7 | 6.7 | 6.9 | 7.11 | 7.4 | 7.93 | 7.93 | 25.09 |
| measured pH | 21-Nov-13 | 2.14 | - | - | - | - | - | - | - | - | - | |
| measured pH | Mean | 2.14 | 6.38 | 6.56 | 6.70 | 6.70 | 6.90 | 7.11 | 7.40 | 7.93 | 7.93 | 25.08 |
| measured pH | σ | NA | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| mV | 13-Nov-13 | - | 26 | 16 | 8 | 8 | -4 | -16 | -32 | -63 | -63 | |
| mV | 14-Nov-13 | - | 27 | 17 | 9 | 9 | -3 | -15 | -32 | -63 | -63 | |
| mV | 15-Nov-13 | - | 28 | 18 | 9 | 9 | -3 | -15 | -32 | -63 | -63 | |
| mV | Mean | 272 | 27 | 17 | 9 | 9 | -3 | -15 | -32 | -63 | -63 | |
| mV | σ | NA | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | | | |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | HCl | 1 | 2 | 3a | 3b | 4 | 5 | 6 | 7a | 7b |
|---|---|---|---|---|---|---|---|---|---|---|---|
| measured pH | 13-Nov-13 | - | 6.39 | 6.57 | 6.70 | 6.70 | 6.90 | 7.10 | 7.39 | 7.92 | 7.92 |
| measured pH | 14-Nov-13 | - | 6.38 | 6.55 | 6.69 | 6.69 | 6.89 | 7.1 | 7.39 | 7.92 | 7.92 |
| measured pH | 15-Nov-13 | - | 6.34 | 6.53 | 6.68 | 6.68 | 6.88 | 7.09 | 7.38 | 7.9 | 7.91 |
| measured pH | 21-Nov-13 | 2.15 | - | - | - | - | - | - | - | - | - |
| measured pH | Mean | 2.15 | 6.37 | 6.55 | 6.69 | 6.69 | 6.89 | 7.10 | 7.39 | 7.91 | 7.92 |
| measured pH | σ | NA | 0.03 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| mV | 13-Nov-13 | - | 45 | 34 | 27 | 27 | 15 | 3 | -13 | -43 | -43 |
| mV | 14-Nov-13 | - | 45 | 35 | 27 | 27 | 16 | 4 | -12 | -43 | -43 |
| mV | 15-Nov-13 | - | 47 | 36 | 28 | 28 | 16 | 4 | -12 | -43 | -43 |
| mV | Mean | 291 | 46 | 35 | 27 | 27 | 16 | 4 | -12 | -43 | -43 |
| mV | σ | NA | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 |

| 1.45x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | HCl | 1 | 2 | 3 | 4 | 5 | 6 | 7a | ° C |
| | *I (mol/kg)* | *6.51* | *7.09* | *7.09* | *7.09* | *7.08* | *7.08* | *7.07* | *7.06* | |
| modelled pH, no $CO_2$ | | 2.74 | 7.08 | 7.31 | 7.48 | 7.60 | 7.87 | 8.05 | 8.35 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 2.74 | 7.06 | 7.30 | 7.46 | 7.58 | 7.83 | 7.98 | 8.19 | 25.00 |
| measured pH | 19-Nov-13 | - | 6.55 | 6.80 | 6.96 | 7.09 | 7.37 | 7.55 | 7.86 | 24.64 |
| measured pH | 20-Nov-13 | - | 6.54 | 6.79 | 6.95 | 7.08 | 7.36 | 7.54 | 7.85 | 25.19 |
| measured pH | 20-Nov-13 | - | 6.55 | 6.80 | 6.96 | 7.09 | 7.38 | 7.56 | 7.86 | 24.34 |
| measured pH | 21-Nov-13 | 2.23 | - | - | - | - | - | - | - | |
| measured pH | Mean | 2.23 | 6.55 | 6.80 | 6.96 | 7.09 | 7.37 | 7.55 | 7.86 | 24.72 |
| measured pH | σ | NA | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.43 |
| mV | 19-Nov-13 | - | 16 | 3 | -7 | -15 | -31 | -41 | -59 | |
| mV | 20-Nov-13 | - | 17 | 3 | -7 | -14 | -30 | -41 | -59 | |
| mV | 20-Nov-13 | - | 16 | 3 | -7 | -15 | -31 | -42 | -60 | |
| mV | 21-Nov-13 | 267 | - | - | - | - | - | - | - | |
| mV | Mean | 267 | 16 | 3 | -7 | -15 | -31 | -41 | -59 | |
| mV | σ | NA | 1 | 0 | 0 | 1 | 1 | 1 | 1 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | |
| | | HCl | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| measured pH | 19-Nov-13 | - | 6.55 | 6.79 | 6.95 | 7.08 | 7.36 | 7.54 | 7.84 | |
| measured pH | 20-Nov-13 | - | 6.53 | 6.77 | 6.94 | 7.06 | 7.33 | 7.52 | 7.83 | |
| measured pH | 20-Nov-13 | - | 6.54 | 6.78 | 6.95 | 7.08 | 7.36 | 7.54 | 7.85 | |
| measured pH | 21-Nov-13 | 2.24 | - | - | - | - | - | - | - | |
| measured pH | Mean | 2.24 | 6.54 | 6.78 | 6.95 | 7.07 | 7.35 | 7.53 | 7.84 | |
| measured pH | σ | NA | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | |
| mV | 19-Nov-13 | - | 35 | 21 | 12 | 5 | -11 | -21 | -39 | |
| mV | 20-Nov-13 | - | 36 | 22 | 13 | 5 | -10 | -20 | -38 | |
| mV | 20-Nov-13 | - | 36 | 22 | 12 | 5 | -11 | -21 | -39 | |
| mV | Mean | 286 | 36 | 22 | 12 | 5 | -11 | -21 | -39 | |
| mV | σ | NA | 1 | 1 | 1 | 0 | 1 | 1 | 1 | |

| 1.34x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | HCl1a | HCl1b | 1 | 2 | 3a | 3b | 3c | 4 | 5 | 6 | 7 | ° C |
| | *I (mol/kg)* | *6.48* | *6.48* | *6.53* | *6.53* | *6.52* | *6.52* | *6.52* | *6.52* | *6.51* | *6.50* | *6.49* | ### |
| modelled pH, no $CO_2$ | | 1.42 | 1.41 | 6.90 | 7.32 | 7.55 | 7.55 | 7.55 | 7.71 | 7.99 | 8.36 | 8.71 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 1.42 | 1.41 | 6.89 | 7.31 | 7.53 | 7.52 | 7.52 | 7.68 | 7.94 | 8.22 | 8.40 | 25.00 |
| measured pH | 27-Nov-13 | - | - | 6.40 | 6.83 | 7.07 | 7.07 | 7.07 | 7.23 | 7.52 | 7.90 | 8.27 | 24.73 |
| measured pH | 28-Nov-13 | - | - | 6.41 | 6.84 | 7.08 | 7.08 | 7.07 | 7.25 | 7.53 | 7.91 | 8.28 | 24.88 |
| measured pH | 28-Nov-13 | - | - | 6.40 | 6.83 | 7.07 | 7.07 | 7.06 | 7.23 | 7.52 | 7.90 | 8.27 | 24.87 |
| measured pH | 3-Feb-14 | 0.94 | 0.94 | - | - | - | - | - | - | - | - | - | 25.18 |
| measured pH | 4-Feb-14 | 0.95 | 0.95 | - | - | - | - | - | - | - | - | - | 24.96 |
| measured pH | 4-Feb-14 | 0.95 | 0.95 | - | - | - | - | - | - | - | - | - | 25.18 |
| measured pH | Mean | 0.95 | 0.95 | 6.40 | 6.83 | 7.07 | 7.07 | 7.07 | 7.24 | 7.52 | 7.90 | 8.27 | 24.83 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.18 |
| mV | 27-Nov-13 | - | - | 24 | 0 | -14 | -14 | -14 | -24 | -41 | -62 | -84 | |
| mV | 28-Nov-13 | - | - | 25 | 0 | -14 | -14 | -13 | -24 | -40 | -62 | -84 | |
| mV | 28-Nov-13 | - | - | 25 | 0 | -14 | -14 | -14 | -24 | -40 | -62 | -84 | |
| mV | 3-Feb-14 | 337 | 337 | - | - | - | - | - | - | - | - | - | |
| mV | 4-Feb-15 | 337 | 337 | - | - | - | - | - | - | - | - | - | |
| mV | 4-Feb-15 | 337 | 337 | - | - | - | - | - | - | - | - | - | |
| mV | Mean | 337 | 337 | 25 | 0 | -14 | -14 | -14 | -24 | -40 | -62 | -84 | |
| mV | σ | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | | | | |
| | | HCl1a | HCl1b | 1 | 2 | 3a | 3b | 3c | 4 | 5 | 6 | 7 | |
| measured pH | 27-Nov-13 | - | - | 6.40 | 6.83 | 7.06 | 7.06 | 7.06 | 7.23 | 7.52 | 7.89 | 8.27 | |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| measured pH | 28-Nov-13 | - | - | 6.39 | 6.83 | 7.06 | 7.06 | 7.06 | 7.24 | 7.54 | 7.92 | 8.31 |
| measured pH | 28-Nov-13 | - | - | 6.39 | 6.81 | 7.05 | 7.05 | 7.05 | 7.22 | 7.51 | 7.80 | 8.25 |
| measured pH | 3-Feb-14 | 0.93 | 0.93 | - | - | - | - | - | - | - | - | - |
| measured pH | 4-Feb-14 | 0.95 | 0.95 | - | - | - | - | - | - | - | - | - |
| measured pH | 4-Feb-14 | 0.95 | 0.96 | - | - | - | - | - | - | - | - | - |
| measured pH | Mean | 0.94 | 0.95 | 6.39 | 6.82 | 7.06 | 7.06 | 7.06 | 7.23 | 7.52 | 7.87 | 8.28 |
| measured pH | σ | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.06 | 0.03 |
| mV | 27-Nov-13 | - | - | 44 | 19 | 6 | 5 | 6 | -3 | -20 | -42 | -64 |
| mV | 28-Nov-13 | - | - | 44 | 19 | 6 | 6 | 6 | -4 | -20 | -42 | -64 |
| mV | 28-Nov-13 | - | - | 44 | 19 | 6 | 6 | 6 | -3 | -20 | -42 | -63 |
| mV | 3-Feb-14 | 356 | 356 | - | - | - | - | - | - | - | - | - |
| mV | 4-Feb-14 | 355 | 355 | - | - | - | - | - | - | - | - | - |
| mV | 4-Feb-14 | 356 | 355 | - | - | - | - | - | - | - | - | - |
| mV | Mean | 356 | 355 | 44 | 19 | 6 | 6 | 6 | -3 | -20 | -42 | -64 |
| mV | σ | 1 | 1 | 0 | 0 | 0 | 1 | 0 | 1 | 0 | 0 | 1 |

| 1.22x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | ° C |
| | *I (mol/kg)* | *5.97* | *5.97* | *5.97* | *5.97* | *5.96* | *5.95* | *5.95* | |
| modelled pH, no $CO_2$ | | 7.09 | 7.33 | 7.55 | 7.72 | 7.89 | 8.13 | 8.36 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 7.07 | 7.31 | 7.53 | 7.69 | 7.85 | 8.06 | 8.23 | 25.00 |
| measured pH | 3-Dec-13 | 6.64 | 6.88 | 7.11 | 7.28 | 7.45 | 7.70 | 7.94 | 24.36 |
| measured pH | 4-Dec-13 | 6.63 | 6.87 | 7.10 | 7.27 | 7.44 | 7.69 | 7.93 | 24.87 |
| measured pH | 4-Dec-13 | 6.63 | 6.87 | 7.10 | 7.27 | 7.45 | 7.69 | 7.93 | 24.83 |
| measured pH | 6-Dec-13 | 6.63 | 6.87 | 7.11 | 7.28 | 7.45 | 7.70 | 7.94 | 24.57 |
| measured pH | Mean | 6.63 | 6.87 | 7.11 | 7.28 | 7.45 | 7.70 | 7.94 | 24.69 |
| measured pH | σ | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.24 |
| mV | 3-Dec-13 | 10 | -4 | -17 | -27 | -37 | -51 | -65 | |
| mV | 4-Dec-13 | 11 | -3 | -17 | -26 | -37 | -51 | -65 | |
| mV | 4-Dec-13 | 11 | -3 | -17 | -27 | -37 | -51 | -65 | |
| mV | 6-Dec-13 | 11 | -3 | -17 | -27 | -37 | -51 | -65 | |
| mV | Mean | 11 | -3 | -17 | -27 | -37 | -51 | -65 | |
| mV | σ | 1 | 1 | 0 | 1 | 0 | 0 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| measured pH | 3-Dec-13 | 6.63 | 6.87 | 7.10 | 7.27 | 7.45 | 7.69 | 7.93 | |
| measured pH | 4-Dec-13 | 6.62 | 6.86 | 7.10 | 7.26 | 7.44 | 7.68 | 7.93 | |
| measured pH | 4-Dec-13 | 6.62 | 6.86 | 7.09 | 7.26 | 7.43 | 7.68 | 7.92 | |
| measured pH | 6-Dec-13 | 6.62 | 6.86 | 7.09 | 7.26 | 7.44 | 7.69 | 7.94 | |
| measured pH | Mean | 6.62 | 6.86 | 7.10 | 7.26 | 7.44 | 7.68 | 7.93 | |
| measured pH | σ | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | |
| mV | 3-Dec-13 | 30 | 16 | 2 | -7 | -17 | -31 | -45 | |
| mV | 4-Dec-13 | 30 | 16 | 3 | -6 | -16 | -30 | -45 | |
| mV | 4-Dec-13 | 30 | 16 | 3 | -6 | -16 | -30 | -44 | |
| mV | 6-Dec-13 | 30 | 16 | 3 | -6 | -17 | -31 | -45 | |
| mV | Mean | 30 | 16 | 3 | -6 | -17 | -31 | -45 | |
| mV | σ | 0 | 0 | 1 | 1 | 1 | 1 | 1 | |

| 1.22x's L-SPWb | | Ross 815600 + Barnant 20 meter | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | temp |
| | *I (mol/kg)* | *5.97* | *5.97* | *5.97* | *5.97* | *5.96* | *5.95* | *5.95* | |
| modelled pH, no $CO_2$ | | 7.09 | 7.33 | 7.55 | 7.72 | 7.89 | 8.13 | 8.36 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 7.08 | 7.31 | 7.53 | 7.69 | 7.85 | 8.06 | 8.23 | 25.00 |
| measured pH | 4-Mar-14 | 6.63 | 6.87 | 7.11 | 7.27 | 7.45 | 7.69 | 7.94 | 25.07 |
| measured pH | 5-Mar-14 | 6.61 | 6.86 | 7.09 | 7.26 | 7.44 | 7.68 | 7.92 | 24.95 |
| measured pH | 5-Mar-14 | 6.61 | 6.86 | 7.09 | 7.26 | 7.43 | 7.68 | 7.92 | 25.00 |
| measured pH | Mean | 6.62 | 6.86 | 7.10 | 7.26 | 7.44 | 7.68 | 7.93 | 25.01 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.06 |
| mV | 4-Mar-14 | 5 | -9 | -23 | -32 | -42 | -57 | -71 | |
| mV | 5-Mar-14 | 6 | -9 | -22 | -32 | -42 | -57 | -70 | |
| mV | 5-Mar-14 | 6 | -9 | -22 | -32 | -42 | -57 | -70 | |
| mV | Mean | 6 | -9 | -22 | -32 | -42 | -57 | -70 | |
| mV | σ | 1 | 0 | 1 | 0 | 0 | 0 | 1 | |

| L-SPW2 | | Ross 815600 + Barnant 20 meter | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | ° C |
| | *I (mol/kg)* | *4.90* | *4.90* | *4.90* | *4.89* | *4.89* | *4.88* | *4.87* | |
| modelled pH, no $CO_2$ | | 6.92 | 7.23 | 7.50 | 7.68 | 7.90 | 8.14 | 8.37 | 25.00 |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| modelled pH, log $PCO_2$ = -3.4 | | 6.91 | 7.22 | 7.48 | 7.65 | 7.86 | 8.08 | 8.26 | 25.00 |
| measured pH | 9-Dec-13 | 6.52 | 6.84 | 7.11 | 7.29 | 7.52 | 7.76 | 8.00 | 24.87 |
| measured pH | 10-Dec-13 | - | - | - | - | - | - | - | 24.91 |
| measured pH | 10-Dec-13 | 6.52 | 6.84 | 7.11 | 7.30 | 7.52 | 7.77 | 8.01 | 24.58 |
| measured pH | Mean | 6.52 | 6.84 | 7.11 | 7.30 | 7.52 | 7.77 | 8.01 | 24.79 |
| measured pH | σ | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.18 |
| mV | 9-Dec-13 | 16 | -2 | -18 | -29 | -42 | -56 | -70 | |
| mV | 10-Dec-13 | - | - | - | - | - | - | - | |
| mV | 10-Dec-13 | 17 | -2 | -18 | -29 | -41 | -56 | -70 | |
| mV | Mean | 17 | -2 | -18 | -29 | -42 | -56 | -70 | |
| mV | σ | 1 | 0 | 0 | 0 | 1 | 0 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| measured pH | 9-Dec-13 | 6.51 | 6.84 | 7.11 | 7.29 | 7.52 | 7.76 | 8.00 | |
| measured pH | 10-Dec-13 | 6.50 | 6.83 | 7.10 | 7.28 | 7.51 | 7.75 | 7.99 | |
| measured pH | 10-Dec-13 | 6.51 | 6.83 | 7.10 | 7.28 | 7.51 | 7.76 | 8.00 | |
| measured pH | Mean | 6.51 | 6.83 | 7.10 | 7.28 | 7.51 | 7.76 | 8.00 | |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | |
| mV | 9-Dec-13 | 36 | 17 | 2 | -8 | -21 | -35 | -49 | |
| mV | 10-Dec-13 | 37 | 18 | 2 | -8 | -21 | -35 | -49 | |
| mV | 10-Dec-13 | 36 | 18 | 2 | -8 | -21 | -35 | -49 | |
| mV | Mean | 36 | 18 | 2 | -8 | -21 | -35 | -49 | |
| mV | σ | 1 | 1 | 0 | 0 | 0 | 0 | 0 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0.75x L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | ° C |
| | *I (mol/kg)* | *3.61* | *3.61* | *3.61* | *3.61* | *3.60* | *3.59* | *3.59* | |
| modelled pH, no $CO_2$ | | 6.91 | 7.23 | 7.50 | 7.68 | 7.90 | 8.14 | 8.38 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 6.90 | 7.22 | 7.48 | 7.66 | 7.87 | 8.09 | 8.28 | 25.00 |
| measured pH | 12-Dec-13 | 6.61 | 6.93 | 7.20 | 7.39 | 7.61 | 7.86 | 8.10 | 24.87 |
| measured pH | 13-Dec-13 | 6.60 | 6.92 | 7.20 | 7.38 | 7.61 | 7.85 | 8.09 | 24.49 |
| measured pH | 13-Dec-13 | 6.59 | 6.91 | 7.19 | 7.37 | 7.60 | 7.84 | 8.08 | 24.86 |
| measured pH | Mean | 6.60 | 6.92 | 7.20 | 7.38 | 7.61 | 7.85 | 8.09 | 24.74 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.22 |
| mV | 12-Dec-13 | 12 | -7 | -23 | -34 | -47 | -61 | -75 | |
| mV | 13-Dec-13 | 12 | -7 | -23 | -34 | -47 | -61 | -75 | |
| mV | 13-Dec-13 | 13 | -7 | -23 | -33 | -46 | -61 | -75 | |
| mV | Mean | 12 | -7 | -23 | -34 | -47 | -61 | -75 | |
| mV | σ | 1 | 0 | 0 | 1 | 1 | 0 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | |
| measured pH | 12-Dec-13 | 6.59 | 6.92 | 7.19 | 7.37 | 7.60 | 7.84 | 8.08 | |
| measured pH | 13-Dec-13 | 6.60 | 6.92 | 7.19 | 7.38 | 7.61 | 7.86 | 8.11 | |
| measured pH | 13-Dec-13 | 6.58 | 6.90 | 7.18 | 7.37 | 7.59 | 7.84 | 8.08 | |
| measured pH | Mean | 6.59 | 6.91 | 7.19 | 7.37 | 7.60 | 7.85 | 8.09 | |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | |
| mV | 12-Dec-13 | 31 | 12 | -2 | -13 | -26 | -40 | -54 | |
| mV | 13-Dec-13 | 31 | 12 | -3 | -13 | -26 | -41 | -55 | |
| mV | 13-Dec-13 | 32 | 13 | -2 | -13 | -26 | -40 | -54 | |
| mV | Mean | 31 | 12 | -2 | -13 | -26 | -40 | -54 | |
| mV | σ | 1 | 1 | 1 | 0 | 0 | 1 | 1 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0.48x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | ° C |
| | *I (mol/kg)* | *2.38* | *2.38* | *2.38* | *2.37* | *2.37* | *2.36* | *2.35* | |
| modelled pH, no $CO_2$ | | 6.90 | 7.22 | 7.41 | 7.67 | 7.89 | 8.07 | 8.37 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 6.89 | 7.21 | 7.39 | 7.65 | 7.86 | 8.03 | 8.29 | 25.00 |
| measured pH | 17-Dec-13 | 6.68 | 7.00 | 7.20 | 7.46 | 7.68 | 7.86 | 8.16 | 24.17 |
| measured pH | 18-Dec-13 | 6.66 | 6.97 | 7.17 | 7.43 | 7.66 | 7.84 | 8.14 | 24.90 |
| measured pH | 18-Dec-13 | 6.65 | 6.97 | 7.17 | 7.43 | 7.66 | 7.84 | 8.15 | 25.04 |
| measured pH | 27-Dec-13 | 6.68 | 7.01 | 7.20 | 7.46 | 7.68 | 7.86 | 8.17 | 24.91 |
| measured pH | Mean | 6.67 | 6.99 | 7.19 | 7.45 | 7.67 | 7.85 | 8.16 | 24.70 |
| measured pH | σ | 0.01 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.40 |
| mV | 17-Dec-13 | 6 | -12 | -24 | -39 | -52 | -62 | -80 | |
| mV | 18-Dec-13 | 8 | -11 | -22 | -38 | -51 | -61 | -79 | |
| mV | 18-Dec-13 | 9 | -10 | -22 | -37 | -51 | -61 | -79 | |
| mV | 27-Dec-13 | 6 | -13 | -24 | -39 | -52 | -62 | -80 | |
| mV | Mean | 7 | -12 | -23 | -38 | -52 | -62 | -80 | |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| mV | σ | 2 | 1 | 1 | 1 | 1 | 1 | 1 | | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | |
| measured pH | 17-Dec-13 | 6.67 | 7.00 | 7.19 | 7.45 | 7.67 | 7.85 | 8.16 | | |
| measured pH | 18-Dec-13 | 6.65 | 6.97 | 7.17 | 7.43 | 7.66 | 7.84 | 8.14 | | |
| measured pH | 18-Dec-13 | 6.64 | 6.96 | 7.16 | 7.43 | 7.65 | 7.83 | 8.14 | | |
| measured pH | 27-Dec-13 | 6.66 | 6.99 | 7.18 | 7.44 | 7.66 | 7.84 | 8.15 | | |
| measured pH | Mean | 6.65 | 6.98 | 7.17 | 7.44 | 7.66 | 7.84 | 8.15 | | |
| measured pH | σ | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | | |
| mV | 17-Dec-13 | 26 | 7 | -3 | -18 | -31 | -42 | -59 | | |
| mV | 18-Dec-13 | 27 | 9 | -2 | -17 | -30 | -41 | -59 | | |
| mV | 18-Dec-13 | 28 | 9 | -2 | -17 | -30 | -40 | -58 | | |
| mV | 27-Dec-13 | 26 | 7 | -3 | -18 | -31 | -42 | -60 | | |
| mV | Mean | 27 | 8 | -3 | -18 | -31 | -41 | -59 | | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | |
| 0.24x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | | |
| | | 1 | 2 | 3 | 4a | 4b | 4c | 5 | 6 | ° C |
| | *I (mol/kg)* | *1.20* | *1.20* | *1.20* | *1.19* | *1.19* | *1.19* | *1.19* | *1.18* | |
| modelled pH, no $CO_2$ | | 6.87 | 7.19 | 7.38 | 7.52 | 7.52 | 7.52 | 7.73 | 8.03 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 6.85 | 7.18 | 7.36 | 7.50 | 7.51 | 7.50 | 7.71 | 8.00 | 25.00 |
| measured pH | 19-Dec-13 | 6.73 | 7.05 | 7.24 | 7.38 | 7.38 | 7.38 | 7.60 | 7.90 | 24.89 |
| measured pH | 20-Dec-13 | 6.71 | 7.03 | 7.23 | 7.37 | 7.37 | 7.37 | 7.58 | 7.89 | 24.96 |
| measured pH | 20-Dec-13 | 6.70 | 7.03 | 7.22 | 7.37 | 7.37 | 7.37 | 7.59 | 7.89 | 25.02 |
| measured pH | Mean | 6.71 | 7.04 | 7.23 | 7.37 | 7.37 | 7.37 | 7.59 | 7.89 | 24.96 |
| measured pH | σ | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.07 |
| mV | 19-Dec-13 | 4 | -15 | -26 | -34 | -34 | -34 | -46 | -64 | |
| mV | 20-Dec-13 | 6 | -13 | -25 | -33 | -33 | -34 | -46 | -64 | |
| mV | 20-Dec-13 | 6 | -13 | -25 | -33 | -33 | -34 | -46 | -64 | |
| mV | Mean | 5 | -14 | -25 | -33 | -33 | -34 | -46 | -64 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | |
| | | 1 | 2 | 3 | 4a | 4b | 4c | 5 | 6 | |
| measured pH | 19-Dec-13 | 6.71 | 7.04 | 7.23 | 7.37 | 7.37 | 7.36 | 7.58 | 7.89 | |
| measured pH | 20-Dec-13 | 6.69 | 7.02 | 7.22 | 7.36 | 7.36 | 7.36 | 7.57 | 7.88 | |
| measured pH | 20-Dec-13 | 6.68 | 7.02 | 7.21 | 7.36 | 7.36 | 7.36 | 7.58 | 7.88 | |
| measured pH | Mean | 6.69 | 7.03 | 7.22 | 7.36 | 7.36 | 7.36 | 7.58 | 7.88 | |
| measured pH | σ | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | |
| mV | 19-Dec-13 | 23 | 5 | -6 | -14 | -14 | -14 | -26 | -44 | |
| mV | 20-Dec-13 | 25 | 6 | -5 | -13 | -13 | -13 | -26 | -43 | |
| mV | 20-Dec-13 | 25 | 6 | -4 | -13 | -13 | -13 | -26 | -43 | |
| mV | Mean | 24 | 6 | -5 | -13 | -13 | -13 | -26 | -43 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | |
| 0.09x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | | |
| | | 1a | 1b | 2 | 3 | 4 | 5 | 6 | ° C | |
| | *I (mol/kg)* | *0.50* | *0.50* | *0.50* | *0.50* | *0.49* | *0.49* | *0.48* | | |
| modelled pH, no $CO_2$ | | 6.89 | 6.90 | 7.21 | 7.41 | 7.56 | 7.78 | 8.10 | 25.00 | |
| modelled pH, log $PCO_2$ = -3.4 | | 6.87 | 6.88 | 7.20 | 7.39 | 7.54 | 7.75 | 8.06 | 25.00 | |
| measured pH | 2-Jan-14 | 6.80 | 6.81 | 7.13 | 7.33 | 7.48 | 7.70 | 8.03 | 25.26 | |
| measured pH | 3-Jan-14 | 6.79 | 6.78 | 7.11 | 7.32 | 7.46 | 7.69 | 8.02 | 25.08 | |
| measured pH | 3-Jan-14 | 6.78 | 6.79 | 7.12 | 7.31 | 7.46 | 7.69 | 8.02 | 24.97 | |
| measured pH | Mean | 6.79 | 6.79 | 7.12 | 7.32 | 7.47 | 7.69 | 8.02 | 25.10 | |
| measured pH | σ | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.15 | |
| mV | 2-Jan-14 | -2 | -2 | -21 | -32 | -41 | -54 | -73 | | |
| mV | 3-Jan-14 | -1 | -1 | -20 | -31 | -40 | -53 | -72 | | |
| mV | 3-Jan-14 | -1 | -1 | -20 | -32 | -40 | -53 | -73 | | |
| mV | Mean | -1 | -1 | -20 | -32 | -40 | -53 | -73 | | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | |
| | | 1a | 1b | 2 | 3 | 4 | 5 | 6 | | |
| measured pH | 2-Jan-14 | 6.80 | 6.81 | 7.13 | 7.33 | 7.48 | 7.70 | 8.03 | | |
| measured pH | 3-Jan-14 | 6.78 | 6.78 | 7.11 | 7.31 | 7.46 | 7.69 | 8.02 | | |
| measured pH | 3-Jan-14 | 6.78 | 6.78 | 7.11 | 7.31 | 7.46 | 7.68 | 8.02 | | |
| measured pH | Mean | 6.79 | 6.79 | 7.12 | 7.32 | 7.47 | 7.69 | 8.02 | | |
| measured pH | σ | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | | |
| mV | 2-Jan-14 | 18 | 17 | 0 | -12 | -21 | -34 | -53 | | |
| mV | 3-Jan-14 | 19 | 19 | 0 | -11 | -20 | -33 | -52 | | |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| mV | 3-Jan-14 | 19 | 19 | 0 | -11 | -20 | -33 | -52 | |
| mV | Mean | 19 | 18 | 0 | -11 | -20 | -33 | -52 | |
| mV | σ | 1 | 1 | 0 | 1 | 1 | 1 | 1 | |
| | | | | | | | | | |
| 0.01x's L-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5a | 5b | 6 | ° C |
| | *I (mol/kg)* | *0.09* | *0.09* | *0.09* | *0.09* | *0.08* | *0.08* | *0.07* | |
| modelled pH, no $CO_2$ | | 6.81 | 7.13 | 7.32 | 7.47 | 7.68 | 7.68 | 8.00 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 6.80 | 7.12 | 7.30 | 7.45 | 7.66 | 7.66 | 7.97 | 25.00 |
| measured pH | 7-Jan-14 | 6.78 | 7.10 | 7.30 | 7.44 | 7.67 | 7.67 | 8.00 | 24.83 |
| measured pH | 8-Jan-14 | 6.77 | 7.10 | 7.29 | 7.44 | 7.66 | 7.66 | 7.99 | 24.78 |
| measured pH | 8-Jan-14 | 6.76 | 7.08 | 7.28 | 7.43 | 7.66 | 7.66 | 7.99 | 24.97 |
| measured pH | Mean | 6.77 | 7.09 | 7.29 | 7.44 | 7.66 | 7.66 | 7.99 | 24.86 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.10 |
| mV | 7-Jan-14 | 0 | -19 | -31 | -39 | -52 | -52 | -71 | |
| mV | 8-Jan-14 | 1 | -19 | -30 | -39 | -52 | -52 | -71 | |
| mV | 8-Jan-14 | 1 | -18 | -30 | -38 | -51 | -51 | -70 | |
| mV | Mean | 1 | -19 | -30 | -39 | -52 | -52 | -71 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5a | 5b | 6 | |
| measured pH | 7-Jan-14 | 6.77 | 7.10 | 7.30 | 7.44 | 7.67 | 7.67 | 8.00 | |
| measured pH | 8-Jan-14 | 6.76 | 7.09 | 7.28 | 7.43 | 7.65 | 7.65 | 7.98 | |
| measured pH | 8-Jan-14 | 6.75 | 7.07 | 7.27 | 7.42 | 7.65 | 7.65 | 7.97 | |
| measured pH | Mean | 6.76 | 7.09 | 7.28 | 7.43 | 7.66 | 7.66 | 7.98 | |
| measured pH | σ | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.02 | |
| mV | 7-Jan-14 | 19 | 0 | -11 | -19 | -32 | -32 | -51 | |
| mV | 8-Jan-14 | 19 | 0 | -10 | -19 | -32 | -32 | -51 | |
| mV | 8-Jan-14 | 20 | 1 | -10 | -18 | -31 | -31 | -51 | |
| mV | Mean | 19 | 0 | -10 | -19 | -32 | -32 | -51 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | 0 | |
| | | | | | | | | | |
| S-SPW | | Ross 815600 + Barnant 20 meter | | | | | | | |
| | | HCl1 | HCl2 | 1 | 2 | 3 | 4a | 4b | 5 | 6 | 7 | ° C |
| | *I (mol/kg)* | *8.01* | *7.85* | *8.22* | *8.22* | *8.22* | *8.21* | *8.21* | *8.21* | *8.20* | *8.20* | |
| modelled pH, no $CO_2$ | | 3.16 | 2.88 | 6.97 | 7.31 | 7.50 | 7.70 | 7.70 | 7.89 | 8.05 | 8.25 | 25.00 |
| modelled pH, log $PCO_2$ = -3.4 | | 3.16 | 2.88 | 6.97 | 7.29 | 7.49 | 7.67 | 7.67 | 7.84 | 7.98 | 8.13 | 25.00 |
| measured pH | 15-Jan-14 | - | - | 6.30 | 6.63 | 6.84 | 7.04 | 7.04 | 7.23 | 7.40 | 7.61 | 24.76 |
| measured pH | 16-Jan-14 | - | - | 6.30 | 6.63 | 6.84 | 7.04 | 7.04 | 7.24 | 7.40 | 7.61 | 24.70 |
| measured pH | 17-Jan-14 | 2.6 | 2.25 | 6.30 | 6.63 | 6.83 | 7.04 | 7.03 | 7.23 | 7.40 | 7.61 | 24.79 |
| measured pH | Mean | 2.60 | 2.25 | 6.30 | 6.63 | 6.84 | 7.04 | 7.04 | 7.23 | 7.40 | 7.61 | 24.75 |
| measured pH | σ | NA | NA | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.05 |
| mV | 15-Jan-14 | - | - | 26 | 7 | -5 | -16 | -16 | -28 | -37 | -49 | |
| mV | 16-Jan-14 | - | - | 26 | 7 | -4 | -16 | -16 | -28 | -37 | -49 | |
| mV | 17-Jan-14 | 242 | 262 | 27 | 8 | -4 | -16 | -16 | -28 | -37 | -49 | |
| mV | Mean | 242 | 262 | 26 | 7 | -4 | -16 | -16 | -28 | -37 | -49 | |
| mV | σ | NA | NA | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | | | |
| | | HCl1 | HCl2 | 1 | 2 | 3 | 4a | 4b | 5 | 6 | 7 | |
| measured pH | 15-Jan-14 | - | - | 6.31 | 6.64 | 6.84 | 7.04 | 7.04 | 7.24 | 7.40 | 7.61 | |
| measured pH | 16-Jan-14 | - | - | 6.31 | 6.64 | 6.84 | 7.04 | 7.04 | 7.24 | 7.40 | 7.61 | |
| measured pH | 17-Jan-14 | 2.61 | 2.27 | 6.3 | 6.62 | 6.83 | 7.04 | 7.03 | 7.23 | 7.39 | 7.60 | |
| measured pH | Mean | 2.61 | 2.27 | 6.31 | 6.63 | 6.84 | 7.04 | 7.04 | 7.24 | 7.40 | 7.61 | |
| measured pH | σ | NA | NA | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | |
| mV | 15-Jan-14 | - | - | 45 | 26 | 14 | 2 | 3 | -8 | -17 | -30 | |
| mV | 16-Jan-14 | - | - | 45 | 26 | 14 | 2 | 3 | -8 | -18 | -30 | |
| mV | 17-Jan-14 | 260 | 280 | 46 | 27 | 15 | 3 | 3 | -8 | -17 | -29 | |
| mV | Mean | 260 | 280 | 45 | 26 | 14 | 2 | 3 | -8 | -17 | -30 | |
| mV | σ | NA | NA | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 1 | |
| | | | | | | | | | | | | |
| 0.81x's S-SPW | | using 6m old (a) or freshly made (b) phenol red stock solution | | | | | | | | | | |
| | | Ross 815600 + Barnant 20 meter | | | | | | | | | | |
| | | 1a | 1b | 2a | 2b | 3a | 3b | 4a | 4b | 5a | 5b | ° C |
| | *I (mol/kg)* | *6.68* | *6.68* | *6.67* | *6.67* | *6.67* | *6.67* | *6.67* | *6.67* | *6.66* | *6.66* | |
| modelled pH, no $CO_2$ | | 7.14 | 7.14 | 7.34 | 7.34 | 7.54 | 7.54 | 7.74 | 7.74 | 7.93 | 7.93 | 25.00 |
| modelled pH, $P_{CO2}$ = -3.4 | | 7.14 | 7.14 | 7.33 | 7.33 | 7.52 | 7.52 | 7.71 | 7.71 | 7.89 | 7.89 | 25.00 |
| measured pH | 27-Feb-14 | 6.56 | 6.56 | 6.76 | 6.75 | 6.96 | 6.96 | 7.16 | 7.16 | 7.36 | 7.36 | 25.08 |
| measured pH | 28-Feb-14 | 6.57 | 6.56 | 6.76 | 6.76 | 6.96 | 6.96 | 7.17 | 7.17 | 7.36 | 7.36 | 25.10 |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| measured pH | 28-Feb-14 | 6.56 | 6.56 | 6.76 | 6.75 | 6.96 | 6.96 | 7.16 | 7.17 | 7.36 | 7.36 | 25.26 |
| measured pH | Mean | 6.56 | 6.56 | 6.76 | 6.75 | 6.96 | 6.96 | 7.16 | 7.17 | 7.36 | 7.36 | 25.15 |
| measured pH | σ | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 | 0.10 |
| mV | 27-Feb-14 | 9 | 9 | -2 | -2 | -14 | -14 | -26 | -26 | -37 | -37 | |
| mV | 28-Feb-14 | 9 | 9 | -2 | -2 | -14 | -14 | -26 | -26 | -38 | -38 | |
| mV | 28-Feb-14 | 9 | 9 | -2 | -2 | -14 | -14 | -26 | -26 | -37 | -37 | |
| mV | Mean | 9 | 9 | -2 | -2 | -14 | -14 | -26 | -26 | -37 | -37 | |
| mV | σ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | | | | |
| | | 1a | 1b | 2a | 2b | 3a | 3b | 4a | 4b | 5a | 5b | |
| measured pH | 27-Feb-14 | 6.56 | 6.56 | 6.76 | 6.75 | 6.96 | 6.96 | 7.16 | 7.16 | 7.36 | 7.36 | |
| measured pH | 28-Feb-14 | 6.56 | 6.56 | 6.75 | 6.75 | 6.96 | 6.96 | 7.16 | 7.16 | 7.35 | 7.35 | |
| measured pH | 28-Feb-14 | 6.55 | 6.55 | 6.74 | 6.74 | 6.95 | 6.95 | 7.15 | 7.15 | 7.35 | 7.35 | |
| measured pH | Mean | 6.56 | 6.56 | 6.75 | 6.75 | 6.96 | 6.96 | 7.16 | 7.16 | 7.35 | 7.35 | |
| measured pH | STD | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | |
| mV | 27-Feb-14 | 27 | 27 | 15 | 15 | 3 | 3 | -7 | -7 | -19 | -19 | |
| mV | 28-Feb-14 | 27 | 27 | 15 | 15 | 3 | 3 | -8 | -7 | -19 | -19 | |
| mV | 28-Feb-14 | 27 | 27 | 16 | 16 | 3 | 4 | -7 | -7 | -18 | -18 | |
| mV | Avg | 27 | 27 | 15 | 15 | 3 | 3 | -7 | -7 | -19 | -19 | |
| mV | STD | 0 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 1 | |

0.60x's S-SPW

| | | Ross 815600 + Barnant 20 meter | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5a | 5b | 6 | ° C |
| | *I (mol/kg)* | *4.96* | *4.95* | *4.95* | *4.95* | *4.94* | *4.94* | *4.93* | |
| modelled pH, no $CO_2$ | | 7.05 | 7.38 | 7.58 | 7.77 | 7.96 | 7.96 | 8.18 | 25.00 |
| modelled pH, $P_{CO2}$ = -3.4 | | 7.04 | 7.36 | 7.56 | 7.75 | 7.93 | 7.93 | 8.12 | 25.00 |
| measured pH | 18-Feb-14 | 6.58 | 6.92 | 7.12 | 7.31 | 7.51 | 7.51 | 7.74 | 24.98 |
| measured pH | 19-Feb-14 | 6.57 | 6.92 | 7.11 | 7.31 | 7.50 | 7.50 | 7.73 | 25.24 |
| measured pH | 19-Feb-14 | 6.56 | 6.91 | 7.11 | 7.31 | 7.50 | 7.50 | 7.73 | 25.41 |
| measured pH | Mean | 6.57 | 6.92 | 7.11 | 7.31 | 7.50 | 7.50 | 7.73 | 25.21 |
| measured pH | σ | 0.01 | 0.01 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | 0.22 |
| mV | 19-Feb-14 | 9 | -12 | -23 | -34 | -46 | -46 | -59 | |
| mV | 19-Feb-14 | 9 | -11 | -23 | -34 | -45 | -45 | -59 | |
| mV | 19-Feb-14 | 10 | -11 | -22 | -34 | -45 | -45 | -58 | |
| mV | Mean | 9 | -11 | -23 | -34 | -45 | -45 | -59 | |
| mV | σ | 1 | 1 | 1 | 0 | 1 | 1 | 1 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | | |
| | | 1 | 2 | 3 | 4 | 5a | 5b | 6 | |
| measured pH | 19-Feb-14 | 6.58 | 6.92 | 7.12 | 7.31 | 7.51 | 7.51 | 7.74 | |
| measured pH | 19-Feb-14 | 6.56 | 6.92 | 7.11 | 7.31 | 7.51 | 7.51 | 7.74 | |
| measured pH | 19-Feb-14 | 6.55 | 6.91 | 7.10 | 7.30 | 7.49 | 7.49 | 7.72 | |
| measured pH | Mean | 6.56 | 6.92 | 7.11 | 7.31 | 7.50 | 7.50 | 7.73 | |
| measured pH | σ | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | |
| mV | 19-Feb-14 | 27 | 7 | -4 | -15 | -27 | -27 | -40 | |
| mV | 19-Feb-14 | 28 | 7 | -3 | -15 | -26 | -26 | -39 | |
| mV | 19-Feb-14 | 28 | 8 | -3 | -14 | -25 | -25 | -39 | |
| mV | Mean | 28 | 7 | -3 | -15 | -26 | -26 | -39 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | |

0.36x's S-SPW Note: there were unusual laboratory temperature fluctuations during the measurements

| | | Ross 815600 + Barnant 20 meter | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | ° C |
| | *I (mol/kg)* | *2.96* | *2.95* | *2.95* | *2.95* | *2.94* | *2.94* | |
| modelled no CO2 | | 7.15 | 7.44 | 7.63 | 7.82 | 7.99 | 8.22 | 25.00 |
| modelled PCO2 = -3.4 | | 7.14 | 7.42 | 7.62 | 7.79 | 7.96 | 8.17 | 25.00 |
| measured pH | 11-Mar-14 | 6.74 | 7.07 | 7.28 | 7.48 | 7.67 | 7.90 | 25.36 |
| measured pH | 12-Mar-14 | 6.74 | 7.07 | 7.28 | 7.48 | 7.68 | 7.90 | 25.45 |
| measured pH | 12-Mar-14 | 6.76 | 7.10 | 7.30 | 7.50 | 7.70 | 7.93 | 24.14 |
| pH | Mean | 6.75 | 7.08 | 7.29 | 7.49 | 7.68 | 7.91 | 24.98 |
| pH | σ | 0.01 | 0.02 | 0.01 | 0.01 | 0.02 | 0.02 | 0.73 |
| mV | 11-Mar-14 | -2 | -21 | -33 | -45 | -56 | -69 | |
| mV | 12-Mar-14 | -3 | -22 | -34 | -46 | -57 | -70 | |
| mV | 12-Mar-14 | -4 | -23 | -35 | -47 | -58 | -71 | |
| mV | Avg | -3 | -22 | -34 | -46 | -57 | -70 | |
| mV | STD | 1 | 1 | 1 | 1 | 1 | 1 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | |
| | | 1 | 2 | 3 | 4 | 5a | 6 | |

## Table B.2: Results from Potentiometric pH Measurements of HCl and Tris Buffer Series

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| measured pH | 11-Mar-14 | 6.73 | 7.06 | 7.26 | 7.46 | 7.65 | 7.88 | |
| measured pH | 12-Mar-14 | 6.72 | 7.05 | 7.26 | 7.46 | 7.65 | 7.88 | |
| measured pH | 12-Mar-14 | 6.74 | 7.07 | 7.28 | 7.48 | 7.67 | 7.90 | |
| pH | Mean | 6.73 | 7.06 | 7.27 | 7.47 | 7.66 | 7.89 | |
| pH | σ | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | |
| mV | 11-Mar-14 | 15 | -3 | -15 | -26 | -38 | -51 | |
| mV | 12-Mar-14 | 15 | -3 | -15 | -27 | -38 | -51 | |
| mV | 12-Mar-14 | 14 | -4 | -16 | -28 | -39 | -53 | |
| mV | Avg | 15 | -3 | -15 | -27 | -38 | -52 | |
| mV | STD | 1 | 1 | 1 | 1 | 1 | 1 | |

0.03x's S-SPW

| | | Ross 815600 + Barnant 20 meter | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | ° C |
| | *I (mol/kg)* | *0.28* | *0.27* | *0.27* | *0.27* | *0.26* | *0.25* | |
| modelled pH, no $CO_2$ | | 7.04 | 7.38 | 7.58 | 7.79 | 7.99 | 8.24 | 25.00 |
| modelled pH, $P_{CO2}$ = -3.4 | | 7.03 | 7.36 | 7.57 | 7.76 | 7.96 | 8.19 | 25.00 |
| measured pH | 20-Feb-14 | 6.97 | 7.31 | 7.52 | 7.73 | 7.94 | 8.19 | 24.37 |
| measured pH | 21-Feb-14 | 6.96 | 7.30 | 7.51 | 7.72 | 7.93 | 8.18 | 25.16 |
| measured pH | 21-Feb-14 | 6.95 | 7.29 | 7.5 | 7.71 | 7.92 | 8.18 | 25.46 |
| measured pH | Avg | 6.96 | 7.30 | 7.51 | 7.72 | 7.93 | 8.18 | 25.00 |
| measured pH | STD | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.56 |
| mV | 20-Feb-14 | -14 | -34 | -46 | -58 | -70 | -85 | |
| mV | 21-Feb-14 | -13 | -33 | -46 | -58 | -70 | -85 | |
| mV | 21-Feb-14 | -13 | -33 | -45 | -57 | -69 | -84 | |
| mV | Mean | -13 | -33 | -46 | -58 | -70 | -85 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | |
| | | SureFlow + Jenco Model-5005 meter | | | | | | |
| | | 1 | 2 | 3 | 4 | 5 | 6 | |
| measured pH | 20-Feb-14 | 6.97 | 7.31 | 7.52 | 7.73 | 7.93 | 8.19 | |
| measured pH | 21-Feb-14 | 6.95 | 7.28 | 7.5 | 7.71 | 7.91 | 8.17 | |
| measured pH | 21-Feb-14 | 6.94 | 7.28 | 7.49 | 7.7 | 7.91 | 8.16 | |
| measured pH | Mean | 6.95 | 7.29 | 7.50 | 7.71 | 7.92 | 8.17 | |
| measured pH | σ | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 | |
| mV | 20-Feb-14 | 4 | -15 | -27 | -39 | -52 | -66 | |
| mV | 21-Feb-14 | 5 | -14 | -26 | -38 | -50 | -66 | |
| mV | 21-Feb-14 | 5 | -13 | -26 | -38 | -50 | -65 | |
| mV | Mean | 5 | -14 | -26 | -38 | -51 | -66 | |
| mV | σ | 1 | 1 | 1 | 1 | 1 | 1 | |

" - " means not measured; NA mean Not Applicable

## B.6 PHENOL RED pK'$_a$ DETERMINATION RESULTS

### Table B.3: pK'a Measurement Results Based on Modelled pH Assuming No Effect from Atmospheric $CO_{2(g)}$

| | | pK'a | | | | pK'a | |
|---|---|---|---|---|---|---|---|
| | °C | Measured | Temperature Corrected | | °C | Measured | Temperature Corrected |
| Just Tris | | | | 0.1m NaCl | | | |
| *Mean I = 0.04 mol/kg* | | | | *Mean I = 0.10 mol/kg* | | | |
| 9-Jan-14 | 24.88 | 7.80 | 7.80 | 9-Sep-13 | 24.0 | 7.69 | 7.72 |
| 10-Jan-14 | 24.48 | 7.79 | 7.81 | 11-Sep-13 | 24.8 | 7.72 | 7.72 |
| 10-Jan-14 | 24.98 | 7.81 | 7.81 | 13-Sep-13 | 25.5 | 7.73 | 7.72 |
| Mean | 24.78 | 7.80 | 7.81 | Mean | 24.8 | 7.71 | 7.72 |
| σ | 0.26 | 0.01 | 0.004 | σ | 0.8 | 0.02 | 0.004 |
| RSD | 1.07% | 0.11% | 0.05% | RSD | 3% | 0.25% | 0.05% |
| 1.0m NaCl | | | | 1.0m NaCl | | | |
| *Mean I = 1.02 mol/kg* | | | | *Mean I = 1.00 mol/kg* | | | |
| 18-Sep-13 | 23.70 | 7.55 | 7.59 | 13-Jan-14 | 24.61 | 7.59 | 7.60 |
| 24-Sep-13 | 25.10 | 7.59 | 7.59 | 13-Jan-14 | 24.69 | 7.61 | 7.61 |
| 24-Sep-13 | 24.60 | 7.59 | 7.60 | 14-Jan-14 | 24.64 | 7.59 | 7.60 |
| Mean | 24.47 | 7.58 | 7.59 | Mean | 24.65 | 7.60 | 7.60 |
| σ | 0.71 | 0.02 | 0.008 | σ | 0.04 | 0.01 | 0.01 |
| RSD | 3% | 0.29% | 0.11% | RSD | 0.16% | 0.11% | 0.12% |
| 5.0m NaCl | | | | L-SPW | | | |
| *Mean I = 5.00 mol/kg* | | | | *Mean I = 4.92 mol/kg* | | | |
| 27-Sep-13 | 25.55 | 7.68 | 7.67 | 24-Oct-13 | 25.01 | 7.73 | 7.73 |
| 30-Sep-13 | 25.32 | 7.68 | 7.67 | 25-Oct-13 | 24.60 | 7.70 | 7.71 |
| 1-Oct-13 | 25.20 | 7.69 | 7.69 | 28-Oct-13 | 24.70 | 7.70 | 7.71 |
| Mean | 25.36 | 7.69 | 7.67 | Mean | | 7.71 | 7.71 |
| σ | 0.18 | 0.00 | 0.01 | σ | | 0.02 | 0.01 |
| RSD | 0.70% | 0.06% | 0.13% | RSD | | 0.25% | 0.17% |
| 1.57x's L-SPW | | | | 1.45x's L-SPW | | | |
| *Mean I = 7.66 mol/kg* | | | | *Mean I = 7.08 mol/kg* | | | |
| 13-Nov-13 | 25.07 | 7.79 | 7.79 | 19-Nov-13 | 24.64 | 7.79 | 7.80 |
| 14-Nov-13 | 25.08 | 7.78 | 7.78 | 20-Nov-13 | 25.19 | 7.77 | 7.77 |
| 15-Nov-13 | 25.09 | 7.79 | 7.79 | 15-Nov-13 | 24.34 | 7.75 | 7.77 |
| Mean | 25.08 | 7.79 | 7.79 | Mean | 24.72 | 7.77 | 7.78 |
| σ | 0.01 | 0.01 | 0.01 | σ | 0.43 | 0.02 | 0.02 |
| RSD | 0.04% | 0.09% | 0.09% | RSD | 1.75% | 0.30% | 0.27% |
| 1.34x's L-SPW | | | | 1.22x's L-SPW | | | |
| *Mean I = 6.52 mol/kg* | | | | *Mean I = 5.96 mol/kg* | | | |
| 27-Nov-13 | 24.73 | 7.77 | 7.78 | 3-Dec-13 | 24.21 | na | na |
| 28-Nov-13 | 24.88 | 7.75 | 7.75 | 4-Dec-13 | 24.93 | na | na |
| 15-Nov-13 | 24.87 | 7.77 | 7.78 | 4-Dec-13 | 24.86 | 7.73 | 7.74 |
| Mean | 24.83 | 7.76 | 7.77 | 6-Dec-13 | 24.52 | na | na |
| σ | 0.09 | 0.01 | 0.01 | Mean | 24.63 | 7.73 | 7.74 |
| RSD | 0.35% | 0.15% | 0.17% | σ | 0.33 | na | na |
| | | | | RSD | 1.35% | na | na |

("na" means there were issues with the flow through)

## Table B.3: pK'a Measurement Results Based on Modelled pH Assuming No Effect from Atmospheric $CO_{2(g)}$

| | °C | pK'a Measured | pK'a Temperature Corrected |
|---|---|---|---|
| 1.22x's L-SPWb | | | |
| *Mean I = 5.96 mol/kg* | | | |
| 4-Mar-14 | 25.07 | 7.74 | 7.74 |
| 5-Mar-14 | 24.95 | 7.73 | 7.73 |
| 5-Mar-14 | 25.00 | 7.73 | 7.73 |
| Mean | 25.01 | 7.73 | 7.73 |
| σ | 0.06 | 0.01 | 0.01 |
| RSD | 0.24% | 0.10% | 0.08% |
| 0.73x's L-SPW | | | |
| *Mean I = 3.60 mol/kg* | | | |
| 12-Dec-13 | 24.87 | 7.64 | 7.64 |
| 13-Dec-13 | 24.49 | 7.64 | 7.66 |
| 13-Dec-13 | 24.86 | 7.66 | 7.66 |
| Mean | 24.74 | 7.65 | 7.65 |
| σ | 0.22 | 0.01 | 0.01 |
| RSD | 0.88% | 0.12% | 0.11% |
| 0.24x's L-SPW | | | |
| *Mean I = 1.19 mol/kg* | | | |
| 19-Dec-13 | 24.89 | 7.60 | 7.61 |
| 20-Dec-13 | 24.96 | 7.62 | 7.62 |
| 20-Dec-13 | 25.02 | 7.62 | 7.62 |
| Mean | 24.96 | 7.61 | 7.61 |
| σ | 0.07 | 0.01 | 0.01 |
| RSD | 0.27% | 0.11% | 0.08% |
| 0.01x's L-SPW | | | |
| *Mean I = 0.09 mol/kg* | | | |
| 7-Jan-14 | 24.83 | 7.74 | 7.74 |
| 8-Jan-14 | 24.78 | 7.75 | 7.76 |
| 8-Jan-14 | 24.97 | 7.75 | 7.75 |
| Mean | 24.86 | 7.75 | 7.75 |
| σ | 0.10 | 0.01 | 0.01 |
| RSD | 0.40% | 0.11% | 0.11% |
| 0.81x's S-SPWa (using 6m old phenol red indicator stock) | | | |
| *Mean I = 4.95 mol/kg* | | | |
| 27-Feb-14 | 25.08 | 7.74 | 7.74 |
| 28-Feb-14 | 25.10 | 7.76 | 7.76 |
| 28-Feb-14 | 25.26 | 7.77 | 7.76 |
| Mean | 25.22 | 7.76 | 7.75 |
| σ | 0.20 | 0.01 | 0.01 |
| RSD | 0.81% | 0.18% | 0.15% |

| | °C | pK'a Measured | pK'a Temperature Corrected |
|---|---|---|---|
| LSPW2 | | | |
| *Mean I = 4.89 mol/kg* | | | |
| 9-Dec-13 | 24.87 | 7.70 | 7.71 |
| 10-Dec-13 | 24.91 | 7.67 | 7.68 |
| 10-Dec-13 | 24.58 | 7.72 | 7.73 |
| Mean | 24.79 | 7.70 | 7.71 |
| σ | 0.18 | 0.02 | 0.03 |
| RSD | 0.72% | 0.29% | 0.35% |
| 0.48x's L-SPW | | | |
| *Mean I = 2.38 mol/kg* | | | |
| 17-Dec-13 | 24.17 | 7.59 | 7.62 |
| 18-Dec-13 | 24.90 | 7.60 | 7.61 |
| 18-Dec-13 | 25.04 | 7.62 | 7.62 |
| 27-Dec-13 | 24.91 | 7.61 | 7.61 |
| Mean | 24.75 | 7.61 | 7.61 |
| σ | 0.40 | 0.01 | 0.005 |
| RSD | 1.60% | 0.16% | 0.06% |
| 0.09x's L-SPW | | | |
| *Mean I = 0.49 mol/kg* | | | |
| 2-Jan-14 | 25.26 | 7.61 | 7.60 |
| 3-Jan-14 | 25.08 | 7.63 | 7.63 |
| 3-Jan-14 | 24.97 | 7.64 | 7.64 |
| Mean | 25.10 | 7.63 | 7.62 |
| | 0.15 | 0.01 | 0.02 |
| RSD | 0.58% | 0.16% | 0.22% |
| S-SPW | | | |
| *Mean I = 8.21 mol/kg* | | | |
| 15-Jan-14 | 24.76 | 7.80 | 7.80 |
| 16-Jan-14 | 24.70 | 7.82 | 7.83 |
| 17-Jan-14 | 24.79 | 7.82 | 7.83 |
| Mean | 24.75 | 7.81 | 7.82 |
| σ | 0.05 | 0.01 | 0.01 |
| RSD | 0.19% | 0.17% | 0.17% |
| 0.81x's S-SPWb (using freshly made phenol red indicator stock) | | | |
| *Mean I = 4.95 mol/kg* | | | |
| 27-Feb-14 | 25.08 | 7.75 | 7.74 |
| 28-Feb-14 | 25.10 | 7.76 | 7.76 |
| 28-Feb-14 | 25.26 | 7.77 | 7.76 |
| Mean | 25.22 | 7.76 | 7.76 |
| σ | 0.20 | 0.01 | 0.01 |
| RSD | 0.81% | 0.18% | 0.15% |

## Table B.3: pK'a Measurement Results Based on Modelled pH Assuming No Effect from Atmospheric $CO_{2(g)}$

| | °C | pK'a Measured | pK'a Temperature Corrected | | °C | pK'a Measured | pK'a Temperature Corrected |
|---|---|---|---|---|---|---|---|
| 0.60x's S-SPW | | | | 0.36x's S-SPW | | | |
| *Mean I = 4.95 mol/kg* | | | | *Mean I = 2.95 mol/kg* | | | |
| 18-Feb-14 | 24.98 | 7.68 | 7.68 | 11-Mar-14 | 25.36 | 7.65 | 7.64 |
| 19-Feb-14 | 25.24 | 7.69 | 7.68 | 12-Mar-14 | 25.45 | 7.67 | 7.65 |
| 19-Feb-14 | 25.41 | 7.71 | 7.70 | 12-Mar-14 | 24.14 | 7.65 | 7.67 |
| Mean | 25.21 | 7.69 | 7.69 | Mean | 24.98 | 7.66 | 7.66 |
| σ | 0.22 | 0.02 | 0.01 | σ | 0.73 | 0.01 | 0.02 |
| RSD | 0.86% | 0.20% | 0.12% | RSD | 2.9% | 0.13% | 0.21% |
| 0.03x's S-SPW | | | | | | | |
| *Mean I = 0.27 mol/kg* | | | | | | | |
| 20-Feb-14 | 24.37 | 7.65 | 7.65 | | | | |
| 21-Feb-14 | 25.16 | 7.67 | 7.66 | Notes: | | | |
| 21-Feb-14 | 25.46 | 7.67 | 7.66 | *I* =ionic strength; σ = standard deviation | | | |
| Mean | 25.00 | 7.66 | 7.65 | | | | |
| σ | 0.56 | 0.01 | 0.00 | | | | |
| RSD | 2.3% | 0.13% | 0.04% | | | | |