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Estimating the Hydrogen Ion Concentration in Concentrated NaCl and Na₂SO₄ Electrolytes

Dhanpat Rai, Andrew R. Felmy, Samuel P. Juracich, Finfeng Rao
Pacific Northwest Laboratory
Richland, WA 99352

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Dhanpat Rai, Andrew R. Felmy, Samuel P. Juracich, and Finfeng Rao
Pacific Northwest Laboratory
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ABSTRACT

The objective of this study was to test a relatively simple method using commercially available combination glass electrodes for determining the H⁺ concentrations in certain concentrated electrolyte solutions, specifically, pure and mixed NaCl and Na₂SO₄ solutions, as well as natural brine systems dominated by these two electrolyte components. A large number of NaCl, Na₂SO₄, and mixtures of NaCl and Na₂SO₄ solutions of various concentrations were analyzed as part of this study. The emphasis of this work was to determine the appropriate correction factors for estimating the pC_H⁺ (negative logarithm of the H⁺ concentration) from the measured/observed pH values. The required Gran-type titrations were done with HCl and/or NaOH. The titration method is described in detail, and a step-by-step procedure is provided. This method has been used previously for determining the pC_H⁺ values of synthetic chloride-dominated brines. It should be emphasized that extra precautions are required to determine correction factors for electrolytes that react with H⁺ or OH⁻ [e.g., sulfate brines for titration with acid, and magnesium brines for titration with base because of the precipitation of Mg(OH)₂].

The correction factors A (pC_H⁺ = pH_{ob} + A) obtained from HCl titrations were similar to those obtained from NaOH titrations where the concentration of free H⁺ was calculated using a thermodynamic model. These values should be applicable to solutions similar in compositions to those titrated in this study and with a very large range in measured pH values (at least 2 to 12). Because a large number of solutions were titrated with HCl and the A values are similar for HCl and NaOH titrations, the A values for NaCl and Na₂SO₄ solutions were fit as a function of molality to allow extrapolation between experimental points. For NaCl solutions ranging in concentrations from 0 to 6.0 molal, the values of A can be obtained by multiplying the molality by 0.159. For Na₂SO₄ solutions ranging in concentrations from 0 to 2.0 molal, the values of A can be obtained from (0.221 - 0.549X + 0.201X²), where X is the molality of Na₂SO₄ solutions.

A limited number of different Orion-Ross electrodes were evaluated to determine the dependence of the A values on an individual electrode. These evaluations indicated that the A values did not differ significantly for different electrodes. The results suggest that the data contained in this report can be used to estimate A values for different NaCl and Na₂SO₄ solutions even if the electrodes are not calibrated.

Although the values of A were different when the reference cell of the combination glass electrode was filled with an electrolyte of the same composition as the test sample (recommended in some procedures proposed in the literature as an effort to reduce the liquid junction potential) or with 3M KCl, the final estimated pC_h+ values were similar. This indicates that reliable results can be obtained with the proposed method using standard Orion-Ross electrodes without filling the reference cell with the electrolyte of the same composition as the test solution.

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Introduction

The hydrogen ion concentration is a critical parameter for determining geochemical equilibria in electrolyte solutions, including concentrated chloride and sulfate brine systems. Unfortunately, determining the hydrogen ion concentration in such concentrated solutions can be difficult because of variations in activity coefficients, formation of species such as HSO_4^- that can consume protons during electrode standardization procedures, and potentially large junction potentials if cells with liquid junctions are used (Pederson et al. 1993; Knauss et al. 1990; Felmy et al. 1989; Dickson 1984; McBryde 1969, 1971). As a result of these difficulties, a variety of different techniques have been used to measure the hydrogen ion concentration in concentrated electrolyte solutions. Some examples of these different methods are described below.

Knauss et al. (1991) have recently discussed in detail the use of cells without liquid junctions. They used a variety of ion selective electrodes (ISEs) to measure thermodynamic quantities such as the activity of HCl (i.e. a_{HCl}) or activity ratios such as $a_{\text{H}^+}/a_{\text{Na}^+}$. The hydrogen ion concentration was then determined from the known concentration of Cl^- , Na^+ ... and the calculated value of γ_{HCl} , or $\gamma_{\text{H}^+}/\gamma_{\text{Na}^+}$ using a thermodynamic model (such as that of Pitzer). This method has the advantage of directly measuring a true thermodynamic quantity, i.e. a_{HCl} , $a_{\text{H}^+}/a_{\text{Na}^+}$, without introducing unknown terms such as liquid junction corrections. It has the disadvantage of needing 1) a thermodynamic model to calculate the value of γ_{HCl} , $\gamma_{\text{H}^+}/\gamma_{\text{Na}^+}$, and 2) assurance that there are no interferences in the measurement made by ISE. For example, Br^- can directly interfere with the Cl^- ISE.

In the case of cells with liquid junctions, for example a glass electrode with a calomel reference, a liquid junction potential (or difference in liquid junction potentials) is introduced and only a combination of single ion activity terms and liquid junction potentials is measured (see Mesmer 1991). This liquid junction term, or a selected combination of liquid junction terms and activity terms, must then be determined either by calculation (such as the use of the Henderson equation) or by selected gran or other titrations with known amounts of acid or base. The advantage of this method is that in certain solutions where no acid or base consuming species are present (such as HSO_4^-), the hydrogen ion concentration can be determined directly without resorting to the use of a thermodynamic model.

The use of organic indicator species is based upon the fact that the pKa values for different organic acids vary with the aqueous electrolyte concentration. If the organic acid pKa can be readily measured and the dependence of the pKa on electrolyte concentration predicted then the use of organic acids to determine pKa values for unknown solutions can be readily used. These methods have the advantage that small amounts of hydrogen ion consuming species, such as HSO_4^- , generally do not affect the pKa values of the organic acids. They have the disadvantage that the pKa values must be known as a function of the concentration of the major electrolytes present in solution.

In this study, we at the Pacific Northwest Laboratory^(a) tested a relatively simple procedure for estimating the hydrogen ion concentration in the $\text{Na}^+ - \text{Cl}^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$ system using commercially available combination glass electrodes. This relatively simple procedure was selected because of its reliability (± 0.05 pC_{H+} units) and ease of use. The method was tested over a wide range of electrolyte concentration and pC_{H+} values (2 to 12).

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute, under Contract DE-AC06-76RLO 1830.

The H^+ concentration (pC_{H^+}) in unknown samples of a given electrolyte of fixed molarity can be estimated using a glass electrode with liquid junction from the following equation (see Appendix A for a derivation):

$$pC_{H^+} = pH_{ob} + A \quad (1)$$

where pH_{ob} is the observed reading with the calibrated combination glass electrode of the unknown sample, and A is defined by

$$A = \log \gamma_{H^+} + (F/2.303RT)\Delta E_j \quad (2)$$

where γ_{H^+} is the convention-dependent molarity-scale activity coefficient of H^+ , and ΔE_j is the difference in liquid junction potential between standards and solutions. Neither term on the right-hand side of Eq. (2) is individually measurable, but the combination can be measured.

Rewriting Eq. (1) in terms of logarithms, taking the antilog of both sides and rearranging, yields

$$H^+_{ob} = 10^A C_{H^+} \quad (3)$$

The constant A is then obtained by a modified Gran titration (as described under "General Procedure") in which the moles of added free acid per liter are plotted against H^+_{ob} (i.e., $10^{-pH_{ob}}$). The logarithm of the slope of this curve is the correction factor A needed to convert the observed pH reading to pC_{H^+} . For additional details of the procedure and calculations, see Appendix B.

Methods and Materials

Stock Solutions

Deionized distilled water was boiled to remove soluble carbonates and was stored under a N_2 atmosphere until used. All solutions were prepared and stored in a controlled atmosphere chamber with prepurified N_2 gas (99.99% N_2 , with a few ppm of O_2). Standard solutions of 0.0935 M NaOH and 0.0104 M HCl were prepared.

Aliquots of NaCl(c) and Na_2SO_4 (c) were dried at 100°C for about two hours to remove hygroscopic moisture and then stored in a desiccator until used. Stock solutions of different molalities (m) of NaCl (1.0, 2.0, 3.0, 4.0, 5.0, 5.5, and 6.0) and of Na_2SO_4 (0.05, 0.1, 0.5, 1.0, 1.5, and 2.0) and mixed salt solutions (5.5 m NaCl + 0.05 m Na_2SO_4 ; 5.5 m NaCl + 0.01 m Na_2SO_4) were prepared.

General Procedure

A radiometer titrator with a combination pH glass electrode (Orion-Ross, semi-micro) was used for titrating the salt solutions with HCl or NaOH. All new electrodes were soaked in a 1.0 pH buffer for several days before use. A given glass electrode was calibrated against standard pH buffers just before starting the titration; all titrations were done at 20°C. In some cases the filling solution (3 M KCl) in the reference cell of the combination glass electrode was replaced with 6.0 m NaCl. A complete list of the solutions used in acid/base titrations along with the titration range in observed pH values is reported in Table 1.

A 25-ml aliquot of a given salt solution was pipetted into the titration vessel, then titrated with 0.0104 M HCl or 0.0935 M NaOH. The acid or base was added in 0.025-ml or 0.036-ml increments. A fresh increment of acid or base was automatically added to the titration vessel when the measured pH stabilized to within 0.005 pH units. After each addition, the stabilized measured pH value and the increment and total volume of the acid or base added to the vessel were recorded. These data were then used to calculate the moles/L of H^+ or OH^- added [(molarity of titrant)(volume in ml of titrant)/(total volume in ml in titration vessel)] at a given measured pH. The titrations were continued until about 6 ml of the titrant was used. However, to avoid complications due to excessive dilution of the original salt solution by the titrant, the data analyses were confined to the region where <2 ml of the titrant was used.

Table 1. Solutions Used in Acid/Base Titrations

Molality and Medium	Observed pH Range of Titrations with ^(a)	
	HCl	NaOH
1.0 m NaCl	6.98-2.63	
2.0 m NaCl	6.38-2.56	
3.0 m NaCl	6.19-2.34	
4.0 m NaCl	6.51-2.26	
5.0 m NaCl	7.81-2.06	
5.5 m NaCl	8.21-1.96 5.98-1.77	8.22-11.84
6.0 m NaCl	8.45-1.91 8.27-1.55 ^(b) 5.71-1.56 ^(c)	
0.05 m Na ₂ SO ₄	5.31-2.96	5.96-12.22
0.1 m Na ₂ SO ₄	6.53-3.19	6.42-12.19
0.5 m Na ₂ SO ₄	8.14-3.47	8.41-12.11
1.0 m Na ₂ SO ₄	8.77-3.60	
1.5 m Na ₂ SO ₄	9.18-3.68	
2.0 m Na ₂ SO ₄	9.20-3.73	8.83-12.24
5.5 m NaCl+0.05 m Na ₂ SO ₄	8.95-1.98	9.00-11.87
5.5 m NaCl+0.01 m Na ₂ SO ₄	8.83-1.91	8.92-11.87
(a) 25 ml of the solution was titrated with 0.0104 M HCl or with 0.0935 M NaOH at 20°C. (b,c) The reference cell was filled with 6.0 m NaCl and measurements made after equilibrating (b = <4 hours and c = 8 days) the solution in electrode; in all other cases the reference cell was filled with 3.0 M KCl.		

Results and Discussion

Sodium chloride and sodium sulfate solutions were titrated with HCl and NaOH solutions to estimate the value of the correction factor A so that the pC_{H^+} values of the salt solutions can reliably be calculated from pH_{ob} . In addition, mixed NaCl and Na_2SO_4 solutions were also titrated to determine whether the method will be applicable to mixed electrolytes. A few titrations were also conducted where the saturated KCl solution in the reference cell of the Orion-Ross electrode was replaced with 6.0 m NaCl. It is expected that a specific electrode precalibrated to obtain A will be used in estimating the pC_{H^+} in electrolyte samples of unknown H^+ concentration. However, to show the general applicability of the correction factors A and the variability in estimated pC_{H^+} if the electrodes were not individually calibrated, factors A were determined for a few Orion-Ross glass electrodes. The details are presented below.

Titration of NaCl

In the NaCl system, there are no minor species (such as HSO_4^-) that can consume added H^+ , other than, perhaps, small amounts of impurities such as soluble bicarbonate. Therefore, the amount of acid added (H^+_{add}) during titration should primarily correspond to the free H^+ concentration added ($H^+_{free,add}$). From a point where the amount of added free H^+ far exceeds the amount of free H^+ /impurities that may be originally present in the sample, the observed pH should vary linearly with each incremental addition of the acid (Eq. 1) as long as the liquid junction potentials and convention-dependent single-ion activity coefficients remain constant.

Because the total amount of acid added during any given titration is, in most cases, at least a factor of 100 times lower in concentration than the original electrolyte, this added acid will not significantly alter the ionic composition or the ionic strength of the solutions. Therefore, γ_{H^+} and E_j that determine the correction factor A (Eq. 2) required for estimating pC_{H^+} (Eq. 1) are not expected to change significantly during titrations.

The plots of the moles/L of the $H^+_{free,add}$ versus the moles/L of H^+ observed (H^+_{ob}) with the pH probe for 1.0, 2.0, 3.0, 4.0, 5.0, 5.5, and 6.0 m NaCl are shown in Figures 1 to 4, and the corresponding raw data are tabulated in Appendix C. Linear regression through the data points indicates that there is very little scatter around the line and that the r^2 values in all cases were greater than 0.99. The slopes of the regression lines and calculated values of the A parameter are reported in Table 2. These values indicate, as expected, that correction factors increase with the increase in the concentration of NaCl and are as high as 0.97 for 6.0 m NaCl. The very slight non-linearity in the titration curves at the highest NaCl concentrations could result from a variety of factors including back diffusion of the high NaCl solutions through the liquid junction.

As discussed above, it is expected that the value of A for a given electrolyte (Table 2) should be applicable to the entire expected environmental range in pC_{H^+} . Therefore, to check this assertion,

Figure 1. Titration of 1.0 m and 2.0 m NaCl Solutions with HCl [$H^+_{\text{free,add}}$ is moles/L of free H^+ added, and H^+_{ob} is Calculated from Observed pH ($H^+_{\text{ob}} = 10^{-\text{pH}}$); linear regression lines are also shown]

Figure 2. Titration of 3.0 m and 4.0 m NaCl Solutions with HCl [$H^+_{free,add}$ is moles/L of free H^+ added, and H^+_{ob} is calculated from observed pH ($H^+_{ob} = 10^{-pH}$); linear regression lines are also shown]

Figure 3. Titration of 5.0 m and 5.5 m NaCl Solutions with HCl [$H^+_{free,add}$ is moles/L of free H^+ added, and H^+_{ob} is calculated from observed pH ($H^+_{ob} = 10^{-pH}$); linear regression lines are also shown]

Figure 4. Titration of 5.5 m NaCl with NaOH and of 6.0 m NaCl Solutions with HCl [$H^+_{free,add}$ is moles/L of free H^+ added, and H^+_{ob} is calculated from observed pH ($H^+_{ob} = 10^{-pH}$); linear regression lines are also shown]

Table 2. Titration of NaCl Solutions

NaCl (molality)	Titrant	Slope ^(a)	Correction Factor A (log slope)
1.0	HCl	1.366	0.14
2.0	HCl	1.722	0.24
3.0	HCl	2.992	0.48
4.0	HCl	3.914	0.59
5.0	HCl	6.248	0.81
5.5	HCl	8.316	0.92
	NaOH	7.206	0.86
6.0	HCl	9.388	0.97
(a) $Y = mX + b$, where Y is the moles/L of H^+_{ob} with pH electrode (i.e., $10^{-pH_{ob}}$); m is the slope; and X is the moles/L of $H^+_{free,add}$.			

The value of K_w° for 5.5 m NaCl needed to determine $H^+_{free,add}$ was found to be 3.904×10^{-15} and was calculated using the GMIN equilibrium code (Felmy 1990), with 25°C values of Pitzer parameters reported in Table 3 and μ°/RT values of chemical species in Table 4. The temperature dependence of these parameters was neglected owing to the small difference between room temperature and 25°C (i.e. 2-5°C). The plot of the $H^+_{free,add}$ versus H^+_{ob} (Figure 4) from the NaOH titrations of 5.5 m NaCl indicates that the data are highly linear. The 0.86 value of A parameter calculated from these data is very close to the 0.92 value obtained from the HCl titrations and therefore the values of A calculated from the HCl or NaOH titrations can be used to calculate pC_H^+ in samples varying considerably in H^+ concentrations. These experiments also demonstrate the ability of the thermodynamic model to accurately calculate the H^+ concentration in the basic chloride solutions.

Titration of Na_2SO_4

Adding acid to aqueous solutions containing Na_2SO_4 results in the formation of bisulfate ions (HSO_4^-). The concentration of bisulfate that is formed is dependent upon the total sulfate concentration and the amount of acid added. In general, unless large amounts of acid are added, the concentration of bisulfate formed does not significantly alter the total free SO_4^{2-} concentration and, as a result, the A correction factor maintains a constant value throughout the titration procedure. However, the formation of bisulfate can consume a significant amount of the total added acid. It is therefore necessary to account for bisulfate formation in order to determine the correct concentration of free H^+ .

a 5.5 m NaCl solution was also titrated with NaOH to determine the value of A compared with that obtained from the HCl titrations. The NaOH added during this titration was converted to calculated $H^+_{free,add}$ through the concentration-dependent dissociation constant of water (K_w^c):

$$H^+_{free,add} = K_w^c / (OH^-_{add}) \quad (4)$$

The value of K_w^c for 5.5 m NaCl needed to determine $H^+_{free,add}$ was found to be 3.904×10^{-15} and was calculated using the GMIN equilibrium code (Felmy 1990), with 25°C values of Pitzer parameters reported in Table 3 and μ^0/RT values of chemical species in Table 4. The temperature dependence of these parameters was neglected owing to the small difference between room temperature and 25°C (i.e. 2-5°C). The plot of the $H^+_{free,add}$ versus H^+_{ob} (Figure 4) from the NaOH titrations of 5.5 m NaCl indicates that the data are highly linear. The 0.86 value of A parameter calculated from these data is very close to the 0.92 value obtained from the HCl titrations and therefore the values of A calculated from the HCl or NaOH titrations can be used to calculate pC_{H^+} in samples varying considerably in H^+ concentrations. These experiments also demonstrate the ability of the thermodynamic model to accurately calculate the H^+ concentration in the basic chloride solutions.

Titration of Na_2SO_4

Adding acid to aqueous solutions containing Na_2SO_4 results in the formation of bisulfate ions (HSO_4^-). The concentration of bisulfate that is formed is dependent upon the total sulfate concentration and the amount of acid added. In general, unless large amounts of acid are added, the concentration of bisulfate formed does not significantly alter the total free SO_4^{2-} concentration and, as a result, the A correction factor maintains a constant value throughout the titration procedure. However, the formation of bisulfate can consume a significant amount of the total added acid. It is therefore necessary to account for bisulfate formation in order to determine the correct concentration of free H^+ . The concentration of bisulfate formed in the solution can be readily calculated if the apparent equilibrium constant (K_{app}) for the bisulfate formation reaction,

can be determined for the Na_2SO_4 concentration of interest. Knowledge of K_{app} then allows a direct calculation of the free H^+ from the relation

$$(H^+_{free,add}) = (H^+_{add}) / [1 + K_{app}(SO_4^{2-})] \quad (6)$$

In this study the values of K_{app} were calculated using the Pitzer thermodynamic model. Table 5 presents a summary of the values for K_{app} for a 2 m Na_2SO_4 solution with varying amounts of added acid. As expected the apparent equilibrium constants in this solution are approximately constant except for the largest additions of acid. The use of the Pitzer thermodynamic model to accurately calculate the apparent equilibrium constants for these Na_2SO_4 solutions is at least partially verified in the next section, on mixed Na_2SO_4 - NaCl solutions.

Table 3. Ion Interaction Parameters Used in This Study (all values from Harvie et al. 1984)

Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ
Binary System Parameters				
$\text{Na}^+ - \text{SO}_4^{2-}$	0.01958	1.1130	0.00	0.00497
$\text{Na}^+ - \text{HSO}_4^-$	0.0454	0.3980	0.00	0.00
$\text{Na}^+ - \text{OH}^-$	0.0864	0.2530	0.00	0.0044
$\text{H}^+ - \text{SO}_4^{2-}$	0.0298	0.00	0.00	0.0438
$\text{H}^+ - \text{HSO}_4^-$	0.2065	0.5556	0.00	0.00
Common Ion Ternary System Interactions				
$\text{Na}^+ - \text{H}^+$	0.036			
$\text{Na}^+ - \text{H}^+ - \text{HSO}_4^-$	-0.0129			
$\text{SO}_4^{2-} - \text{HSO}_4^- - \text{Na}^+$	-0.0094			
$\text{SO}_4^{2-} - \text{OH}^-$	-0.013			
$\text{SO}_4^{2-} - \text{OH}^- - \text{Na}^+$	-0.009			

Table 4. Chemical Potentials of the Species Used in Calculations (all values from Harvie et al. 1984)

Species	μ°/RT
$\text{H}_2\text{O}(\text{l})$	-95.664
H^+	0.00
OH^-	-63.435
Na^+	-105.651
Cl^-	-52.955
SO_4^{2-}	-300.386
HSO_4^-	-304.942

The plots of the moles/L of the $H^{+}_{free,add}$ versus the moles/L of H^{+} observed (H^{+}_{ob}) with the pH probe for 0.05, 0.1, 0.5, 1.0, 1.5, and 2.0 m Na_2SO_4 are shown in Figures 5 to 7, and the corresponding raw data are tabulated in Appendix D. Linear regression through the data points indicates that there is very little scatter around the line and that the r^2 values in all cases were greater than 0.99. The slopes of the regression lines and calculated values of the A parameter are reported in Table 6. The values of A range from 0.19 to -0.35 and, with the exception of the value for 0.05 m Na_2SO_4 , all values are negative. It is important to note (Appendix D) that H^{+}_{add} is significantly different than $H^{+}_{free,add}$. Therefore, the values of A based on $H^{+}_{free,add}$ are expected to be significantly different than those based on total H^{+}_{add} . Hence, to obtain reliable values of A, $H^{+}_{free,add}$ must be used in calculations.

As found for NaCl titrations, the values of correction factors A calculated from the titrations of Na_2SO_4 with HCl are expected to be similar to those calculated from Na_2SO_4 titrations with NaOH. The log value of the formation constant for HSO_4^- is 1.98 (Harvie et al. 1984), such that $\log(HSO_4^-) = \log(SO_4^{2-}) + 1.98 - pH$. Therefore, under alkaline conditions the proportion of HSO_4^- compared with SO_4^{2-} is insignificant and thus it can be ignored as a source for consumption of added OH during titrations of Na_2SO_4 with NaOH. Furthermore, the hydrolysis of Na^+ at titration pH values is not important. Therefore, the total H^{+}_{add} ($K_w^c / (OH^{+}_{add})$, from Eq. (4), under alkaline conditions should equal $H^{+}_{free,add}$.

Table 5. Variation in K_{app} as a function of H^{+}_{add} for 2 molal Na_2SO_4

H^{+}_{add} (Moles/L)	K_{app}
0.00001	2.395
0.0001	2.395
0.001	2.395
0.005	2.396
0.008	2.397
0.001	2.397
0.05	2.406

Figure 5. Titration of 0.05 m and 0.10 m Na₂SO₄ with HCl [$H^+_{\text{free,add}}$ is moles/L of free H^+ added, and H^+_{ob} is calculated from observed pH ($H^+_{\text{ob}} = 10^{-\text{pH}}$); linear regression lines are also shown (for regression coefficients, see Table 7)]

Figure 6. Titration of 0.50 m and 1.00 m Na_2SO_4 with HCl [$H^+_{\text{free,add}}$ is moles/L of free H^+ added, and H^+_{ob} is calculated from observed pH ($H^+_{\text{ob}} = 10^{-\text{pH}}$); linear regression lines are also shown (for regression coefficients, see Table 7)]

Figure 7. Titration of 1.50 m and 2.0 m Na₂SO₄ with HCl [$H^+_{free,add}$ is moles/L of free H^+ added, and H^+_{ob} is calculated from observed pH ($H^+_{ob} = 10^{-pH}$); linear regression lines are also shown (for regression coefficients, see Table 7)]

The values of K_w^c for different Na_2SO_4 solutions containing 0.0001 to 0.01 M NaOH were calculated using the GMIN equilibrium code (Felmy 1990) with the values of Pitzer parameters and μ^*/RT reported in Tables 3 and 4, respectively. These K_w^c values for a given electrolyte concentration, as expected, were found to be relatively constant. For example, K_w^c values for 2 m Na_2SO_4 ranged from 3.28×10^{-14} to 3.29×10^{-14} (Table 7). The average values of K_w^c for 0.05, 0.1, 0.5, and 2.0 m Na_2SO_4 solutions are reported in Table 8. The plots of the $\text{H}^+_{\text{free,add}}$ (calculated using Eq. 4) versus H^+_{ob} (Figures 8 and 9) show that the data are highly linear. The values of the A parameter calculated from NaOH titrations are in fairly good agreement (average difference of 0.13 units) with those calculated from HCl titrations (Table 6).

Table 6. Titration of Na_2SO_4 Solutions

Na_2SO_4 (molality)	Titratant	Slope ^(a)	Correction factor A (log slope)
0.05	HCl	1.183	0.07
	NaOH	0.641	0.19
0.10	HCl	0.804	- 0.10
	NaOH	0.565	- 0.25
0.50	HCl	0.566	- 0.25
	NaOH	0.444	- 0.35
1.00	HCl	0.486	- 0.31
1.50	HCl	0.479	- 0.32
2.00	HCl	0.508	- 0.29
	NaOH	0.444	- 0.35
^(a) $Y = mX + b$; where Y is the moles/L of $0.486\text{H}^+_{\text{ob}}$ with pH electrode (i.e., $10^{-\text{pH}_{\text{ob}}}$), m is the slope, 0.479 and X is the moles/L of $\text{H}^+_{\text{free,add}}$ (see text). 0.508			

Table 7. Values of Apparent Dissociation Constant of Water (K_w^c) for 2 m Na_2SO_4 Solutions Titrated with NaOH

OH_{add}	K_w^c
0.0001	3.29×10^{-14}
0.001	3.29×10^{-14}
0.0015	3.29×10^{-14}
0.003	3.29×10^{-14}
0.01	3.28×10^{-14}

Figure 8. Titration of 0.05 m and 0.10 m Na_2SO_4 Solutions with NaOH [$H^+_{free,add}$ is moles/L of free H^+ added, and H^+_{ob} is calculated from observed pH ($H^+_{ob} = 10^{-pH}$); linear regression lines are also shown]

Table 8. Factors to Calculate $H^{+}_{\text{free,add}}$ from Total H^{+}_{add} or OH^{-}_{add} for Na_2SO_4 Solutions

Na_2SO_4 (molality)	K_{app}	K_w^c
0.05	25.74	2.02×10^{-14}
0.10	17.69	2.45×10^{-14}
0.50	5.614	4.015×10^{-14}
1.00	3.267	NC
1.50	2.572	NC
2.00	2.395	3.29×10^{-14}
NC = not calculated		

Titration of Mixed Na_2SO_4 and $NaCl$ Electrolytes

Two mixed electrolytes (5.5 m $NaCl$ + 0.01 m Na_2SO_4 , and 5.5 m $NaCl$ + 0.05 m Na_2SO_4) were titrated with HCl and $NaOH$ to determine the values of correction factor A for their use in estimating pC_H^{+} of mixed salt solutions (raw data are presented in Appendix E). The procedures used for titrations and for calculations were analogous to those described above for titrations of pure $NaCl$ and Na_2SO_4 . The values for K_{app} and K_w^c needed to convert the H^{+}_{add} to $H^{+}_{\text{free,add}}$ for these solutions are listed in Table 9. The values of A based on titrations of (5.5 m $NaCl$ + 0.01 m Na_2SO_4) and (5.5 m $NaCl$ + 0.05 m Na_2SO_4) with $NaOH$ were 0.87 and 0.83, respectively (Figure 10), whereas they were 0.95 and 0.99, respectively, when titrations were done with HCl and the $H^{+}_{\text{free,add}}$ was calculated from H^{+}_{add} using Eq. (6) (Figure 11). As discussed earlier for Na_2SO_4 solutions, the values of A were considerably different if Eq. 6 was not used to account for the consumption of a portion of the H^{+}_{add} in the formation of HSO_4^{-} . The Figures 10 and 11 show that there is very little scatter in the data. Since (5.5 m $NaCl$ + 0.01 m Na_2SO_4) and (5.5 m $NaCl$ + 0.05 m Na_2SO_4) solutions are primarily $NaCl$ solutions, it was not surprising to find values of A based on HCl titrations for these solutions (0.95 to 0.99) similar to that observed (0.92) for pure 5.5 m $NaCl$ (Table 2). These results indicate that the Pitzer thermodynamic model is effective in calculating the values of K_{app} needed to account for bisulfate formation in these solutions and that the H^{+} concentration determination method is applicable to mixed $NaCl$ and Na_2SO_4 solutions.

Table 9. Factors to Calculate $H^{+}_{\text{free,add}}$ from Total H^{+}_{add} or OH^{-}_{add} for Mixed $NaCl$ and Na_2SO_4 Solutions

Electrolyte	K_{app}	K_w^c
5.5 m $NaCl$ + 0.01 m Na_2SO_4	2.6	3.899×10^{-15}
5.5 m $NaCl$ + 0.05 m Na_2SO_4	2.6	3.868×10^{-15}

Figure 10. Titration of (5.5 m NaCl + 0.01 m Na_2SO_4) and (5.5 m NaCl + 0.05 m Na_2SO_4) with NaOH [$H^+_{free,add}$ is moles/L of free H^+ added and H^+_{ob} is calculated from observed pH ($H^+_{ob} = 10^{-pH}$); linear regression lines are also shown]

Titration When the Reference Cell Filled with NaCl

To minimize the liquid junction effects, some of the investigators suggest filling the reference cell of the combination glass electrode with a similar medium as the sample. We would expect the values of correction factor A to be different for the electrodes filled with 3.0 M KCl or standard NaCl. However, we wanted to test whether the H^+ concentrations calculated from these two different electrodes with two different correction factors are the same. Therefore, the reference cell of the Orion-Ross electrode was filled with 6 m NaCl and the titrations of 6.0 m NaCl with HCl were conducted to obtain the values of A . The plots of the moles/L of the $H^+_{free,add}$ versus the moles/L of H^+ observed (H^+_{ob}) with the pH probe are shown in Figure 12 for the titration data corresponding to <4 hours and 8 days (Appendix F) after filling the reference cell with 6 m NaCl. The titration data (Figure 12) and the calculated values of A (1.30 and 1.27) are almost identical. A 25-ml test solution of 6.0 m NaCl spiked with 0.140 ml of 0.0104 M HCl was prepared. The observed pH value was 4.185 with the calibrated pH electrode containing 3.0 M KCl solution, and it was 3.933 with the electrode containing 6.0 m NaCl. Using the values of pH_{ob} and of A in Eq. (1), the calculated values of pC_{H^+} were 5.16 and 5.22 for the electrodes containing KCl and NaCl, respectively. The excellent agreement between the final calculated pC_{H^+} values suggests that no advantage is gained by filling the electrode with an electrolyte similar in composition to the test solution, if the proposed method is used.

Figure 12. Titration of 6.0 m NaCl with HCl When the Reference Cell of the Glass Electrode was Filled with 6.0 m NaCl Instead of 3.0 M KCl and When the Titrations Were Performed <4 Hours and 8 Days after Filling the Cell with NaCl [$H^+_{free,add}$ is moles/L of free H⁺ added, and H^+_{ob} is calculated from observed pH ($H^+_{ob} = 10^{-pH}$) linear regression lines are also shown]

Figure 13. Values of A as a Function of Molality of Electrolyte for NaCl solutions [$A = (0.159)(\text{molality of NaCl})$] and for Na₂SO₄ solutions ($A = 0.221 - 0.549X + 0.201X^2$), where X is the molality of Na₂SO₄

Summary and Conclusions

A large number of NaCl, Na₂SO₄, and mixtures of NaCl and Na₂SO₄ solutions varying in concentrations were titrated to determine the correction factors A to estimate the pC_H⁺ (negative logarithm of H⁺ concentration) from the measured/observed pH values (pC_H⁺ = pH_{obs} + A). The titrations were done with HCl and NaOH. The titration method is described in detail. This method is equally applicable to determining the pC_H⁺ values of natural and synthetic brines (e.g., Felmy et al. 1989; Pederson et al. 1993). It should be emphasized that extra precautions are required to determine correction factors for electrolytes that react with H⁺ or OH⁻ [e.g., sulfate brines for titration with acid, as discussed in the text; and magnesium brines for titration with base because of the precipitation of Mg(OH)₂]. It should be noted that the presence of minor H⁺ consuming species, such as trace levels of HCO₃⁻, CO₃²⁻, or B species, does not effect the procedure outlined here as long as data from the acid side of the titration curve are used. Also other minor species, (i.e. species such as K⁺ which may be present at concentrations ten or twenty times lower than the bulk Na⁺ concentration), do not effect the calculated A values since such minor species do not effect the convention dependent activity coefficient of H⁺ or the liquid junction term.

The values of A obtained from HCl titrations were similar to those obtained from NaOH titrations. These values should be applicable to solutions similar in compositions to those titrated in this study and with a very large range in measured pH values (approximately 2 to 12). Because a large number of solutions were titrated with HCl and that the A values are similar for HCl and NaOH titrations, A values for any given NaCl or Na₂SO₄ solutions can be obtained from fitting the data for A values as a function of molality of the given electrolyte (Figure 13). A limited number of different Orion-Ross electrodes were evaluated to determine the dependence of the A values on an individual electrode. These evaluations indicated that the A values did not differ significantly for different electrodes (+/- ~ 0.05 pC_H⁺ units). The results suggest that the data reported in Figure 13 can be used to estimate A values for different NaCl and Na₂SO₄ solutions without having to calibrate each and every electrode.

Although the values of A were different when the reference cell of the combination glass electrode was filled with an electrolyte of the same composition as the test sample (as recommended in some procedures proposed in the literature) or with 3 M KCl, the final estimated pC_H⁺ values in both cases were similar. These results indicate that reliable results can be obtained with the proposed method that uses standard Orion-Ross electrode without filling the reference cell with the electrolyte of the same composition as the test solution.

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Appendix A

Derivation of the Equations Relating the Measured EMF of a Glass Electrode with Liquid Junction to the Measured Hydrogen Ion Concentration

Appendix A

Derivation of the Equations Relating the Measured EMF of a Glass Electrode with Liquid Junction to the Measured Hydrogen Ion Concentration

The following paragraphs derive the equations relating the measured EMF to the hydrogen ion concentration for a glass electrode with liquid junction.

The equation for the EMF of a glass electrode with a liquid junction is

$$E_x = (\mu_{H^+}(\text{soln } x) - \mu_{H^+}(\text{glass}))/F + E_j^x + C \quad (A1)$$

where E_x is the measured EMF, μ is the chemical potential, F is Faraday's constant, E_j^x is the liquid junction potential, and C represents the sum of all other electrostatic potential differences in the electrode system such as potential differences between Pt wires. In our case C is a constant since none of these potentials are related to the solution composition. Equation (A1) is derived from the phase equilibrium relating the electrochemical potential of H^+ in the unknown solution to the electrochemical potential of H^+ at the surface of the glass electrode. When this same electrode is immersed in a standard solution we can write

$$E_s = (\mu_{H^+}(\text{soln } s) - \mu_{H^+}(\text{glass}))/F + E_j^s + C \quad (A2)$$

Taking the difference between these two equations and assuming that the chemical potential of H^+ at the glass surface remains constant as a result of the HCl or other solution on the inside of the glass (Note: this assumption may not be true if large asymmetry potentials develop at the glass surface) yields

$$E_x - E_s = RT/F(\ln a_{H^+}(\text{soln } s) - \ln a_{H^+}(\text{soln } x)) + \Delta E_j \quad (A3)$$

or, upon rearranging and using base 10 logarithms

$$p a_{H^+}(x) - p a_{H^+}(s) = (F/2.303RT)(E_x - E_s + \Delta E_j) \quad (A4)$$

where $p a_{H^+}$ is the negative logarithm of the activity of H^+ . The operational definition of pH is

$$pH(x) = pH(s) + (E_x - E_s)F/2.303RT \quad (A5)$$

where $pH(x)$ is the "observed" pH meter reading using the unknown solution and $pH(s)$ is the meter reading using a standard solution. Combining these two equations and assigning the pH of the standard solution to be equal to the negative logarithm of the thermodynamic activity of H^+ in the standard solution yields

$$pa_H^+ = pH(x) + \Delta E_j F / 2.303RT \quad (A6)$$

or

$$pc_{H^+} = pH(x) + \log \gamma_{H^+} + \Delta E_j F / 2.303RT \quad (A7)$$

which, for a solution of constant electrolyte composition, yields

$$pC_{H^+} = pH_{ob} + A \quad (A8)$$

where A is a constant owing to the fact that the convention-dependent activity coefficient of H^+ and the difference in liquid junction remain constant in the solution as the H^+ concentration changes.

Appendix B

Determination of Hydrogen Ion Concentrations in Brines

Appendix B

Determination of Hydrogen Ion Concentrations in Brines

1.0 OBJECTIVE

This procedure describes a method to estimate pC_{H^+} (negative logarithm of H^+ concentration) of concentrated salt brines using a pH meter and combination glass pH electrode.

2.0 APPLICABILITY

This procedure is addressed to the project manager, task leader, and trained and qualified personnel who will be performing the pH measurements in concentrated brines.

3.0 DEFINITIONS

N: normality of standard HCl solution.

V_i : volume of standardized acid addition, ml

X_i : $\frac{V_i N}{25.0 + V_i}$, moles of standard HCl per liter added to titration vessel containing 25.0 ml of salt solution. In the case of electrolytes that do not chemically react with added H^+ (such as NaCl), the added H^+ equals free H^+ added ($H^+_{free, add}$). However, for Na_2SO_4 that reacts with added H^+ to form HSO_4 species, the $H^+_{free, add}$ is calculated by dividing the moles/L of H^+ added by $(1 + K_{app}(SO_4^{2-}))$ (for details see text). X_i is $H^+_{free, add}$ in moles/L.

4.0 RESPONSIBILITIES

4.1 Cognizant Scientist

4.1.1 Train the technician in the use of this procedure and provide help and guidance in data reduction.

4.1.2 Ensure that the work is done according to this procedure.

4.2 Technicians

4.2.1 Ensure that the applicable equipment is in proper working order.

4.2.2 Conduct tests according to this procedure.

4.2.3 Comply with laboratory data storage and reduction practices.

4.2.4 Implement QA requirements related to this procedure.

4.2.5 Report completed test results to the cognizant scientist.

5.0 PROCEDURE

5.1 Equipment and Materials Required

- 5.1.1 pH meter equipped to read out in pH units to a precision of at least 0.01 units.
- 5.1.2 Combination glass pH electrode (e.g., Orion-Ross).
- 5.1.3 pH buffer solutions 2, 4, 7, and 10.
- 5.1.4 A buret capable of delivering titrant accurate to 0.001 mL.
- 5.1.5 Standardized HCl solution, 0.01 M to 0.10 M (see 5.2.5).
- 5.1.6 Transfer pipette, 25.0 ± 0.1 ml.
- 5.1.7 Titration vessel with cover.
- 5.1.8 N_2 gas for sparging.

5.2 Calibration of pH Electrode Response in Brines

- 5.2.1 Calibrate pH electrode and meter using pH buffer solution at 4 and 7, using pH meter manuals as a guide. Measure and record the electrode response in pH 2 and 10 buffers (but do not readjust meter).
- 5.2.2 Deliver 25.0 ± 0.1 ml brine for which a pH calibration is required into a titration vessel. The method also applies to blanks (deionized water rather than brines).
- 5.2.3 Sparge with an inert gas for 5 minutes before beginning the titration. Continue sparging throughout the titration procedure. In addition, the solution should be continuously stirred.
- 5.2.4 Measure and record the temperature of the solution to a precision of $\pm 1^\circ\text{C}$.
- 5.2.5 Add standardized HCl to the titration vessel containing the sparged brine solution until an appropriate pH change is observed. Select the molarity of the HCl so that 1) the volume of acid can be accurately measured to observe pH changes as reported in step 5.2.6, and 2) the total volume of acid used by the end of titration is far less than 10% of the original volume of brine used for titration. Record both the measured pH (pH_{ob}) and the corresponding volume addition of standardized HCl.
- 5.2.6 Repeat step 5.2.4 every 0.2 to 0.4 pH units above pH 4.5 and every 0.1 pH unit for pH < 4.5 . Liquid junction errors will depress the measured pH values from the actual value by approximately 0.9 pH unit in saturated NaCl solution at 20°C and by approximately 3 units in saturated MgCl_2 solutions, requiring some adjustment in the measured pH range over which the data is taken.

5.3 Data Records

Record in the appropriate laboratory record books, all information and data called for by this procedure including pH meter and electrode used, calibration of pH meter and pH buffer

readings, molality of the acid used in titration, volume of electrolyte used in titration, temperature, incremental volume of acid added, total volume of acid added, and observed pH after each incremental acid addition.

5.4 Calculations

5.4.1 Calculation of acid added and measured:

Equivalents H^+/L measured, $Y_i = 10^{-pH}$

Equivalents HCl/L added ($H^+_{free,add}$) to titration vessel, X_i (see 3.0 above)

5.4.2 Data set selection for calculation of correction factor A

Plot Y_i (acid detected using pH probe) versus X_i ($H^+_{free,add}$ in moles/L added to titration vessel). Select for further calculations those data X_i, Y_i that yield a linear relationship by visual inspection.

5.4.3 Least-Squares Calculation

For the selected data set X_i, Y_i , calculate the slope, defined as

$$\text{slope} = \frac{X_i Y_i - \frac{X_i Y_i}{n}}{X_i^2 - \frac{(X_i)^2}{n}}$$

5.4.4 Calculation of correction factor A

$A = \log (\text{slope})$

5.4.5 Calculation of H^+ concentration (pC_{H^+}) from measured/observed pH

$pC_{H^+} = pH_{ob} + A$

6.0 EXAMPLE DATA SETS AND CALCULATIONS

For examples of data to be obtained and the necessary calculations, see Appendices C, D, and E and the text of this document.

Appendix C
Titration of NaCl Solutions

Appendix C

Titration of NaCl Solutions

Table C.1 Titration of 25 ml of 1.0 Molal NaCl with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
6.976	0.000	0.000E+00
5.740	0.025	1.042E-05
5.012	0.050	2.082E-05
4.934	0.054	2.248E-05
4.849	0.060	2.497E-05
4.759	0.066	2.746E-05
4.684	0.073	3.037E-05
4.601	0.082	3.410E-05
4.558	0.091	3.783E-05
4.420	0.107	4.445E-05
4.379	0.114	4.734E-05
4.313	0.126	5.230E-05
4.242	0.142	5.891E-05
4.181	0.159	6.592E-05
4.107	0.180	7.456E-05
4.048	0.202	8.360E-05
3.976	0.229	9.467E-05
3.915	0.257	1.061E-04
3.854	0.290	1.196E-04
3.792	0.328	1.351E-04
3.738	0.371	1.525E-04
3.673	0.423	1.735E-04
3.612	0.477	1.953E-04
3.559	0.535	2.185E-04
3.502	0.604	2.460E-04
3.454	0.678	2.754E-04
3.391	0.769	3.113E-04
3.347	0.845	3.410E-04
3.303	0.944	3.795E-04
3.249	1.062	4.250E-04
3.204	1.173	4.674E-04
3.162	1.297	5.144E-04
3.119	1.438	5.673E-04
3.074	1.588	6.229E-04
3.034	1.739	6.783E-04
3.028	1.903	7.378E-04
2.958	2.103	8.093E-04
2.949	2.169	8.327E-04
2.940	2.301	8.791E-04
2.888	2.501	9.485E-04
2.883	2.592	9.798E-04
2.865	2.774	1.042E-03
2.820	2.974	1.109E-03
2.817	3.084	1.145E-03
2.782	3.284	1.211E-03

Table C.1 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
2.777	3.399	1.248E-03
2.752	3.599	1.313E-03
2.740	3.758	1.363E-03
2.717	3.958	1.426E-03
2.708	4.147	1.484E-03
2.678	4.347	1.545E-03
2.674	4.484	1.586E-03
2.659	4.684	1.646E-03
2.640	4.884	1.705E-03
2.631	5.000	1.738E-03

Table C.2 Titration of 25 ml of 2.0 Molal NaCl with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
6.376	0.000	0.000E+00
5.066	0.025	1.042E-05
4.607	0.050	2.082E-05
4.539	0.056	2.331E-05
4.466	0.063	2.622E-05
4.389	0.072	2.995E-05
4.316	0.082	3.410E-05
4.254	0.094	3.907E-05
4.175	0.109	4.528E-05
4.108	0.124	5.148E-05
4.043	0.141	5.850E-05
3.981	0.162	6.715E-05
3.910	0.186	7.703E-05
3.848	0.212	8.770E-05
3.789	0.242	9.999E-05
3.720	0.278	1.147E-04
3.663	0.315	1.298E-04
3.603	0.360	1.481E-04
3.543	0.410	1.683E-04
3.487	0.466	1.909E-04
3.430	0.529	2.161E-04
3.378	0.599	2.441E-04
3.324	0.679	2.758E-04
3.271	0.767	3.105E-04
3.223	0.862	3.476E-04
3.174	0.970	3.896E-04
3.124	1.086	4.342E-04
3.083	1.208	4.807E-04
3.037	1.347	5.332E-04
2.999	1.491	5.870E-04
2.957	1.653	6.469E-04

Table C.2 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
2.919	1.818	7.071E-04
2.886	1.995	7.708E-04
2.848	2.190	8.401E-04
2.818	2.376	9.052E-04
2.787	2.576	9.743E-04
2.760	2.776	1.042E-03
2.735	2.976	1.110E-03
2.718	3.176	1.176E-03
2.694	3.376	1.241E-03
2.676	3.574	1.305E-03
2.656	3.774	1.368E-03
2.638	3.974	1.431E-03
2.623	4.174	1.492E-03
2.605	4.374	1.553E-03
2.592	4.574	1.613E-03
2.577	4.774	1.672E-03
2.564	4.974	1.731E-03
2.562	5.000	1.738E-03

Table C.3 Titration of 25 ml of 3.0 Molal NaCl with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
6.194	0.000	0.000E+00
5.136	0.025	1.042E-05
4.524	0.050	2.082E-05
4.450	0.055	2.290E-05
4.381	0.061	2.539E-05
4.288	0.069	2.871E-05
4.220	0.076	3.161E-05
4.144	0.086	3.576E-05
4.073	0.096	3.990E-05
4.004	0.109	4.528E-05
3.931	0.123	5.106E-05
3.862	0.139	5.767E-05
3.796	0.157	6.509E-05
3.726	0.178	7.374E-05
3.669	0.200	8.278E-05
3.602	0.229	9.467E-05
3.542	0.261	1.078E-04
3.472	0.298	1.229E-04
3.416	0.335	1.379E-04
3.354	0.381	1.566E-04
3.298	0.430	1.764E-04
3.244	0.488	1.997E-04

Table C.3 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
3.182	0.556	2.269E-04
3.129	0.625	2.544E-04
3.076	0.705	2.861E-04
3.025	0.792	3.203E-04
2.976	0.889	3.582E-04
2.926	0.997	4.000E-04
2.881	1.112	4.442E-04
2.837	1.239	4.925E-04
2.793	1.377	5.445E-04
2.753	1.525	5.997E-04
2.713	1.686	6.590E-04
2.676	1.855	7.204E-04
2.641	2.036	7.855E-04
2.609	2.227	8.531E-04
2.575	2.427	9.229E-04
2.551	2.627	9.918E-04
2.521	2.827	1.060E-03
2.499	3.016	1.123E-03
2.485	3.216	1.189E-03
2.457	3.416	1.254E-03
2.451	3.573	1.304E-03
2.424	3.773	1.368E-03
2.420	3.915	1.412E-03
2.399	4.115	1.474E-03
2.391	4.278	1.524E-03
2.374	4.478	1.584E-03
2.360	4.678	1.644E-03
2.347	4.878	1.703E-03
2.339	5.000	1.738E-03

Table C.4 Titration of 25 ml of 4.0 Molal NaCl with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
6.508	0.000	0.000E+00
5.590	0.025	1.042E-05
4.738	0.050	2.082E-05
4.622	0.054	2.248E-05
4.536	0.058	2.414E-05
4.443	0.063	2.622E-05
4.350	0.068	2.829E-05
4.290	0.074	3.078E-05
4.177	0.083	3.451E-05
4.116	0.089	3.700E-05

Table C.4 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
4.054	0.097	4.031E-05
3.979	0.108	4.486E-05
3.898	0.120	4.982E-05
3.828	0.133	5.519E-05
3.760	0.147	6.097E-05
3.701	0.164	6.797E-05
3.627	0.185	7.662E-05
3.562	0.207	8.565E-05
3.496	0.233	9.631E-05
3.429	0.261	1.078E-04
3.377	0.292	1.204E-04
3.308	0.333	1.371E-04
3.252	0.375	1.541E-04
3.189	0.425	1.743E-04
3.136	0.478	1.957E-04
3.080	0.542	2.213E-04
3.026	0.613	2.496E-04
2.964	0.693	2.813E-04
2.920	0.771	3.120E-04
2.868	0.870	3.508E-04
2.819	0.975	3.915E-04
2.775	1.088	4.350E-04
2.732	1.217	4.842E-04
2.684	1.359	5.377E-04
2.646	1.498	5.896E-04
2.607	1.658	6.487E-04
2.569	1.827	7.103E-04
2.539	2.007	7.751E-04
2.506	2.207	8.461E-04
2.474	2.407	9.160E-04
2.447	2.607	9.849E-04
2.423	2.807	1.053E-03
2.402	3.007	1.120E-03
2.386	3.207	1.186E-03
2.363	3.407	1.251E-03
2.345	3.600	1.313E-03
2.327	3.800	1.376E-03
2.314	4.000	1.439E-03
2.302	4.200	1.500E-03
2.290	4.400	1.561E-03
2.278	4.600	1.621E-03
2.267	4.800	1.680E-03
2.256	5.000	1.738E-03

Table C.5 Titration of 25 ml of 5.0 Molal NaCl with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
7.810	0.000	0.000E+00
7.144	0.025	1.042E-05
5.717	0.050	2.082E-05
5.388	0.052	2.165E-05
5.293	0.054	2.248E-05
5.179	0.056	2.331E-05
5.071	0.059	2.456E-05
4.955	0.063	2.622E-05
4.828	0.067	2.788E-05
4.708	0.071	2.954E-05
4.613	0.075	3.120E-05
4.496	0.079	3.285E-05
4.413	0.083	3.451E-05
4.346	0.088	3.658E-05
4.225	0.095	3.948E-05
4.161	0.100	4.155E-05
4.084	0.106	4.404E-05
3.998	0.114	4.734E-05
3.931	0.122	5.065E-05
3.857	0.132	5.478E-05
3.768	0.143	5.932E-05
3.722	0.154	6.386E-05
3.614	0.171	7.086E-05
3.574	0.180	7.456E-05
3.501	0.198	8.196E-05
3.446	0.216	8.934E-05
3.372	0.241	9.959E-05
3.301	0.266	1.098E-04
3.244	0.292	1.204E-04
3.193	0.325	1.338E-04
3.109	0.369	1.517E-04
3.072	0.398	1.634E-04
3.009	0.449	1.840E-04
2.950	0.503	2.057E-04
2.891	0.562	2.293E-04
2.837	0.626	2.548E-04
2.786	0.699	2.837E-04
2.729	0.785	3.175E-04
2.680	0.873	3.519E-04
2.634	0.974	3.911E-04
2.585	1.089	4.354E-04
2.540	1.210	4.815E-04
2.494	1.344	5.321E-04
2.456	1.484	5.844E-04
2.419	1.644	6.436E-04
2.379	1.818	7.071E-04
2.343	1.994	7.704E-04
2.311	2.181	8.369E-04
2.280	2.381	9.070E-04
2.253	2.581	9.760E-04
2.228	2.781	1.044E-03

Table C.5 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
2.207	2.981	1.111E-03
2.187	3.181	1.177E-03
2.169	3.381	1.243E-03
2.152	3.581	1.307E-03
2.136	3.781	1.370E-03
2.123	3.981	1.433E-03
2.109	4.181	1.494E-03
2.090	4.381	1.555E-03
2.085	4.581	1.615E-03
2.076	4.781	1.674E-03
2.066	4.981	1.733E-03
2.064	5.000	1.738E-03

Table C.6 Titration of 25 ml of 5.5 Molal NaCl with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
8.210	0.000	0.000E+00
7.840	0.025	1.042E-05
7.110	0.050	2.082E-05
6.801	0.053	2.206E-05
6.598	0.055	2.290E-05
6.432	0.057	2.373E-05
6.138	0.060	2.497E-05
5.924	0.062	2.580E-05
5.756	0.064	2.663E-05
5.606	0.066	2.746E-05
5.450	0.069	2.871E-05
5.309	0.071	2.954E-05
5.159	0.074	3.078E-05
4.998	0.077	3.203E-05
4.884	0.080	3.327E-05
4.761	0.083	3.451E-05
4.639	0.086	3.576E-05
4.548	0.090	3.741E-05
4.423	0.094	3.907E-05
4.323	0.098	4.073E-05
4.222	0.103	4.280E-05
4.138	0.108	4.486E-05
4.040	0.114	4.734E-05
3.963	0.120	4.982E-05
3.884	0.127	5.272E-05
3.804	0.135	5.602E-05
3.727	0.144	5.973E-05
3.656	0.154	6.386E-05
3.577	0.165	6.839E-05

Table C.6 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
3.515	0.177	7.333E-05
3.439	0.193	7.990E-05
3.383	0.209	8.647E-05
3.300	0.231	9.549E-05
3.246	0.249	1.029E-04
3.179	0.274	1.131E-04
3.118	0.301	1.241E-04
3.055	0.334	1.375E-04
2.998	0.370	1.521E-04
2.929	0.414	1.699E-04
2.874	0.458	1.876E-04
2.816	0.511	2.089E-04
2.764	0.570	2.325E-04
2.702	0.642	2.611E-04
2.649	0.713	2.892E-04
2.599	0.795	3.215E-04
2.551	0.888	3.578E-04
2.499	0.995	3.992E-04
2.457	1.105	4.415E-04
2.410	1.236	4.914E-04
2.368	1.370	5.419E-04
2.325	1.518	5.971E-04
2.287	1.673	6.542E-04
2.254	1.843	7.161E-04
2.217	2.034	7.847E-04
2.209	2.225	8.524E-04
2.155	2.425	9.223E-04
2.152	2.507	9.506E-04
2.125	2.670	1.006E-03
2.120	2.792	1.048E-03
2.089	2.992	1.115E-03
2.086	3.127	1.160E-03
2.057	3.327	1.225E-03
2.055	3.453	1.266E-03
2.033	3.653	1.330E-03
2.028	3.808	1.379E-03
2.011	4.008	1.441E-03
1.997	4.201	1.501E-03
1.986	4.401	1.561E-03
1.976	4.601	1.621E-03
1.966	4.801	1.680E-03
1.958	5.000	1.738E-03

Table C.7 Titration of 25 ml of 6.0 Molal NaCl with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
8.445	0.000	0.000E+00
8.150	0.025	1.042E-05
7.313	0.050	2.082E-05
7.206	0.053	2.206E-05
7.123	0.055	2.290E-05
7.003	0.059	2.456E-05
6.835	0.063	2.622E-05
6.657	0.066	2.746E-05
6.459	0.068	2.829E-05
6.294	0.070	2.912E-05
6.140	0.072	2.995E-05
5.996	0.075	3.120E-05
5.849	0.078	3.244E-05
5.718	0.081	3.368E-05
5.585	0.084	3.493E-05
5.454	0.087	3.617E-05
5.351	0.090	3.741E-05
5.219	0.093	3.866E-05
5.096	0.096	3.990E-05
4.992	0.099	4.114E-05
4.881	0.103	4.280E-05
4.758	0.107	4.445E-05
4.639	0.111	4.610E-05
4.531	0.115	4.776E-05
4.406	0.119	4.941E-05
4.304	0.123	5.106E-05
4.220	0.128	5.313E-05
4.123	0.133	5.519E-05
4.026	0.139	5.767E-05
3.951	0.144	5.973E-05
3.866	0.151	6.262E-05
3.777	0.159	6.592E-05
3.718	0.166	6.880E-05
3.636	0.177	7.333E-05
3.562	0.189	7.826E-05
3.481	0.202	8.360E-05
3.422	0.215	8.893E-05
3.344	0.232	9.590E-05
3.287	0.250	1.033E-04
3.204	0.273	1.127E-04
3.151	0.291	1.200E-04
3.105	0.317	1.306E-04
3.013	0.357	1.468E-04
2.979	0.379	1.558E-04
2.906	0.423	1.735E-04
2.853	0.462	1.892E-04
2.792	0.512	2.093E-04
2.742	0.565	2.305E-04
2.678	0.634	2.580E-04
2.635	0.697	2.829E-04
2.574	0.786	3.179E-04

Table C.7 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added (moles/L)
2.525	0.865	3.488E-04
2.480	0.959	3.853E-04
2.428	1.071	4.285E-04
2.383	1.185	4.720E-04
2.341	1.313	5.204E-04
2.299	1.457	5.744E-04
2.257	1.610	6.311E-04
2.221	1.771	6.900E-04
2.185	1.948	7.540E-04
2.151	2.135	8.206E-04
2.119	2.334	8.906E-04
2.091	2.534	9.599E-04
2.068	2.734	1.028E-03
2.046	2.934	1.095E-03
2.027	3.134	1.162E-03
2.009	3.334	1.227E-03
1.992	3.534	1.292E-03
1.976	3.734	1.355E-03
1.964	3.934	1.418E-03
1.951	4.134	1.480E-03
1.939	4.334	1.541E-03
1.929	4.534	1.601E-03
1.920	4.734	1.661E-03
1.910	4.934	1.719E-03
1.908	5.000	1.738E-03

Table C.8 Titration of 25 ml of 5.5 Molal NaCl with 0.0935 M NaOH

Observed pH	Volume of NaOH Added (ml)	NaOH Added ^(a) (moles/L)	H ⁺ _{free,add} ^(b) (moles/L)
8.219	0.000	0.000E+00	0.00
9.616	0.036	1.344E-04	2.90172E-11
9.956	0.071	2.647E-04	1.47335E-11
10.064	0.089	3.316E-04	1.17621E-11
10.189	0.115	4.280E-04	9.11229E-12
10.303	0.147	5.464E-04	7.13775E-12
10.420	0.189	7.013E-04	5.56085E-12
10.524	0.241	8.924E-04	4.37000E-12
10.639	0.311	1.148E-03	3.39579E-12
10.737	0.395	1.454E-03	2.68252E-12
10.840	0.507	1.858E-03	2.09915E-12
10.940	0.642	2.340E-03	1.66652E-12
11.035	0.805	2.916E-03	1.33752E-12
11.123	0.997	3.585E-03	1.08798E-12
11.201	1.197	4.271E-03	9.13166E-13
11.267	1.397	4.947E-03	7.88407E-13

Table C.8 (contd)

Observed pH	Volume of NaOH Added (ml)	NaOH Added ^(a) (moles/L)	H ⁺ _{free,add} ^(b) (moles/L)
11.320	1.597	5.612E-03	6.94896E-13
11.369	1.797	6.268E-03	6.22201E-13
11.412	1.997	6.914E-03	5.64066E-13
11.453	2.197	7.551E-03	5.16515E-13
11.488	2.397	8.178E-03	4.76900E-13
11.521	2.597	8.796E-03	4.43386E-13
11.551	2.797	9.405E-03	4.14665E-13
11.578	2.997	1.001E-02	3.89778E-13
11.602	3.197	1.060E-02	3.68004E-13
11.628	3.397	1.118E-02	3.48794E-13
11.650	3.597	1.176E-02	3.31721E-13
11.668	3.797	1.232E-02	3.16446E-13
11.692	3.997	1.288E-02	3.02699E-13
11.708	4.197	1.344E-02	2.90263E-13
11.724	4.397	1.398E-02	2.78958E-13
11.743	4.597	1.452E-02	2.68637E-13
11.759	4.797	1.505E-02	2.59176E-13
11.774	4.997	1.557E-02	2.50473E-13
11.790	5.197	1.609E-02	2.42440E-13
11.805	5.397	1.660E-02	2.35002E-13
11.816	5.597	1.710E-02	2.28095E-13
11.829	5.797	1.759E-02	2.21665E-13
11.843	5.997	1.808E-02	2.15664E-13
11.842	6.000	1.809E-02	2.15577E-13

(a) NaOH added in moles/L = [(volume of NaOH added)(0.0935)]/
(sample volume + volume NaOH added).

(b) $H^+_{\text{free,add}} = (3.90 \times 10^{-15}) / (\text{NaOH added in moles/L})$.

Appendix D

Titration of Na_2SO_4 Solutions with HCl and NaOH

Appendix D

Titration of Na₂SO₄ Solutions with HCl and NaOH

Table D.1 Titration of 25 ml of 0.05 Molal Na₂SO₄ Solutions with 0.0104 M HCl

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
5.307	0.000	0.000E+00	0.000E+00
4.932	0.036	1.500E-05	6.558E-06
4.728	0.071	2.954E-05	1.292E-05
4.611	0.099	4.114E-05	1.799E-05
4.497	0.135	5.602E-05	2.449E-05
4.391	0.181	7.497E-05	3.278E-05
4.266	0.244	1.008E-04	4.408E-05
4.171	0.314	1.294E-04	5.657E-05
4.057	0.413	1.695E-04	7.412E-05
3.953	0.527	2.153E-04	9.415E-05
3.859	0.663	2.695E-04	1.178E-04
3.759	0.834	3.367E-04	1.472E-04
3.674	1.027	4.116E-04	1.800E-04
3.597	1.227	4.880E-04	2.134E-04
3.534	1.427	5.632E-04	2.463E-04
3.481	1.627	6.373E-04	2.787E-04
3.432	1.827	7.103E-04	3.106E-04
3.388	2.027	7.822E-04	3.420E-04
3.350	2.227	8.531E-04	3.730E-04
3.316	2.427	9.229E-04	4.036E-04
3.283	2.627	9.918E-04	4.337E-04
3.254	2.827	1.060E-03	4.633E-04
3.227	3.027	1.126E-03	4.926E-04
3.202	3.227	1.192E-03	5.214E-04
3.178	3.427	1.257E-03	5.498E-04
3.157	3.627	1.321E-03	5.778E-04
3.136	3.827	1.385E-03	6.054E-04
3.113	4.027	1.447E-03	6.327E-04
3.096	4.227	1.508E-03	6.596E-04
3.077	4.427	1.569E-03	6.861E-04
3.059	4.627	1.629E-03	7.122E-04
3.044	4.827	1.688E-03	7.381E-04
3.028	5.027	1.746E-03	7.635E-04
3.012	5.227	1.804E-03	7.886E-04
2.997	5.427	1.860E-03	8.134E-04
2.984	5.627	1.916E-03	8.379E-04
2.971	5.827	1.972E-03	8.620E-04
2.957	6.000	2.019E-03	8.827E-04

^(a) HCl added in moles per liter = [(vol HCl added)(0.0104)]/
(Sample volume + volume of HCl added).

^(b) H⁺_{free, add} in moles per liter = [HCl added in moles per liter]/2.287.

Table D.2 Titration of 25 ml of 0.1 Molal Na₂SO₄ Solutions with 0.0104 M HCl

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
6.530	0.000	0.000E+00	0.000E+00
5.585	0.036	1.500E-05	5.416E-06
5.233	0.071	2.954E-05	1.067E-05
5.128	0.088	3.658E-05	1.321E-05
4.988	0.114	4.734E-05	1.710E-05
4.877	0.142	5.891E-05	2.127E-05
4.758	0.181	7.497E-05	2.707E-05
4.641	0.229	9.467E-05	3.419E-05
4.531	0.289	1.192E-04	4.305E-05
4.422	0.364	1.497E-04	5.406E-05
4.318	0.457	1.872E-04	6.762E-05
4.212	0.573	2.337E-04	8.440E-05
4.116	0.711	2.884E-04	1.042E-04
4.019	0.879	3.543E-04	1.279E-04
3.929	1.075	4.300E-04	1.553E-04
3.851	1.275	5.061E-04	1.828E-04
3.788	1.475	5.811E-04	2.099E-04
3.732	1.675	6.549E-04	2.365E-04
3.682	1.875	7.277E-04	2.628E-04
3.637	2.075	7.993E-04	2.887E-04
3.597	2.275	8.700E-04	3.142E-04
3.560	2.475	9.396E-04	3.393E-04
3.526	2.675	1.008E-03	3.641E-04
3.494	2.875	1.076E-03	3.885E-04
3.465	3.075	1.142E-03	4.126E-04
3.441	3.275	1.208E-03	4.363E-04
3.414	3.475	1.273E-03	4.597E-04
3.394	3.675	1.337E-03	4.827E-04
3.368	3.875	1.400E-03	5.055E-04
3.352	4.075	1.462E-03	5.279E-04
3.329	4.275	1.523E-03	5.500E-04
3.315	4.475	1.584E-03	5.719E-04
3.293	4.675	1.643E-03	5.934E-04
3.273	4.875	1.702E-03	6.147E-04
3.258	5.075	1.760E-03	6.356E-04
3.241	5.275	1.817E-03	6.563E-04
3.224	5.475	1.874E-03	6.767E-04
3.209	5.675	1.930E-03	6.969E-04
3.196	5.875	1.985E-03	7.167E-04
3.189	6.000	2.019E-03	7.290E-04

^(a) HCl added in moles per liter = [(vol HCl added)(0.0104)]/
(Sample volume + volume of HCl added).

^(b) H⁺_{free, add} in moles per liter = [HCl added in moles per liter]/2.769.

Table D.3 Titration of 25 ml of 0.5 Molal Na₂SO₄ Solutions with 0.0104 M HCl

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
8.139	0.000	0.000E+00	0.000E+00
6.632	0.036	1.500E-05	3.939E-06
5.986	0.071	2.954E-05	7.759E-06
5.868	0.082	3.410E-05	8.957E-06
5.735	0.097	4.031E-05	1.059E-05
5.588	0.115	4.776E-05	1.254E-05
5.477	0.136	5.643E-05	1.482E-05
5.328	0.165	6.839E-05	1.796E-05
5.222	0.195	8.072E-05	2.120E-05
5.083	0.237	9.795E-05	2.573E-05
4.967	0.282	1.163E-04	3.056E-05
4.871	0.338	1.391E-04	3.655E-05
4.739	0.418	1.715E-04	4.505E-05
4.636	0.502	2.053E-04	5.393E-05
4.541	0.609	2.480E-04	6.515E-05
4.427	0.749	3.034E-04	7.969E-05
4.334	0.899	3.620E-04	9.510E-05
4.243	1.084	4.335E-04	1.139E-04
4.162	1.284	5.095E-04	1.338E-04
4.099	1.484	5.844E-04	1.535E-04
4.037	1.684	6.582E-04	1.729E-04
3.984	1.884	7.309E-04	1.920E-04
3.936	2.084	8.025E-04	2.108E-04
3.895	2.284	8.731E-04	2.293E-04
3.857	2.484	9.427E-04	2.476E-04
3.821	2.684	1.011E-03	2.656E-04
3.790	2.884	1.079E-03	2.834E-04
3.761	3.084	1.145E-03	3.009E-04
3.732	3.284	1.211E-03	3.181E-04
3.705	3.484	1.276E-03	3.351E-04
3.683	3.684	1.340E-03	3.519E-04
3.659	3.884	1.403E-03	3.684E-04
3.639	4.084	1.465E-03	3.847E-04
3.617	4.284	1.526E-03	4.008E-04
3.598	4.484	1.586E-03	4.167E-04
3.577	4.684	1.646E-03	4.323E-04
3.562	4.884	1.705E-03	4.478E-04
3.545	5.084	1.763E-03	4.630E-04
3.529	5.284	1.820E-03	4.780E-04
3.514	5.484	1.876E-03	4.929E-04
3.498	5.684	1.932E-03	5.075E-04
3.486	5.884	1.987E-03	5.220E-04
3.473	6.000	2.019E-03	5.303E-04

^(a) HCl added in moles per liter = [(vol HCl added)(0.0104)]/
(Sample volume + volume of HCl added).

^(b) H⁺_{free, add} in moles per liter = [HCl added in moles per liter]/3.807.

Table D.4 Titration of 25 ml of 1 Molal Na₂SO₄ Solutions with 0.0104 M HCl

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
8.772	0.000	0.000E+00	0.000E+00
8.338	0.036	1.500E-05	3.515E-06
7.089	0.071	2.954E-05	6.922E-06
6.884	0.075	3.120E-05	7.311E-06
6.765	0.079	3.285E-05	7.700E-06
6.598	0.086	3.576E-05	8.380E-06
6.438	0.095	3.948E-05	9.253E-06
6.290	0.105	4.362E-05	1.022E-05
6.148	0.117	4.859E-05	1.139E-05
6.010	0.131	5.437E-05	1.274E-05
5.859	0.149	6.179E-05	1.448E-05
5.732	0.168	6.962E-05	1.632E-05
5.618	0.192	7.949E-05	1.863E-05
5.482	0.224	9.262E-05	2.171E-05
5.347	0.261	0.0001078	2.526E-05
5.232	0.302	0.0001245	2.918E-05
5.111	0.354	0.0001456	3.413E-05
4.990	0.415	0.0001703	3.991E-05
4.883	0.487	0.0001993	4.671E-05
4.772	0.577	0.0002353	5.514E-05
4.672	0.685	0.0002782	6.519E-05
4.558	0.820	0.0003312	7.763E-05
4.467	0.966	0.0003880	9.094E-05
4.374	1.150	0.0004587	0.0001075
4.288	1.350	0.0005344	0.0001252
4.220	1.550	0.0006089	0.0001427
4.158	1.750	0.0006823	0.0001599
4.106	1.950	0.0007547	0.0001769
4.058	2.150	0.0008259	0.0001936
4.017	2.350	0.0008962	0.0002100
3.977	2.550	0.0009654	0.0002262
3.942	2.750	0.001034E-03	0.0002422
3.910	2.950	0.001101E-03	0.0002580
3.881	3.150	0.001167E-03	0.0002735
3.853	3.350	0.001232E-03	0.0002888
3.827	3.550	0.001297E-03	0.0003039
3.803	3.750	0.001360E-03	0.0003188
3.780	3.950	0.001423E-03	0.0003335
3.757	4.150	0.001485E-03	0.0003480
3.734	4.350	0.001546E-03	0.0003623
3.717	4.550	0.001606E-03	0.0003764
3.699	4.750	0.001665E-03	0.0003903
3.680	4.950	0.001724E-03	0.0004040
3.664	5.150	0.001782E-03	0.0004175
3.648	5.350	0.001839E-03	0.0004309
3.633	5.550	0.001895E-03	0.0004441
3.619	5.750	0.001950E-03	0.0004571
3.603	5.950	0.002005E-03	0.0004699
3.598	6.000	0.002019E-03	0.0004731

(a) HCl added in moles per liter = [(vol HCl added)(0.0104)]/
(Sample volume + volume of HCl added).

(b) H⁺_{free, add} in moles per liter = [HCl added in moles per liter]/4.267.

Table D.5 Titration of 25 ml of 1.5 Molal Na_2SO_4 Solutions with 0.0104 M HCl

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H^+ _{free, add} ^(b) (moles/L)
9.176	0.000	0.000E+00	0.000E+00
9.065	0.036	1.500E-05	3.087E-06
8.926	0.071	2.954E-05	6.080E-06
8.778	0.100	4.155E-05	8.554E-06
8.647	0.121	5.024E-05	1.034E-05
8.485	0.141	5.850E-05	1.204E-05
8.336	0.155	6.427E-05	1.323E-05
8.134	0.168	6.962E-05	1.433E-05
7.990	0.175	7.250E-05	1.492E-05
7.745	0.183	7.579E-05	1.560E-05
7.577	0.188	7.785E-05	1.602E-05
7.348	0.194	8.031E-05	1.653E-05
7.098	0.200	8.278E-05	1.704E-05
6.932	0.204	8.442E-05	1.738E-05
6.766	0.210	8.688E-05	1.788E-05
6.607	0.218	9.016E-05	1.856E-05
6.460	0.227	9.385E-05	1.932E-05
6.319	0.238	9.836E-05	2.025E-05
6.170	0.251	1.037E-04	2.134E-05
6.018	0.267	1.102E-04	2.269E-05
5.934	0.284	1.172E-04	2.412E-05
5.758	0.315	1.298E-04	2.672E-05
5.661	0.339	1.395E-04	2.872E-05
5.533	0.375	1.541E-04	3.173E-05
5.383	0.418	1.715E-04	3.531E-05
5.280	0.461	1.888E-04	3.887E-05
5.148	0.520	2.125E-04	4.375E-05
5.037	0.584	2.381E-04	4.901E-05
4.926	0.664	2.699E-04	5.555E-05
4.810	0.760	3.077E-04	6.334E-05
4.712	0.869	3.504E-04	7.212E-05
4.610	1.007	4.039E-04	8.313E-05
4.512	1.170	4.663E-04	9.599E-05
4.416	1.358	5.374E-04	1.106E-04
4.334	1.558	6.119E-04	1.260E-04
4.263	1.758	6.853E-04	1.411E-04
4.208	1.958	7.575E-04	1.559E-04
4.155	2.158	8.288E-04	1.706E-04
4.109	2.358	8.990E-04	1.850E-04
4.069	2.558	9.681E-04	1.993E-04
4.032	2.758	1.036E-03	2.133E-04
3.996	2.958	1.104E-03	2.272E-04
3.965	3.158	1.170E-03	2.408E-04
3.943	3.358	1.235E-03	2.542E-04
3.908	3.558	1.299E-03	2.675E-04
3.886	3.758	1.363E-03	2.806E-04
3.862	3.958	1.426E-03	2.934E-04
3.841	4.158	1.487E-03	3.062E-04
3.816	4.358	1.548E-03	3.187E-04

Table D.5 (contd)

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
3.798	4.558	1.608E-03	3.311E-04
3.774	4.758	1.668E-03	3.433E-04
3.765	4.958	1.726E-03	3.553E-04
3.744	5.158	1.784E-03	3.672E-04
3.725	5.358	1.841E-03	3.789E-04
3.712	5.558	1.897E-03	3.905E-04
3.698	5.758	1.953E-03	4.019E-04
3.682	5.958	2.007E-03	4.132E-04
3.679	6.000	2.019E-03	4.155E-04

(a) HCl added in moles per liter = [(vol HCl added)(0.0104)]/

(Sample volume + volume of HCl added)

(b) H⁺_{free, add} in moles per liter = [HCl added in moles per liter]/4.858

Table D.6 Titration of 25 ml of 2 Molal Na₂SO₄ Solutions with 0.0104 M HCl

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
9.204	0.000	0.000E+00	0.000E+00
9.123	0.036	1.500E-05	2.591E-06
9.011	0.071	2.954E-05	5.102E-06
8.906	0.103	4.280E-05	7.393E-06
8.740	0.144	5.973E-05	1.032E-05
8.585	0.172	7.127E-05	1.231E-05
8.450	0.192	7.949E-05	1.373E-05
8.287	0.210	8.688E-05	1.501E-05
8.137	0.223	9.221E-05	1.593E-05
7.944	0.234	9.672E-05	1.671E-05
7.779	0.241	9.959E-05	1.720E-05
7.604	0.248	1.024E-04	1.770E-05
7.385	0.254	1.049E-04	1.812E-05
7.189	0.260	1.074E-04	1.854E-05
6.998	0.266	1.098E-04	1.897E-05
6.822	0.273	1.127E-04	1.946E-05
6.658	0.281	1.159E-04	2.003E-05
6.495	0.290	1.196E-04	2.066E-05
6.367	0.301	1.241E-04	2.143E-05
6.228	0.316	1.302E-04	2.249E-05
6.101	0.334	1.375E-04	2.375E-05
5.933	0.357	1.468E-04	2.537E-05
5.833	0.378	1.554E-04	2.684E-05
5.706	0.410	1.683E-04	2.907E-05
5.576	0.448	1.836E-04	3.172E-05
5.465	0.491	2.009E-04	3.470E-05
5.315	0.548	2.237E-04	3.865E-05
5.233	0.600	2.445E-04	4.223E-05
5.084	0.686	2.786E-04	4.812E-05

Table D.6 (contd)

Observed pH	HCl Volume Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
4.988	0.755	3.058E-04	5.282E-05
4.870	0.852	3.437E-04	5.938E-05
4.781	0.959	3.853E-04	6.656E-05
4.660	1.107	4.423E-04	7.640E-05
4.567	1.257	4.993E-04	8.625E-05
4.479	1.442	5.688E-04	9.825E-05
4.397	1.642	6.428E-04	1.110E-04
4.323	1.842	7.157E-04	1.236E-04
4.263	2.042	7.876E-04	1.360E-04
4.210	2.242	8.584E-04	1.483E-04
4.164	2.442	9.281E-04	1.603E-04
4.119	2.642	9.969E-04	1.722E-04
4.086	2.842	1.065E-03	1.839E-04
4.050	3.042	1.131E-03	1.954E-04
4.018	3.242	1.197E-03	2.068E-04
3.987	3.442	1.262E-03	2.180E-04
3.960	3.642	1.326E-03	2.291E-04
3.934	3.842	1.389E-03	2.400E-04
3.912	4.042	1.452E-03	2.508E-04
3.889	4.242	1.513E-03	2.614E-04
3.868	4.442	1.574E-03	2.718E-04
3.853	4.642	1.633E-03	2.821E-04
3.834	4.842	1.692E-03	2.923E-04
3.810	5.042	1.750E-03	3.024E-04
3.794	5.242	1.808E-03	3.123E-04
3.780	5.442	1.865E-03	3.221E-04
3.761	5.642	1.920E-03	3.317E-04
3.749	5.842	1.976E-03	3.413E-04
3.734	6.000	2.019E-03	3.487E-04

^(a) HCl added in moles per liter = [(vol HCl added)(0.0104)]/
(Sample volume + volume of HCl added).

^(b) H⁺_{free, add} in moles per liter = [HCl added in moles per liter]/5.789.

Table D.7 Titration of 25 ml of 0.05 Molal Na₂SO₄ Solutions with 0.0935 M NaOH

Observed pH	NaOH Volume Added (ml)	NaOH Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
5.955	0.000	0.000E+00	0.00
9.951	0.036	1.344E-04	1.50E-10
10.303	0.071	2.647E-04	7.63E-11
10.412	0.088	3.279E-04	6.16E-11
10.537	0.113	4.206E-04	4.80E-11
10.649	0.144	5.353E-04	3.77E-11
10.772	0.186	6.903E-04	2.93E-11
10.878	0.233	8.704E-04	2.32E-11
10.984	0.302	1.116E-03	1.81E-11
11.097	0.387	1.425E-03	1.42E-11
11.195	0.488	1.790E-03	1.13E-11
11.301	0.617	2.251E-03	8.97E-12
11.392	0.767	2.782E-03	7.26E-12
11.485	0.954	3.436E-03	5.88E-12
11.565	1.154	4.124E-03	4.90E-12
11.634	1.354	4.802E-03	4.21E-12
11.691	1.554	5.470E-03	3.69E-12
11.741	1.754	6.128E-03	3.30E-12
11.786	1.954	6.776E-03	2.98E-12
11.826	2.154	7.415E-03	2.72E-12
11.862	2.354	8.044E-03	2.51E-12
11.895	2.554	8.664E-03	2.33E-12
11.925	2.754	9.275E-03	2.18E-12
11.953	2.954	9.877E-03	2.05E-12
11.980	3.154	1.047E-02	1.93E-12
12.003	3.354	1.106E-02	1.83E-12
12.023	3.554	1.163E-02	1.74E-12
12.046	3.754	1.220E-02	1.66E-12
12.061	3.954	1.276E-02	1.58E-12
12.083	4.154	1.332E-02	1.52E-12
12.100	4.354	1.386E-02	1.46E-12
12.116	4.554	1.440E-02	1.40E-12
12.131	4.754	1.493E-02	1.35E-12
12.148	4.954	1.546E-02	1.31E-12
12.161	5.154	1.598E-02	1.26E-12
12.177	5.354	1.649E-02	1.23E-12
12.188	5.554	1.699E-02	1.19E-12
12.200	5.754	1.749E-02	1.16E-12
12.212	5.954	1.798E-02	1.12E-12
12.215	6.000	1.809E-02	1.12E-12

^(a) NaOH added in moles per liter = [(volume NaOH added)(0.0935)]/
(Sample volume + volume of NaOH added).

^(b) H⁺_{free, add} in moles per liter = (2.02x10⁻¹⁴)/(NaOH added in moles
per liter).

Table D.8 Titration of 25 ml of 0.1 Molal Na_2SO_4 Solutions with 0.0935 M NaOH

Observed pH	NaOH Volume Added (ml)	NaOH Added ^(a) (moles/L)	H^+ _{free, add} ^(b) (moles/L)
6.415	0.000	0.000E+00	0.00
9.933	0.036	1.344E-04	1.82287E-10
10.275	0.071	2.647E-04	9.25565E-11
10.388	0.089	3.316E-04	7.38903E-11
10.504	0.113	4.206E-04	5.82524E-11
10.629	0.146	5.427E-04	4.51450E-11
10.744	0.185	6.866E-04	3.56832E-11
10.842	0.234	8.668E-04	2.82660E-11
10.961	0.306	1.130E-03	2.16768E-11
11.072	0.388	1.428E-03	1.71510E-11
11.168	0.488	1.790E-03	1.36902E-11
11.275	0.619	2.258E-03	1.08484E-11
11.364	0.768	2.786E-03	8.79454E-12
11.460	0.959	3.453E-03	7.09518E-12
11.544	1.159	4.141E-03	5.91605E-12
11.609	1.359	4.819E-03	5.08397E-12
11.668	1.559	5.487E-03	4.46539E-12
11.719	1.759	6.144E-03	3.98747E-12
11.763	1.959	6.792E-03	3.60714E-12
11.804	2.159	7.430E-03	3.29727E-12
11.840	2.359	8.059E-03	3.03995E-12
11.874	2.559	8.679E-03	2.82284E-12
11.904	2.759	9.290E-03	2.63722E-12
11.932	2.959	9.892E-03	2.47668E-12
11.957	3.159	1.049E-02	2.33648E-12
11.982	3.359	1.107E-02	2.21297E-12
12.005	3.559	1.165E-02	2.10334E-12
12.024	3.759	1.222E-02	2.00537E-12
12.044	3.959	1.278E-02	1.91731E-12
12.062	4.159	1.333E-02	1.83771E-12
12.079	4.359	1.388E-02	1.76542E-12
12.095	4.559	1.442E-02	1.69947E-12
12.111	4.759	1.495E-02	1.63907E-12
12.126	4.959	1.547E-02	1.58353E-12
12.141	5.159	1.599E-02	1.53231E-12
12.154	5.359	1.650E-02	1.48490E-12
12.168	5.559	1.700E-02	1.44091E-12
12.180	5.759	1.750E-02	1.39997E-12
12.192	5.959	1.799E-02	1.36178E-12
12.194	6.000	1.809E-02	1.35427E-12

^(a) NaOH added in moles per liter = [(volume NaOH added)(0.0935)]/
(Sample volume + volume of NaOH added).

^(b) H^+ _{free, add} in moles per liter = (2.45×10^{-14}) /(NaOH added in moles
per liter).

Table D.9 Titration of 25 ml of 0.5 Molal Na₂SO₄ Solutions with 0.0935 M NaOH

Observed pH	NaOH Volume Added (ml)	NaOH Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
8.412	0.000	0.000E+00	0.00
9.826	0.036	1.344E-04	2.98728E-10
10.167	0.071	2.647E-04	1.51679E-10
10.278	0.089	3.316E-04	1.21090E-10
10.399	0.114	4.243E-04	9.46290E-11
10.518	0.145	5.390E-04	7.44898E-11
10.626	0.185	6.866E-04	5.84768E-11
10.752	0.239	8.851E-04	4.53615E-11
10.852	0.300	1.108E-03	3.62253E-11
10.967	0.385	1.418E-03	2.83224E-11
11.071	0.482	1.768E-03	2.27091E-11
11.161	0.604	2.205E-03	1.82089E-11
11.266	0.765	2.775E-03	1.44671E-11
11.357	0.943	3.398E-03	1.18174E-11
11.441	1.143	4.087E-03	9.82477E-12
11.510	1.343	4.765E-03	8.42563E-12
11.570	1.543	5.434E-03	7.38920E-12
11.621	1.743	6.092E-03	6.59062E-12
11.668	1.943	6.741E-03	5.95644E-12
11.709	2.143	7.380E-03	5.44063E-12
11.747	2.343	8.009E-03	5.01288E-12
11.779	2.543	8.630E-03	4.65241E-12
11.810	2.743	9.242E-03	4.34451E-12
11.839	2.943	9.844E-03	4.07846E-12
11.866	3.143	1.044E-02	3.84627E-12
11.891	3.343	1.102E-02	3.64186E-12
11.907	3.543	1.160E-02	3.46052E-12
11.934	3.743	1.217E-02	3.29857E-12
11.955	3.943	1.273E-02	3.15304E-12
11.975	4.143	1.329E-02	3.02157E-12
11.990	4.343	1.383E-02	2.90220E-12
12.008	4.543	1.437E-02	2.79335E-12
12.023	4.743	1.491E-02	2.69367E-12
12.039	4.943	1.543E-02	2.60206E-12
12.054	5.143	1.595E-02	2.51758E-12
12.069	5.343	1.646E-02	2.43942E-12
12.080	5.543	1.696E-02	2.36690E-12
12.095	5.743	1.746E-02	2.29943E-12
12.107	5.943	1.795E-02	2.23651E-12
12.107	6.000	1.809E-02	2.21934E-12

^(a) NaOH added in moles per liter = [(volume NaOH added)(0.0935)]/
(Sample volume + volume of NaOH added).

^(b) H⁺_{free, add} in moles per liter = (4.015x10⁻¹⁴)/(NaOH added in moles
per liter).

Table D.10 Titration of 25 ml of 2 Molal Na₂SO₄ Solutions with 0.0935 M NaOH

Observed pH	NaOH Volume Added (ml)	NaOH Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
8.830	0.000	0.000E+00	0.00
9.842	0.036	1.671E-04	1.96889E-10
10.286	0.071	3.290E-04	1.00005E-10
10.396	0.085	3.936E-04	8.35922E-11
10.517	0.106	4.903E-04	6.71016E-11
10.609	0.133	6.144E-04	5.35513E-11
10.776	0.176	8.113E-04	4.05542E-11
10.867	0.209	9.618E-04	3.42067E-11
10.972	0.261	1.198E-03	2.74621E-11
11.086	0.331	1.514E-03	2.17292E-11
11.185	0.415	1.891E-03	1.74026E-11
11.289	0.525	2.379E-03	1.38305E-11
11.387	0.659	2.967E-03	1.10901E-11
11.484	0.822	3.671E-03	8.96115E-12
11.576	1.013	4.483E-03	7.33823E-12
11.654	1.235	5.409E-03	6.08273E-12
11.726	1.485	6.428E-03	5.11825E-12
11.793	1.735	7.424E-03	4.43173E-12
11.844	1.985	8.397E-03	3.91813E-12
11.894	2.235	9.348E-03	3.51943E-12
11.930	2.485	1.028E-02	3.20095E-12
11.968	2.735	1.119E-02	2.94070E-12
12.002	2.985	1.208E-02	2.72404E-12
12.025	3.235	1.295E-02	2.54086E-12
12.058	3.485	1.380E-02	2.38397E-12
12.085	3.735	1.463E-02	2.24808E-12
12.105	3.985	1.545E-02	2.12924E-12
12.128	4.235	1.625E-02	2.02443E-12
12.144	4.485	1.704E-02	1.93130E-12
12.168	4.735	1.780E-02	1.84801E-12
12.181	4.985	1.856E-02	1.77308E-12
12.195	5.235	1.929E-02	1.70530E-12
12.207	5.485	2.002E-02	1.64369E-12
12.226	5.735	2.072E-02	1.58746E-12
12.242	5.985	2.142E-02	1.53593E-12
12.242	6.000	2.146E-02	1.53297E-12

^(a) NaOH added in moles per liter = [(volume NaOH added)(0.0935)]/
(Sample volume + volume of NaOH added).

^(b) H⁺_{free, add} in moles per liter = (3.29x10⁻¹⁴)/(NaOH added in moles
per liter).

Appendix E

Titration of Mixed NaCl and Na₂SO₄ Solutions

Appendix E

Titration of Mixed NaCl and Na₂SO₄ Solutions

Table E.1 Titration of 25 ml of (5.5 m NaCl+0.01 m Na₂SO₄) with 0.0935 M NaOH

Observed pH	Volume of NaOH Added (ml)	NaOH Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
8.919	0.000	0.000E+00	0.00
9.659	0.036	1.344E-04	2.90023E-11
9.976	0.071	2.647E-04	1.47259E-11
10.095	0.090	3.353E-04	1.16259E-11
10.207	0.114	4.243E-04	9.18715E-12
10.321	0.148	5.501E-04	7.08617E-12
10.442	0.191	7.087E-04	5.50024E-12
10.549	0.244	9.034E-04	4.31457E-12
10.659	0.313	1.156E-03	3.37263E-12
10.763	0.399	1.468E-03	2.65469E-12
10.867	0.507	1.858E-03	2.09808E-12
10.967	0.639	2.330E-03	1.67328E-12
11.060	0.798	2.891E-03	1.34820E-12
11.151	0.991	3.564E-03	1.09375E-12
11.228	1.191	4.250E-03	9.17086E-13
11.291	1.391	4.927E-03	7.91222E-13
11.346	1.591	5.593E-03	6.97002E-13
11.396	1.791	6.249E-03	6.23825E-13
11.440	1.991	6.895E-03	5.65350E-13
11.479	2.191	7.532E-03	5.17550E-13
11.515	2.391	8.159E-03	4.77747E-13
11.548	2.591	8.778E-03	4.44089E-13
11.580	2.791	9.387E-03	4.15254E-13
11.601	2.991	9.988E-03	3.90276E-13
11.632	3.191	1.058E-02	3.68429E-13
11.649	3.391	1.116E-02	3.49158E-13
11.679	3.591	1.174E-02	3.32035E-13
11.695	3.791	1.231E-02	3.16718E-13
11.713	3.991	1.287E-02	3.02936E-13
11.735	4.191	1.342E-02	2.90470E-13
11.753	4.391	1.396E-02	2.79139E-13
11.762	4.591	1.450E-02	2.68795E-13
11.785	4.791	1.503E-02	2.59316E-13
11.800	4.991	1.555E-02	2.50595E-13
11.813	5.191	1.607E-02	2.42547E-13
11.829	5.391	1.658E-02	2.35096E-13
11.842	5.591	1.708E-02	2.28178E-13
11.855	5.791	1.758E-02	2.21738E-13
11.867	5.991	1.807E-02	2.15728E-13
11.871	6.000	1.809E-02	2.15467E-13

^(a) NaOH added in moles/L = [(NaOH volume added)(0.0935)]/
(volume of sample + volume of NaOH added).

^(b) H⁺_{free, add} = (3.898x10⁻¹⁵)/(NaOH added in moles/L).

Table E.2 Titration of 25 ml of (5.5 m NaCl+0.05 m Na₂SO₄) with 0.0935 M NaOH

Observed pH	Volume of NaOH Added (ml)	NaOH Added ^(a) (moles/L)	H ⁺ _{free, add} ^(b) (moles/L)
9.000	0.000	0.000E+00	0.00
9.692	0.036	1.344E-04	2.87791E-11
9.996	0.071	2.647E-04	1.46126E-11
10.110	0.090	3.353E-04	1.15365E-11
10.231	0.117	4.354E-04	8.88375E-12
10.345	0.150	5.575E-04	6.93843E-12
10.458	0.194	7.197E-04	5.37415E-12
10.558	0.250	9.254E-04	4.17961E-12
10.690	0.329	1.214E-03	3.18593E-12
10.782	0.410	1.508E-03	2.56469E-12
10.880	0.525	1.922E-03	2.01197E-12
10.984	0.669	2.436E-03	1.58780E-12
11.083	0.834	3.017E-03	1.28186E-12
11.165	1.023	3.674E-03	1.05268E-12
11.241	1.223	4.359E-03	8.87299E-13
11.304	1.423	5.034E-03	7.68407E-13
11.361	1.623	5.698E-03	6.78817E-13
11.408	1.823	6.353E-03	6.08884E-13
11.451	2.023	6.997E-03	5.52779E-13
11.493	2.223	7.633E-03	5.06770E-13
11.526	2.423	8.259E-03	4.68356E-13
11.561	2.623	8.876E-03	4.35800E-13
11.588	2.823	9.484E-03	4.07856E-13
11.616	3.023	1.008E-02	3.83611E-13
11.642	3.223	1.067E-02	3.62374E-13
11.663	3.423	1.126E-02	3.43619E-13
11.685	3.623	1.183E-02	3.26935E-13
11.709	3.823	1.240E-02	3.11996E-13
11.730	4.023	1.296E-02	2.98543E-13
11.745	4.223	1.351E-02	2.86364E-13
11.761	4.423	1.405E-02	2.75286E-13
11.779	4.623	1.459E-02	2.65167E-13
11.795	4.823	1.512E-02	2.55887E-13
11.812	5.023	1.564E-02	2.47346E-13
11.825	5.223	1.615E-02	2.39459E-13
11.833	5.423	1.666E-02	2.32154E-13
11.852	5.623	1.716E-02	2.25369E-13
11.866	5.823	1.766E-02	2.19050E-13
11.873	6.000	1.809E-02	2.13808E-13

^(a) NaOH added in moles/L = [(NaOH volume added)(0.0935)]/
(volume of sample + volume of NaOH added).

^(b) H⁺_{free, add} = (3.868x10⁻¹⁵)/(NaOH added in moles/L).

Table E.3 Titration of 25 ml of (5.5 m NaCl+0.01 m Na₂SO₄) with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free,add} ^(b) (moles/L)
8.883	0.000	0.000	0.000
8.721	0.036	1.500E-05	1.332E-05
8.489	0.071	2.954E-05	2.623E-05
8.378	0.087	3.617E-05	3.212E-05
8.135	0.108	4.486E-05	3.984E-05
7.982	0.118	4.900E-05	4.352E-05
7.812	0.126	5.230E-05	4.645E-05
7.600	0.133	5.519E-05	4.902E-05
7.332	0.138	5.726E-05	5.085E-05
7.144	0.141	5.850E-05	5.195E-05
6.957	0.146	6.056E-05	5.378E-05
6.708	0.152	6.303E-05	5.598E-05
6.441	0.157	6.509E-05	5.781E-05
6.160	0.161	6.674E-05	5.927E-05
5.917	0.165	6.839E-05	6.073E-05
5.722	0.169	7.003E-05	6.220E-05
5.521	0.175	7.250E-05	6.439E-05
5.326	0.181	7.497E-05	6.658E-05
5.138	0.187	7.744E-05	6.877E-05
4.905	0.195	8.072E-05	7.169E-05
4.711	0.201	8.319E-05	7.388E-05
4.529	0.208	8.606E-05	7.643E-05
4.346	0.216	8.934E-05	7.935E-05
4.175	0.225	9.303E-05	8.262E-05
4.031	0.234	9.672E-05	8.590E-05
3.895	0.246	1.016E-04	9.026E-05
3.765	0.261	1.078E-04	9.571E-05
3.636	0.280	1.155E-04	1.026E-04
3.505	0.304	1.253E-04	1.113E-04
3.392	0.332	1.367E-04	1.214E-04
3.275	0.369	1.517E-04	1.347E-04
3.163	0.417	1.711E-04	1.520E-04
3.051	0.478	1.957E-04	1.738E-04
2.939	0.553	2.257E-04	2.005E-04
2.842	0.644	2.619E-04	2.326E-04
2.737	0.765	3.097E-04	2.750E-04
2.645	0.907	3.652E-04	3.243E-04
2.548	1.086	4.342E-04	3.856E-04
2.465	1.286	5.103E-04	4.532E-04
2.399	1.486	5.852E-04	5.197E-04
2.342	1.686	6.590E-04	5.852E-04
2.294	1.886	7.316E-04	6.498E-04
2.255	2.086	8.033E-04	7.134E-04
2.219	2.286	8.738E-04	7.760E-04
2.189	2.486	9.434E-04	8.378E-04
2.159	2.686	1.012E-03	8.987E-04
2.135	2.886	1.079E-03	9.586E-04
2.117	3.086	1.146E-03	1.018E-03
2.093	3.286	1.212E-03	1.076E-03
2.077	3.486	1.276E-03	1.134E-03
2.058	3.686	1.340E-03	1.190E-03

Table E.3 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free,add} ^(b) (moles/L)
2.040	3.886	1.403E-03	1.246E-03
2.028	4.086	1.465E-03	1.301E-03
2.014	4.286	1.526E-03	1.356E-03
2.001	4.486	1.587E-03	1.409E-03
1.990	4.686	1.646E-03	1.462E-03
1.980	4.886	1.705E-03	1.514E-03
1.970	5.086	1.763E-03	1.566E-03
1.960	5.286	1.820E-03	1.617E-03
1.951	5.486	1.877E-03	1.667E-03
1.945	5.686	1.933E-03	1.716E-03
1.937	5.886	1.988E-03	1.765E-03
1.929	6.086	2.042E-03	1.813E-03
1.921	6.286	2.096E-03	1.861E-03
1.916	6.486	2.149E-03	1.908E-03
1.911	6.686	2.201E-03	1.955E-03
1.907	6.886	2.252E-03	2.000E-03
1.900	7.086	2.303E-03	2.046E-03
1.896	7.286	2.354E-03	2.090E-03
1.891	7.486	2.403E-03	2.135E-03
1.890	7.500	2.407E-03	2.138E-03

^(a) HCl added in moles/L = [(HCl volume added)(0.0104)]/
(volume of sample + volume of HCl added).

^(b) H⁺_{free, add} = (HCl added in moles per liter)/1.126.

Table E.4 Titration of 25 ml of (5.5 m NaCl+0.05 m Na₂SO₄) with 0.0104 M HCl

Observed pH	Volume of HCl Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free,add} ^(b) (moles/L)
8.952	0.000	0.000E+00	0.000
8.814	0.036	1.500E-05	9.207E-06
8.609	0.071	2.954E-05	1.813E-05
8.486	0.089	3.700E-05	2.271E-05
8.334	0.106	4.404E-05	2.703E-05
8.192	0.121	5.024E-05	3.084E-05
7.975	0.135	5.602E-05	3.439E-05
7.838	0.143	5.932E-05	3.642E-05
7.525	0.152	6.303E-05	3.869E-05
7.255	0.157	6.509E-05	3.996E-05
7.111	0.160	6.633E-05	4.072E-05
6.872	0.166	6.880E-05	4.223E-05
6.537	0.172	7.127E-05	4.375E-05
6.258	0.176	7.291E-05	4.476E-05
6.044	0.180	7.456E-05	4.577E-05
5.840	0.184	7.620E-05	4.678E-05
5.620	0.190	7.867E-05	4.829E-05
5.450	0.196	8.114E-05	4.981E-05
5.220	0.203	8.401E-05	5.157E-05
5.042	0.210	8.688E-05	5.333E-05
4.867	0.217	8.975E-05	5.510E-05
4.674	0.226	9.344E-05	5.736E-05
4.484	0.234	9.672E-05	5.937E-05
4.331	0.243	1.004E-04	6.164E-05
4.150	0.254	1.049E-04	6.440E-05
4.030	0.265	1.094E-04	6.716E-05
3.912	0.281	1.159E-04	7.117E-05
3.740	0.302	1.245E-04	7.642E-05
3.648	0.321	1.322E-04	8.117E-05
3.527	0.353	1.452E-04	8.915E-05
3.392	0.393	1.614E-04	9.909E-05
3.305	0.437	1.792E-04	1.100E-04
3.163	0.508	2.077E-04	1.275E-04
3.059	0.576	2.349E-04	1.442E-04
2.974	0.665	2.702E-04	1.659E-04
2.859	0.796	3.218E-04	1.976E-04
2.767	0.938	3.772E-04	2.315E-04
2.671	1.117	4.461E-04	2.738E-04
2.586	1.317	5.220E-04	3.204E-04
2.519	1.517	5.967E-04	3.663E-04
2.466	1.717	6.703E-04	4.115E-04
2.415	1.917	7.428E-04	4.560E-04
2.371	2.117	8.143E-04	4.999E-04
2.341	2.317	8.847E-04	5.431E-04
2.310	2.517	9.540E-04	5.857E-04
2.276	2.717	1.022E-03	6.276E-04
2.252	2.917	1.090E-03	6.690E-04
2.226	3.117	1.156E-03	7.098E-04
2.204	3.317	1.222E-03	7.500E-04
2.186	3.517	1.286E-03	7.896E-04
2.166	3.717	1.350E-03	8.287E-04
2.149	3.917	1.413E-03	8.673E-04
2.131	4.117	1.475E-03	9.053E-04
2.118	4.317	1.536E-03	9.428E-04

Table E.4 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added ^(a) (moles/L)	H ⁺ _{free,add} ^(b) (moles/L)
2.102	4.517	1.596E-03	9.798E-04
2.094	4.717	1.656E-03	1.016E-03
2.083	4.917	1.714E-03	1.052E-03
2.069	5.117	1.772E-03	1.088E-03
2.054	5.317	1.829E-03	1.123E-03
2.053	5.517	1.886E-03	1.158E-03
2.043	5.717	1.941E-03	1.192E-03
2.035	5.917	1.996E-03	1.225E-03
2.026	6.117	2.050E-03	1.259E-03
2.018	6.317	2.104E-03	1.291E-03
2.012	6.517	2.157E-03	1.324E-03
2.007	6.717	2.209E-03	1.356E-03
2.001	6.917	2.260E-03	1.388E-03
1.995	7.117	2.311E-03	1.419E-03
1.989	7.317	2.361E-03	1.450E-03
1.980	7.500	2.407E-03	1.478E-03

(a) $\text{HCl added in moles/L} = [(\text{HCl volume added})(0.0104)] /$
 $(\text{volume of sample} + \text{volume of HCl added}).$

(b) $\text{H}^+_{\text{free,add}} = (\text{HCl added in moles per liter}) / 1.629.$

Appendix F

**Titration of 6.0 Molal NaCl Solutions
with Reference Cell of Orion-Ross Electrode
Filled with 6.0 Molal NaCl Instead of Saturated KCl**

Appendix F

Titration of 6.0 Molal NaCl Solutions with Reference Cell of Orion-Ross, Electrode Filled with 6.0 Molal NaCl Instead of 3 M KCl

Table F.1 Titration of 25 ml of 6.0 Molal NaCl with 0.0104 M HCl
(reference cell filled with 6.0 molal NaCl and allowed to
equilibrate for <4 hours)

Observed pH	Volume of HCl Added (ml)	HCL Added ^(a) (moles/L)
8.268	0.000	0.000E+00
7.734	0.036	1.500E-05
6.813	0.071	2.954E-05
6.460	0.077	3.203E-05
6.312	0.080	3.327E-05
5.898	0.085	3.534E-05
5.697	0.088	3.658E-05
5.508	0.092	3.824E-05
5.266	0.098	4.073E-05
5.054	0.103	4.280E-05
4.834	0.109	4.528E-05
4.641	0.115	4.776E-05
4.385	0.122	5.065E-05
4.248	0.127	5.272E-05
4.014	0.134	5.561E-05
3.902	0.140	5.808E-05
3.722	0.150	6.221E-05
3.560	0.161	6.674E-05
3.442	0.172	7.127E-05
3.302	0.189	7.826E-05
3.186	0.208	8.606E-05
3.049	0.235	9.713E-05
2.933	0.265	1.094E-04
2.824	0.304	1.253E-04
2.711	0.356	1.464E-04
2.590	0.421	1.727E-04
2.496	0.497	2.033E-04
2.387	0.602	2.452E-04
2.291	0.726	2.943E-04
2.191	0.882	3.554E-04
2.105	1.063	4.254E-04
2.033	1.263	5.016E-04
1.973	1.463	5.766E-04
1.922	1.663	6.505E-04
1.879	1.863	7.233E-04
1.844	2.063	7.951E-04
1.808	2.263	8.658E-04

Table F.1 (contd)

Observed pH	Volume of HCl Added (ml)	HCL Added ^(a) (moles/L)
1.781	2.463	9.354E-04
1.756	2.663	1.004E-03
1.735	2.863	1.072E-03
1.714	3.063	1.138E-03
1.694	3.263	1.204E-03
1.674	3.463	1.269E-03
1.667	3.663	1.333E-03
1.647	3.863	1.396E-03
1.639	4.063	1.458E-03
1.628	4.263	1.519E-03
1.618	4.463	1.580E-03
1.609	4.663	1.640E-03
1.598	4.863	1.698E-03
1.589	5.063	1.757E-03
1.585	5.263	1.814E-03
1.576	5.463	1.870E-03
1.570	5.663	1.926E-03
1.564	5.863	1.981E-03
1.559	6.063	2.036E-03
1.553	6.263	2.089E-03
1.549	6.463	2.142E-03
1.549	6.500	2.152E-03

^(a) HCl added in moles/L = [(HCl volume added) (0.0104)]/
(volume of sample + volume of HCl added).

Table F.2 Titration of 25 ml of 6.0 Molal NaCl with 0.0104 M HCl
(reference cell filled with 6.0 molal NaCl and allowed to
equilibrate for 8 days)

Observed pH	Volume of HCl Added (ml)	HCl Added ^(a) (moles/L)
5.714	0.000	0.000E+00
5.657	0.036	1.500E-05
5.206	0.071	2.954E-05
5.083	0.078	3.244E-05
5.008	0.085	3.534E-05
4.673	0.098	4.073E-05
4.560	0.103	4.280E-05
4.349	0.112	4.652E-05
4.197	0.119	4.941E-05
3.997	0.129	5.354E-05
3.850	0.137	5.684E-05
3.696	0.148	6.138E-05

Table F.2 (contd)

Observed pH	Volume of HCl Added (ml)	HCl Added ^(a) (moles/L)
3.612	0.160	6.633E-05
3.355	0.183	7.579E-05
3.300	0.193	7.990E-05
3.191	0.212	8.770E-05
3.076	0.239	9.877E-05
2.934	0.275	1.135E-04
2.849	0.313	1.290E-04
2.697	0.377	1.549E-04
2.618	0.431	1.768E-04
2.517	0.523	2.137E-04
2.401	0.641	2.607E-04
2.301	0.769	3.113E-04
2.198	0.925	3.721E-04
2.134	1.102	4.403E-04
2.046	1.302	5.163E-04
1.988	1.497	5.893E-04
1.938	1.697	6.630E-04
1.897	1.897	7.356E-04
1.862	2.097	8.072E-04
1.819	2.297	8.777E-04
1.794	2.497	9.471E-04
1.769	2.697	1.016E-03
1.747	2.897	1.083E-03
1.730	3.097	1.150E-03
1.711	3.297	1.215E-03
1.694	3.497	1.280E-03
1.679	3.697	1.344E-03
1.664	3.897	1.407E-03
1.651	4.097	1.469E-03
1.639	4.297	1.530E-03
1.628	4.497	1.590E-03
1.620	4.697	1.650E-03
1.610	4.897	1.708E-03
1.601	5.097	1.766E-03
1.595	5.297	1.824E-03
1.587	5.497	1.880E-03
1.581	5.697	1.936E-03
1.574	5.897	1.991E-03
1.567	6.097	2.045E-03
1.563	6.297	2.099E-03
1.558	6.497	2.151E-03
1.557	6.500	2.152E-03

^(a) HCl added in moles/L = [(HCl volume added) (0.0104)]/
(volume of sample + volume of HCl added).

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Dr. Andy R. Felmy (25)
Geochemistry Section
3110 Port of Benton Boulevard
Battelle, PNL
Richland, WA 99352

Dr. Ilham Al Mahamid (5)
Mail Stop 70A-1115
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

Dr. Wolfgang Runde (5)
Mail Stop 70A-1115
Lawrence Berkeley Laboratory
1 Cyclotron Road Berkeley, CA 94720

Dr. Cynthia E. A. Palmer (5)
Lawrence Livermore National Laboratory
Mail Stop L-232
P.O. Box 808
Livermore, CA 94551

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Oxyrase, Incorporated
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Knoxville, TN 37931

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Board of Radioactive Waste Management
GF456
2101 Constitution Ave.
Washington, DC 20418

Rodney C. Ewing
Department of Geology
University of New Mexico
Albuquerque, NM 87131

Charles Fairhurst
Department of Civil and Mineral Engineering
University of Minnesota
500 Pillsbury Dr. SE
Minneapolis, MN 55455-0220

B. John Garrick
PLG Incorporated
4590 MacArthur Blvd., Suite 400
Newport Beach, CA 92660-2027

Leonard F. Konikow
US Geological Survey
431 National Center
Reston, VA 22092

Carl A. Anderson, Director
Board of Radioactive Waste Management
National Research Council
HA 456
2101 Constitution Ave. NW
Washington, DC 20418

Christopher G. Whipple
ICF Kaiser Engineers
1800 Harrison St., 7th Floor
Oakland, CA 94612-3430

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Sue B. Clark
University of Georgia
Savannah River Ecology Lab
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Aiken, SC 29802

Konrad B. Krauskopf
Department of Geology
Stanford University
Stanford, CA 94305-2115

Della Roy
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UNITED KINGDOM

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