

# **Thermodynamic Properties of Chlorides in Hydrothermal Fluids: Evaluation and Regression of Experimental Data**

Oluwatobiloba Odukoya

March 16, 2025

# 1. Introduction

An important branch of materials studied by geologists are the various fluids that originate from the depths of the earth. These fluids are the result of an often complex mixture of solutes and solvents which have combined at high temperatures and pressures. One of the tools used to study these fluids is thermodynamics and it can be summarily defined as a conceptual field that seeks to describe the relationship between energy and matter. The study approach of thermodynamics often deconstructs the components of a system, followed by defining each component and lastly, rebuilding the system from the understanding gleaned from each component. This is achieved through a combination of empirical data and predictive modelling.

This study falls within the second stage of the thermodynamic approach discussed above and seeks to understand the properties of the components of a system. The system studied being hydrothermal fluids and the components of the system are aqueous chlorides; sodium chloride ( $\text{NaCl}$ ) and hydrochloric acid ( $\text{HCl}$ ). The chosen partial molar properties at infinite dilution of these chlorides have been compiled from various authors and processed by fitting the data points to models which yield coefficients used to describe the behaviour of the chlorides over a wide range of temperatures and pressures. These partial molar properties have been measured from just below standard states to high temperatures (slightly above the critical temperature of water) and high pressures (pressures experienced around to the Mohorovičić discontinuity). The usefulness of these properties are many fold, but as it relates to geology, such knowledge can be used as a better predictor on the chemical composition of materials at great depths as well as the paths (thermobarometric and compositional) through which these materials navigate.

## 2. Thermodynamics of Aqueous Dissolution

According to Dolejš and Manning (2010)<sup>[19]</sup>, the energy that results in the dissolution of a solute in water can be broken down into three energy contributions [9], [19]: (1) localized distortion of the solutes crystal lattice, (2) formation of hydration shell(s) around the solute, and (3) volumetric compression due to electrostriction (solute-solvent interaction). These energy considerations have been mathematically expressed in the literature<sup>[19]</sup> through Equations (1)-(3),

$$\Delta_{ds}G = \underbrace{\Delta_{cl}G}_{(1)+(2)} + \underbrace{\Delta_{co}G}_{(3)} \quad (1)$$

expanding the terms gives,

$$\Delta_{ds}G = \underbrace{\Delta H + \int_{T_{ref}}^T c_P dT - T \left( \Delta S + \int_{T_{ref}}^T \frac{c_P}{T} dT \right)}_{\Delta_{cl}G} + \underbrace{RT \ln \frac{\rho_{hs}}{\rho_w}}_{\Delta_{co}G} \quad (2)$$

which can be simplified to,

$$\Delta_{ds}G = \underbrace{a + bT + cT \ln T + dT^2}_{\Delta_{cl}G} + \underbrace{eT \ln \rho_w}_{\Delta_{co}G} \quad (3)$$

where: (1)-(3) indicate the energy contributions discussed in the paragraph above;  $\Delta_{ds}G$ ,  $\Delta_{cl}G$  and  $\Delta_{co}G$  are the Gibbs energies defined as the energy of dissolution, the caloric contribution to dissolution and the volumetric contribution to dissolution, respectively;  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy;  $\rho_{hs}$  and  $\rho_w$  are the densities of the solution and pure water respectively;  $T$  and  $P$  are the temperature and pressure of the solution, while  $T_{ref}$  is a specified temperature at which standard thermodynamic properties have been measured (Usually 25 °C);  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  are coefficients related to enthalpy, entropy, electrostriction, and the heat capacity polynomial.

The Gibbs energy in Equations (1)-(3) are linked to the solubility product ( $K$ )

of the solute through an equilibrium equation given in Equation (4),

$$0 = \Delta_{ds}G + RT \ln K \quad (4)$$

Which can be rewritten explicitly in terms of  $K$  as

$$K = e^{\left(\frac{\Delta_{ds}G}{RT}\right)} \quad (5)$$

The partial molar volume at infinite dilution and partial molar heat capacity of component  $i$  ( $V_{m,i}$  and  $c_{P,i}$ ) are given by Equations (6) & (7),

$$V_{m,i} = \left( \frac{\partial V}{\partial n_i} \right)_{T,P,n_j \neq i} \quad (6)$$

$$c_{P,i} = \left( \frac{\partial c_P}{\partial n_i} \right)_{T,P,n_j \neq i} \quad (7)$$

which measure the change in volume and heat capacity when an infinitesimal amount of  $i$  is added to the solution. This means that the amount of solute  $i$  is so small that every molecule is surrounded by solvent molecules and there are no solute-solute interactions in the solution. While Equations (1)-(3) refer to the thermodynamic properties of the solution, the same equations with values of the partial molar properties of  $i$  inserted would yield the partial molar Gibbs energy of  $i$  ( $d\mu_i$ )<sup>[53]</sup>. This leads to further equations for  $V_{m,i}$  and  $c_{P,i}$  which relate them to their associated Gibbs energies,

$$V_{m,i} = \left( \frac{\partial \mu_i}{\partial P} \right)_T \quad (8)$$

$$c_{P,i} = -T \left( \frac{\partial^2 \mu_i}{\partial T^2} \right)_P \quad (9)$$

The combination of the Equations (1)-(5) give information on the sum of thermodynamic interactions of all solution components, while Equations (6)-(9) gives information on the thermodynamic properties of the interaction of components relative to the other components in the solution. The halides studied dissolve in

water to produce strongly polarized chemical species. The different approaches to analyzing what goes on when substances are mixed helps to reveal how natural systems deviate from ideality and to further improve our models regarding them.

### 3. Experiments and Models

The previous section shows the link between the properties studied here and the Gibbs free energy, which is a determinant of the spontaneity of chemical reactions. The theory behind the properties have been discussed and now we briefly discuss the practical set up for obtaining the molar properties.

The partial molar volumes of dilute solutions are chiefly obtained by measuring properties that are directly related to the volume<sup>[9]</sup>, such as the density of solution ( $\rho$ ), the density change ( $\Delta\rho - \Delta\rho^\circ$ ) or the volume of the mixture ( $V^M$ ). The choice of instrumentation for measurements is governed by the conditions (temperature, pressure and molality) at which one chooses to measure. However, the most common instruments include established methods like pycnometry and buoyancy/magnetic floats, as well as newer methods like vibrating-tube densitometry and dilatometry [9], [38], [72]. For partial molar heat capacities on the other hand, thermal energy is measured at constant pressure by flow calorimetry, bomb calorimetry and differential scanning calorimetry.

In addition to direct measurements of related properties, some studies that have attempted to mathematically express or model the chemical interactions of solutions, have derived partial molar properties of the components. These derived partial molar properties are then usually compared to those obtained from experimental studies to prove the efficacy of the models. The most prominent of such models include Debye-Hückel theory<sup>[15]</sup>, Bjerrum theory<sup>[5]</sup>, Pitzer Equations<sup>[49]</sup>

and Davies Equations<sup>[14]</sup>. The models mostly seek to improve the equation of the Debye-Hückel theory by adding terms to the equation to address the shortcomings of the equation. The model in its original form is given as,

$$\log_{10} \gamma \pm = -Az_j^2 \frac{\sqrt{I}}{1 + Ba_o \sqrt{I}} \quad (10)$$

where:

$\gamma$  = activity coefficient

$A$  = Debye radius (a term that shows the magnitude of charge carriers' net electrostatic effect in solution)

$z_j$  = charge of component  $j$

$I$  = ionic strength of the solution

$Ba_o$  = correction term for short-range solute interactions

The constants  $A$  and  $B$  in the equation vary with temperature and have values of approximately  $0.51 \text{ mol}^{-1/2} \text{ dm}^{1/2}$  and  $0.3 \text{ mol}^{-1/2} \text{ dm}^{1/2}$  respectively at  $25^\circ\text{C}$  and  $1 \text{ atm}$ . The resulting activities from such models are inserted into equations that yield the energy of the solution and the partial molar properties are subsequently calculated through Equations (8) and (9). The advantage of models is that they can predict properties in  $P$ - $T$  domains where experimental set-ups may be physically limited in terms of available materials or practicality. The disadvantage however is that there is yet to be a model that remains valid at all  $P$ - $T$ - $x$  conditions, as they are mostly only valid over short ranges.

## 4. Data Sources

Data on the partial molar properties of NaCl and HCl have been obtained from papers spanning almost a century. The data selected includes empirical and predicted values of  $c_{P,i}$  and  $V_{m,i}$  for the halides. Studies from peer-reviewed articles which employed well-established experimental techniques and explicitly reported uncertainties or provided error analyses were prioritized. Additionally, multiple papers covering overlapping temperature and pressure conditions were included to mitigate potential biases and improve the reliability of the compiled dataset by averaging out discrepancies across different experimental methods. There are a combined 600 data points for  $V_{m,i}$  and 299 points for  $c_{P,i}$ . For convenience,  $T$  is reported in degrees Celsius ( $^{\circ}\text{C}$ ) and pressure in  $\text{bar}$ , while all  $V_{m,i}$  data has been converted to  $\text{cm}^3 \text{mol}^{-1}$  and  $c_{P,i}$  to  $\text{J mol}^{-1} \text{K}^{-1}$ . The summary of the  $P$ - $T$  conditions of the chosen data are shown in Figures 4.1-4.4<sup>1</sup>.

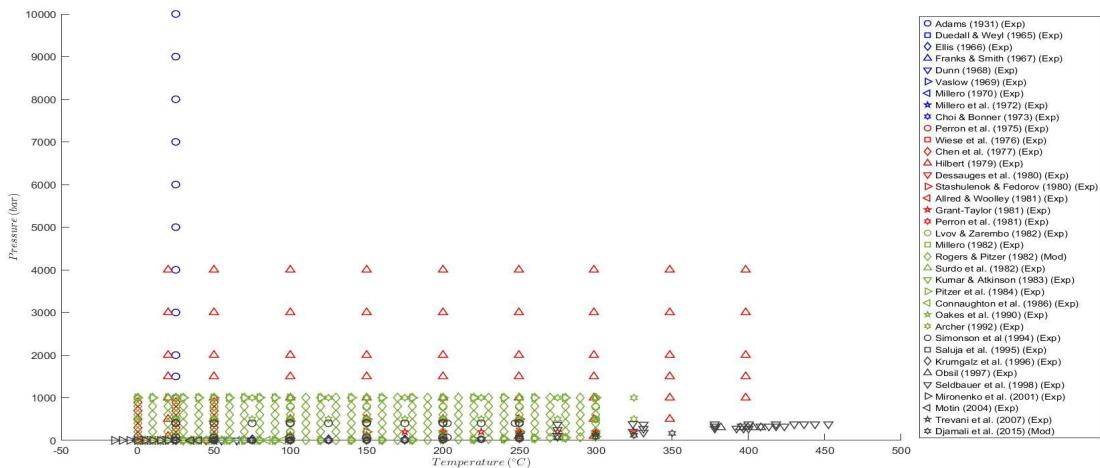


Figure 4.1.: Plot showing  $P$ - $T$  conditions of all  $V_{m,\text{NaCl}}$  data (Experiments and Models) (zoomed plots are shown in Figure A.1 [2] [20] [23] [25] [21] [71] [39] [41] [8] [47] [73] [7] [31] [16] [65] [3] [28] [48] [37] [40] [53] [66] [35] [50] [11] [44] [4] [62] [54] [34] [45] [57] [42] [43] [70] [17])

<sup>1</sup>Figures A.1-A.4 are found on pages I-III of Appendix A

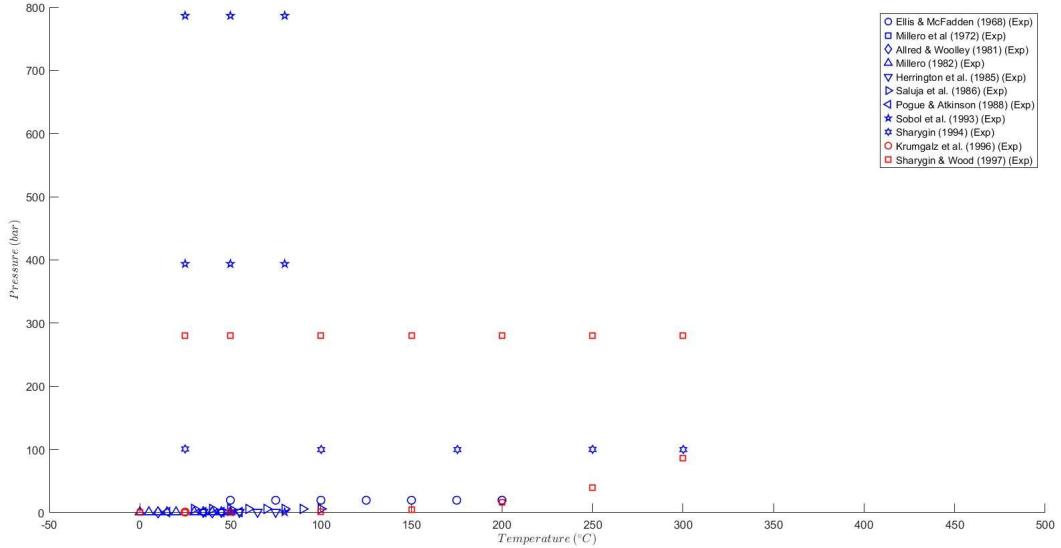


Figure 4.2.: Plot showing  $P$ - $T$  conditions of all  $V_{m,HCl}$  data (Experiments and Models) (zoomed plots are shown in Figure A.2) [24] [41] [3] [40] [30] [55] [52] [64] [58] [34] [59]

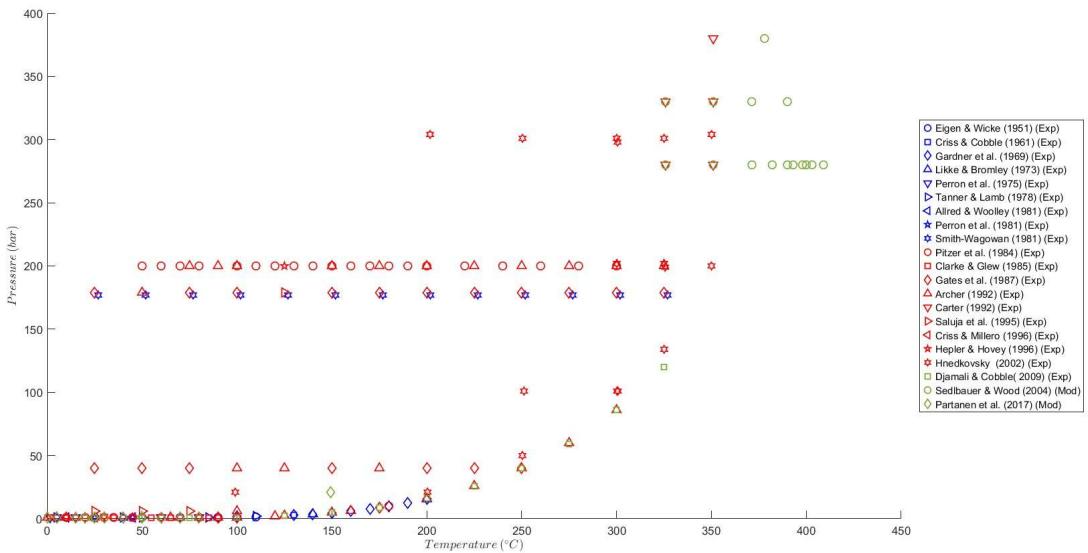


Figure 4.3.: Plot showing  $P$ - $T$  conditions of all  $c_{P,NaCl}$  data (Experiments and Models) (zoomed plots are shown in Figure A.3) [22] [13] [26] [36] [47] [68] [3] [48] [63] [50] [10] [27] [4] [6] [54] [12] [29] [32] [56] [18] [46]

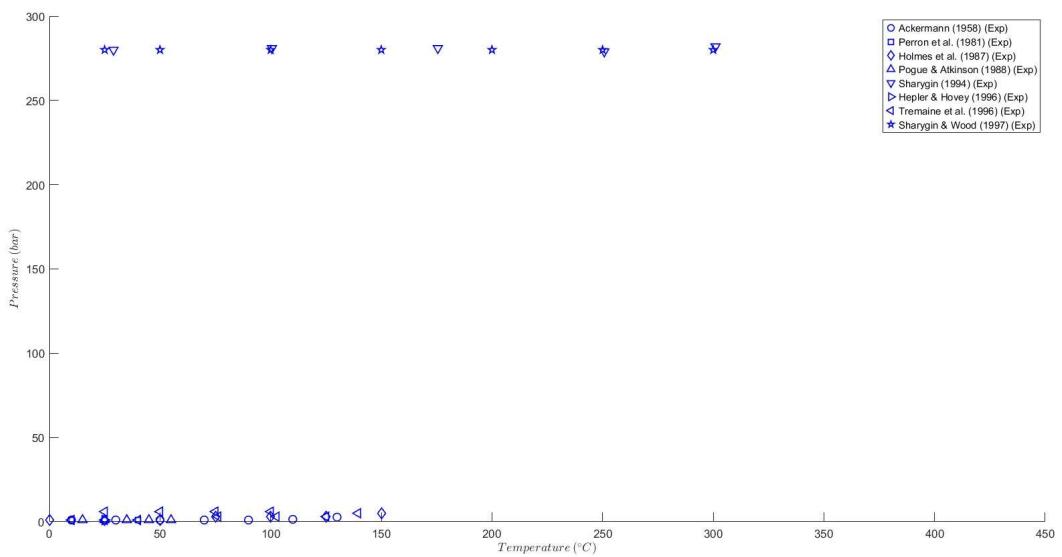


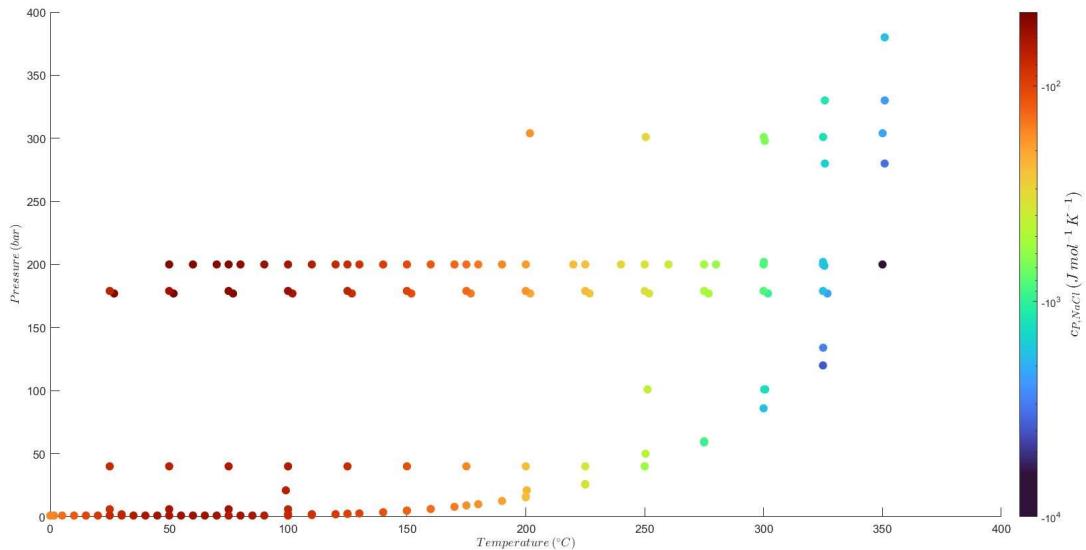
Figure 4.4.: Plot showing  $P$ - $T$  conditions of all  $c_{P,HCl}$  data (Experiments and Models) (zoomed plots are shown in Figure A.4) [1] [48] [33] [52] [58] [29] [69] [59]

## 5. Plots of Experimental Data: Heat Capacity and Volume

### 5.1. Partial Molar Heat Capacity ( $c_{P,i}$ )

$c_{P,NaCl}$

(A)



(B)

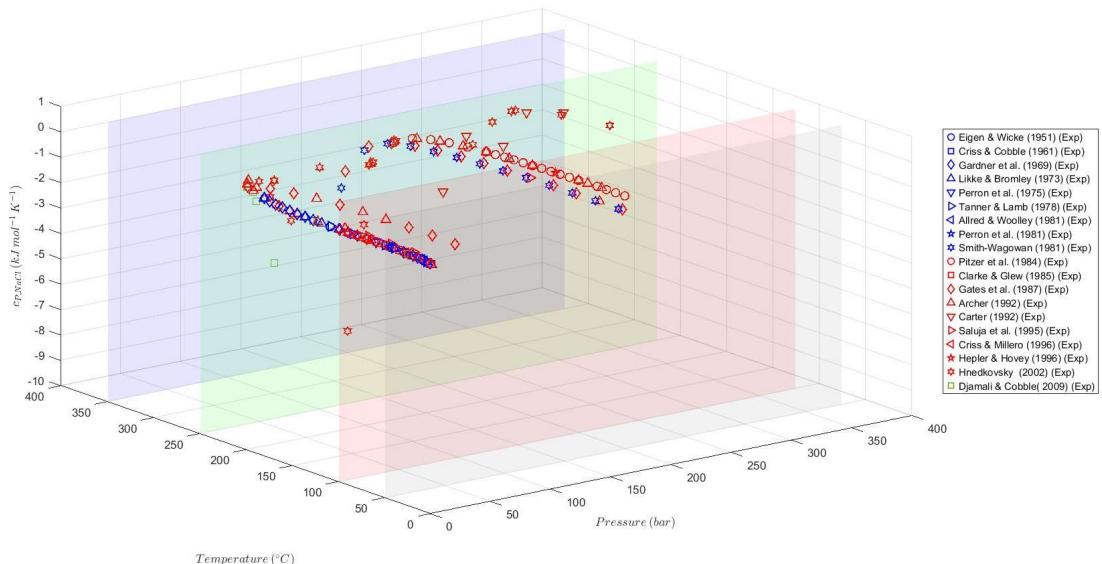


Figure 5.1.: Plots of  $c_{P,NaCl}$  showing spread of heat capacity experiments in a  $P$ - $T$  space. (A) 2D plot with  $c_{P,NaCl}$  values indicated using a colorbar. (B) 3D plot of ( $c_{P,NaCl}$ ) with temperature slices (shown in Figures B.1-B.2)<sup>2</sup>.

(C)

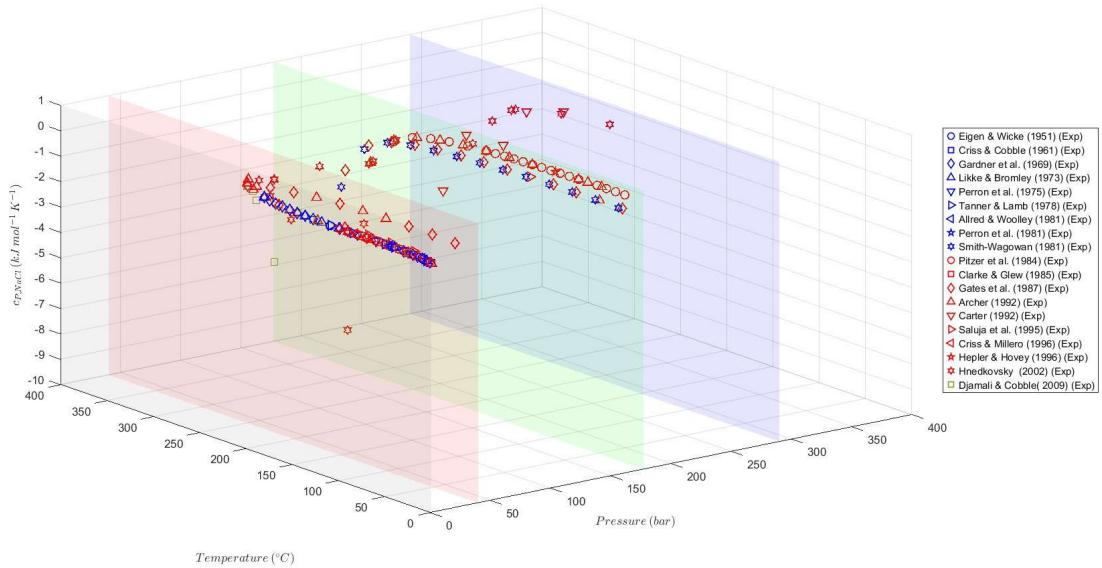


Figure 5.2.: 3D plot of  $c_{P,NaCl}$  with pressure slices (shown in Figures B.3-B.5).

<sup>2</sup>Figures B.1-B.16 are found on pages IV-XVIII of Appendix B

(C)

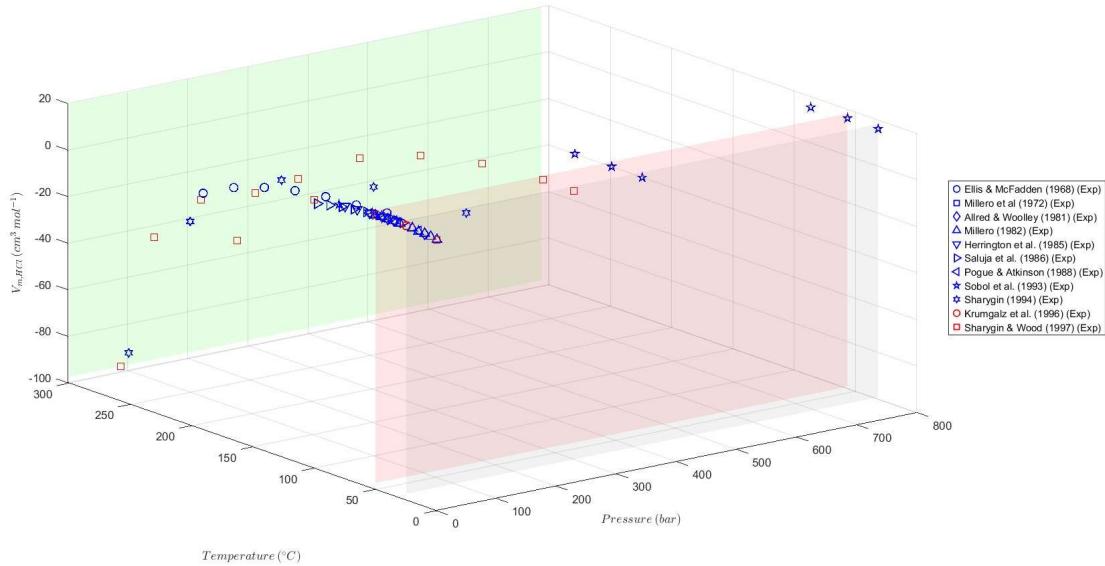


Figure 5.8.: 3D plot of  $V_{m,HCl}$  showing temperature slices (plotted in Figures B.15(E)-B.16(G))

## 6. Regression and Evaluation of Experimental Data

Experimental data were fitted to equations to see which modelled molecular interactions affected the partial molar properties of the halides the most. Four equations for molar volume and two equations for molar heat capacity were fitted to the data. In addition to these fits, the interactions between the volumes/densities of the solute and solvent with temperature were additionally plotted. The choice of using  $25^{\circ}\text{C}$  as the minimum temperature was due to the unreliability of  $\alpha_w$  and  $\beta_w$  values at low temperatures. The aforementioned equations are shown below in Equations (11)-(16):

For Volume,

$$V_{m,i} = a_0 + a_1 \beta_w \quad (11)$$

$$V_{m,i} = a_0 + a_1 T \beta_w \quad (12)$$

$$V_{m,i} - 2RT\beta_w = a_0 + a_1 \beta_w \quad (13)$$

$$V_{m,i} - 2RT\beta_w = a_0 + a_1 \frac{1}{\epsilon_w^2} \left( \frac{\partial \epsilon_w}{\partial P} \right)_T \quad (14)$$

For Heat Capacity,

$$c_{P,i} = a_0 + a_1 T \left( \frac{\partial \alpha_w}{\partial T} \right)_P \quad (15)$$

$$c_{P,i} = a_0 + a_1 \left[ 2T\alpha_w + T^2 \left( \frac{\partial \alpha_w}{\partial T} \right)_P \right] \quad (16)$$

where:

$\beta_w$  = Isothermal compressibility of water

$\epsilon_w$  = Static dielectric constant of water

$\alpha_w$  = Isobaric expansivity of water

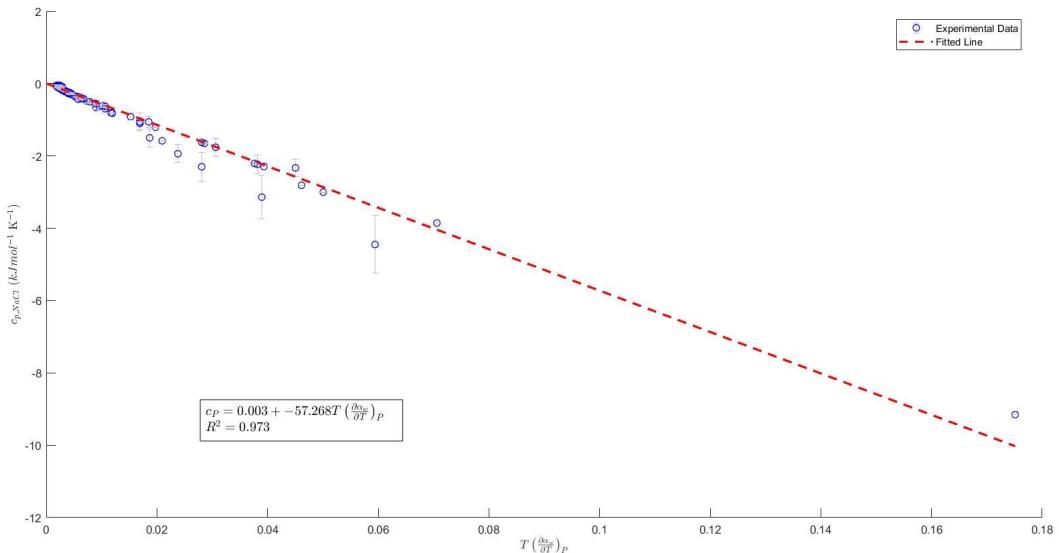
$(-2RT\beta_w)$  = Correction factor for water

$a_0$  &  $a_1$  = Coefficients of the fitted model

## 6.1. Heat Capacity Fits

**NaCl**

(A)



(B)

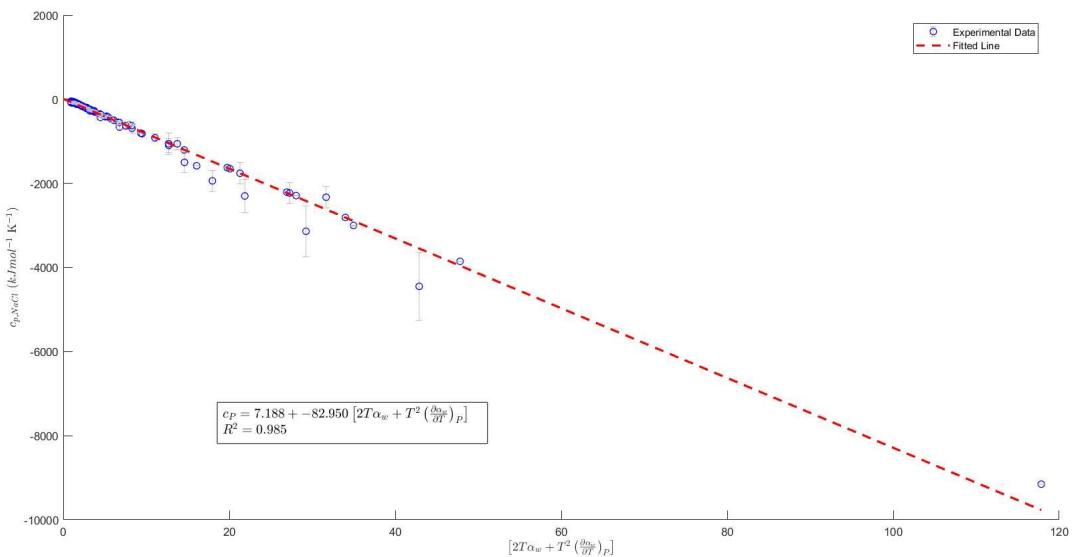
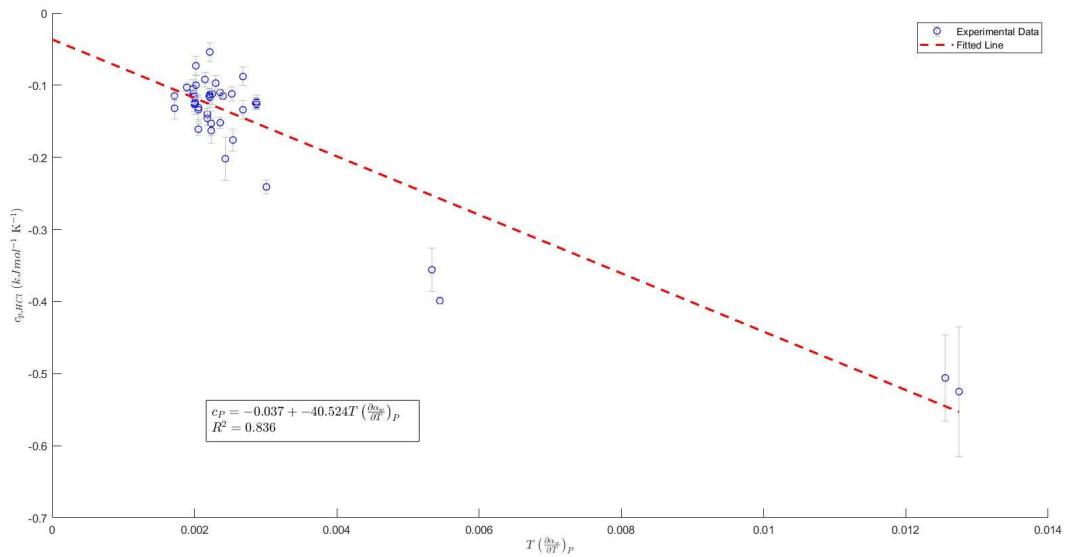


Figure 6.1.: Fit of NaCl heat capacity data to: (A) Equation (15) & (B) Equation (16)

(A)



(B)

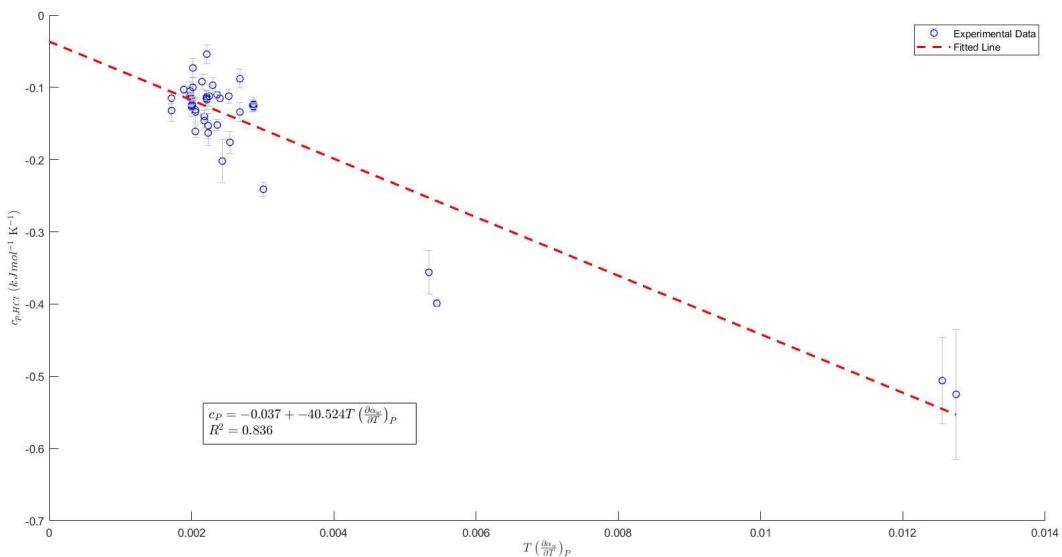
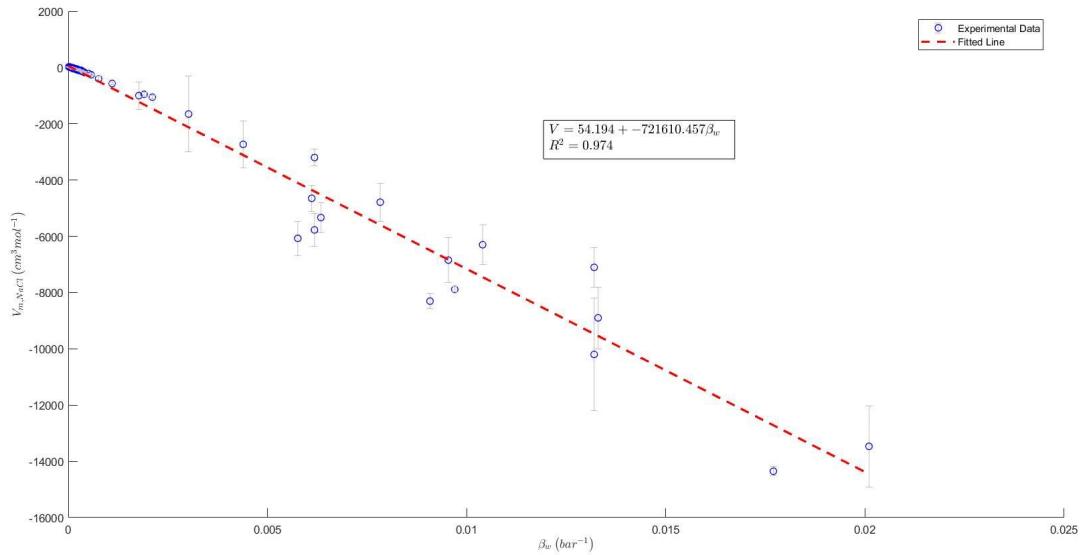


Figure 6.2.: Fit of HCl heat capacity data to: (A) Equation (15) & (B) Equation (16)

## 6.2. Volume Fits

**NaCl**

(A)



(B)

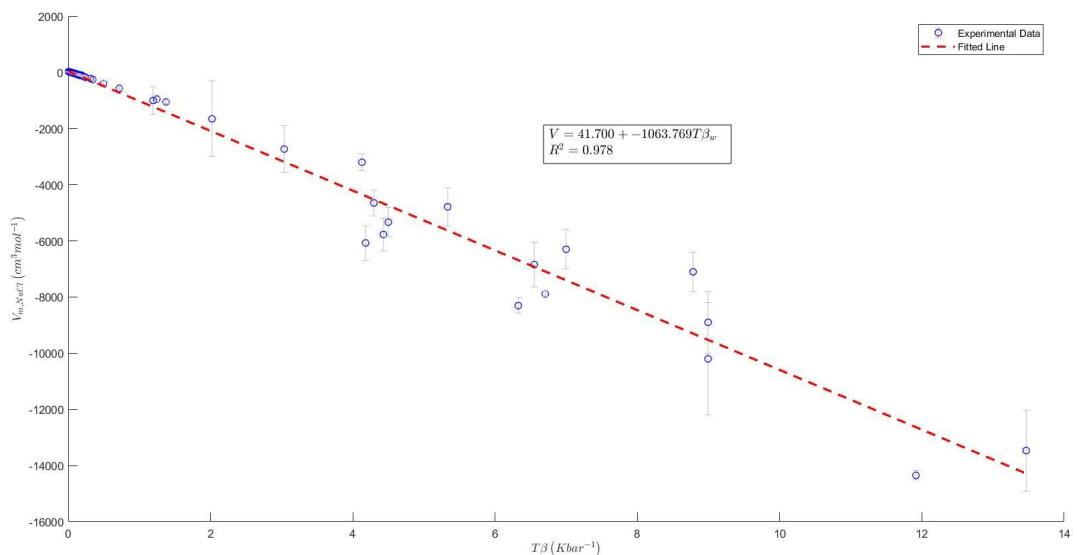
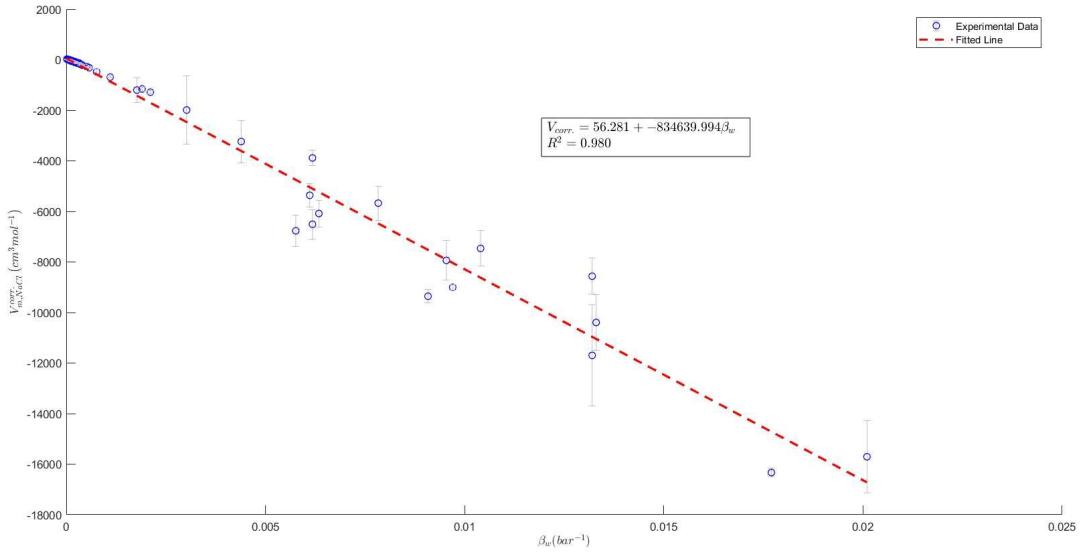


Figure 6.3.: Fit of NaCl volume data to: (A) Equation (11) & (B) Equation (12)

(C)



(D)

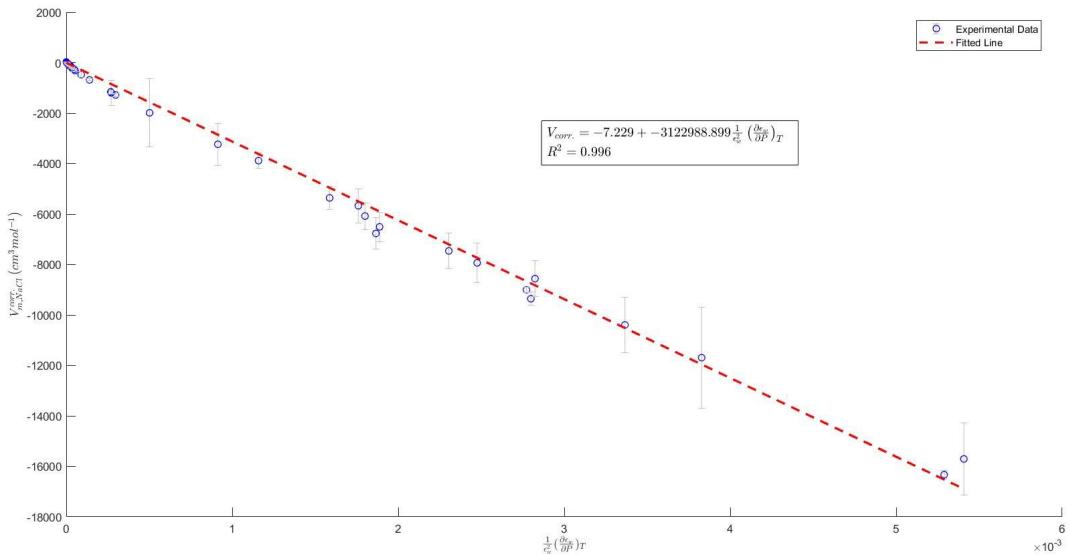
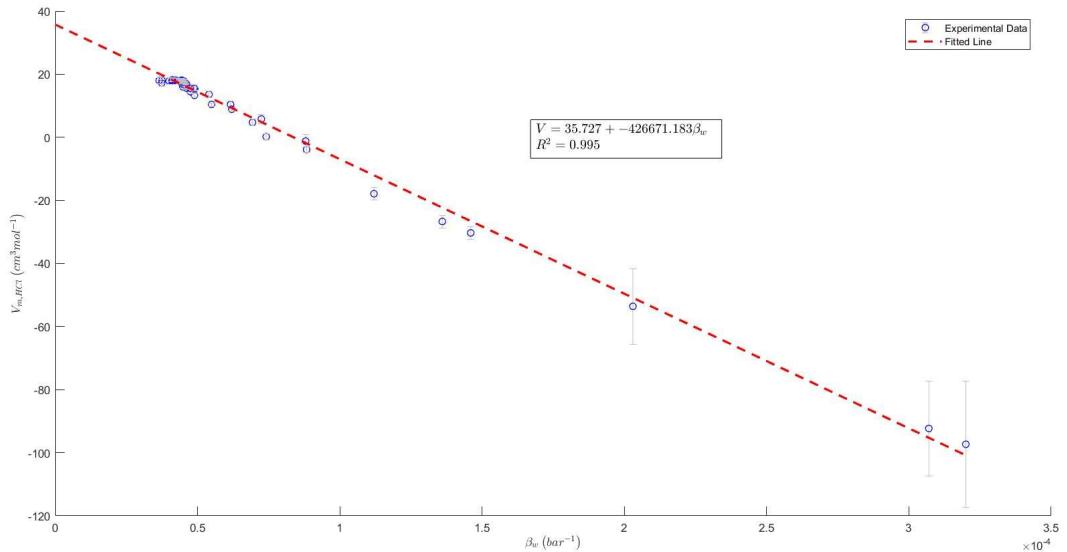


Figure 6.4.: Fit of NaCl volume data to: (C) Equation (13) & (B) Equation (14)

# HCl

(A)



(B)

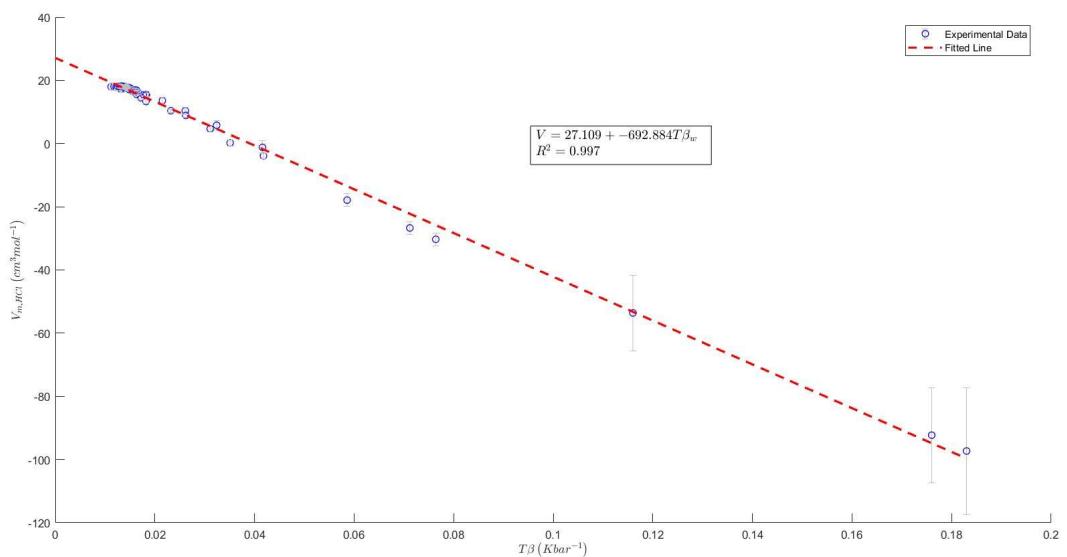
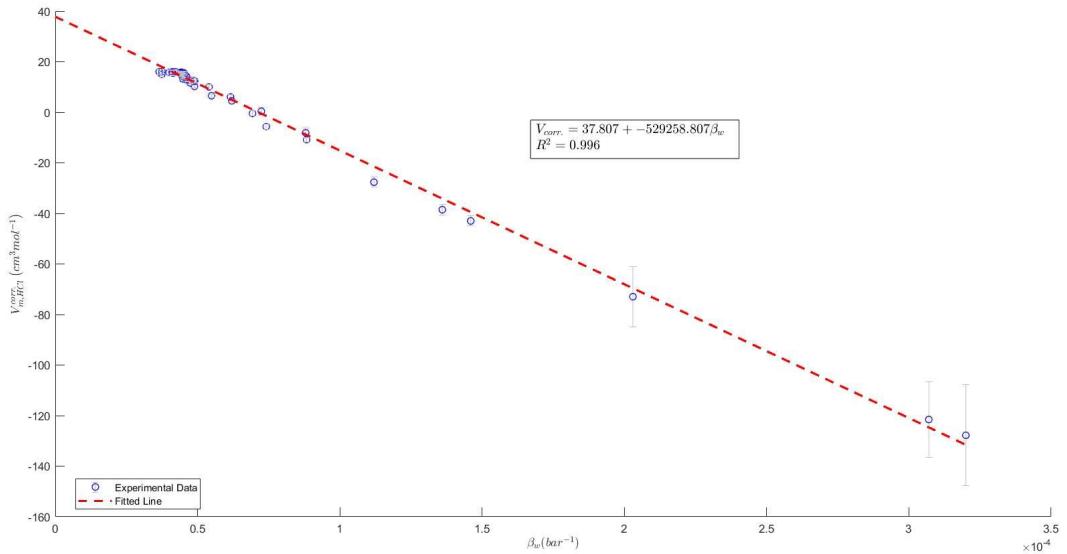


Figure 6.5.: Fit of HCl volume data to: (A) Equation (11) & (B) Equation (12)

(C)



(D)

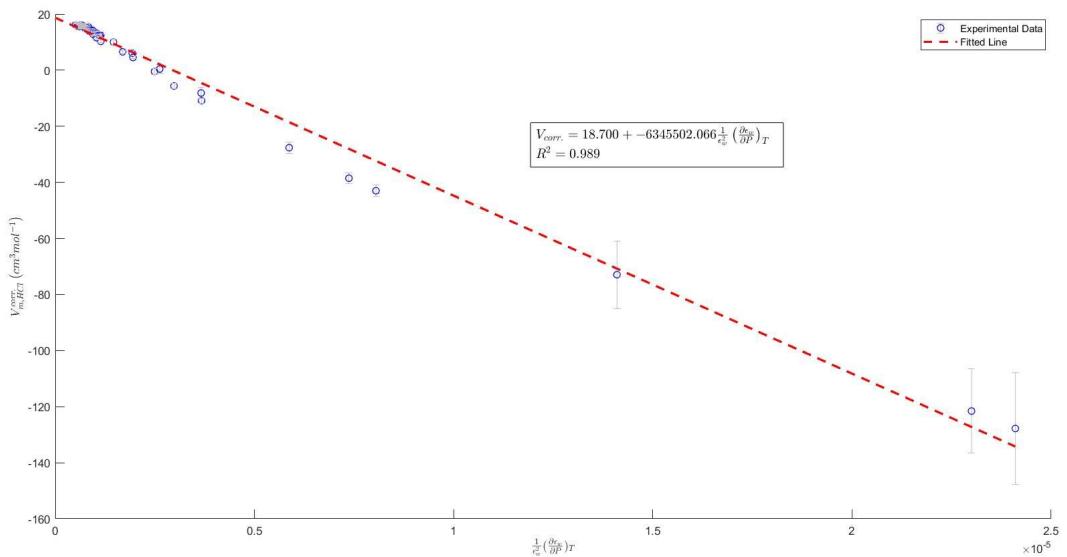
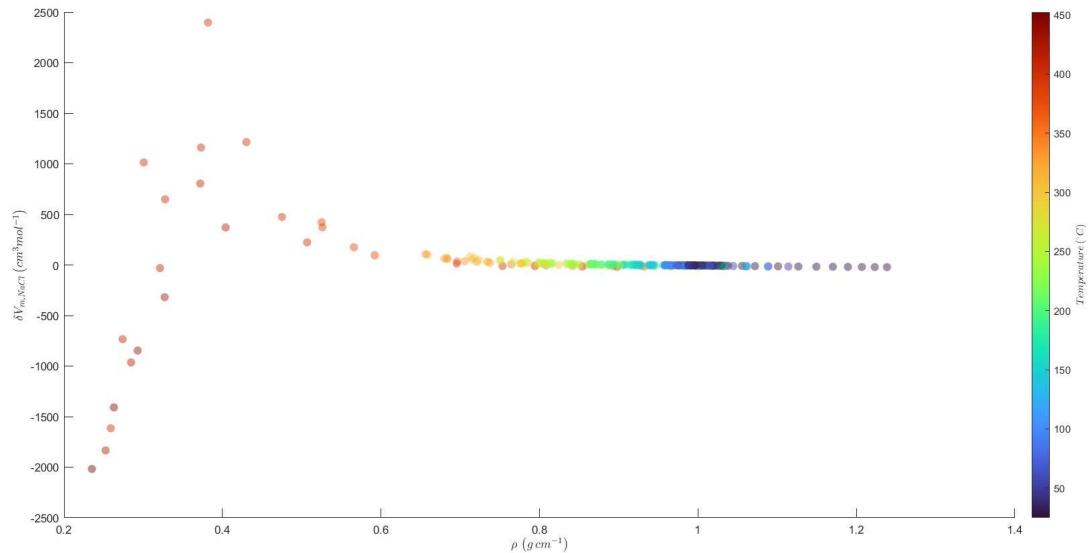


Figure 6.6.: Fit of HCl volume data to: (A) Equation (13) &amp; (B) Equation (14)

## 6.3. Volume-Density Plots

### NaCl Volume Density Plots

(A)



(B)

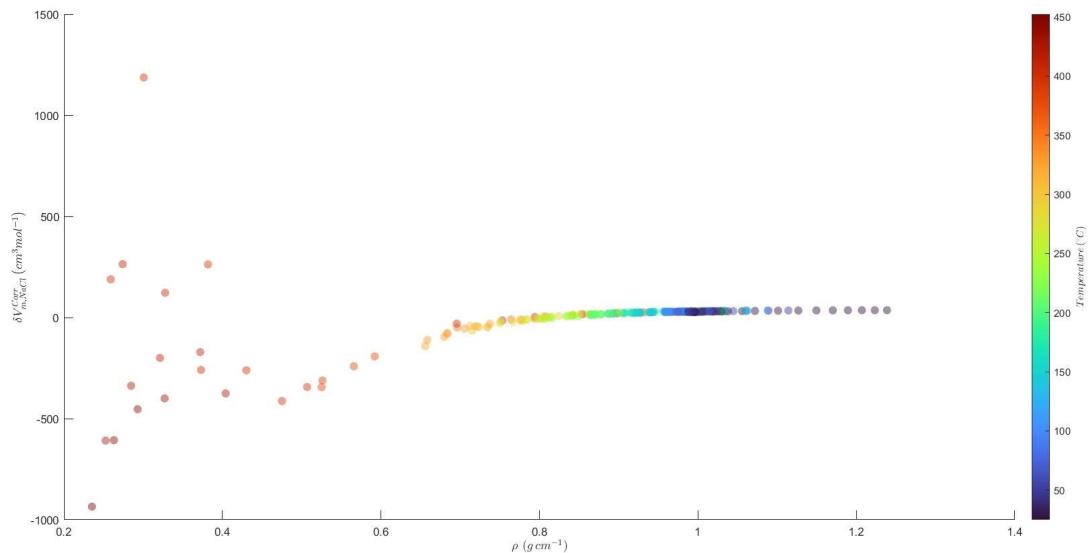
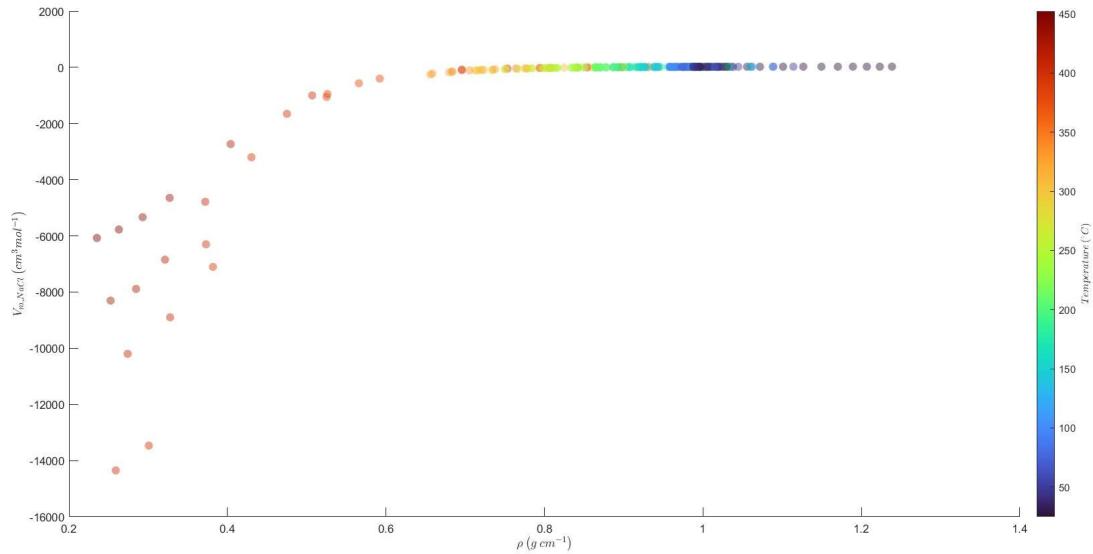


Figure 6.7.: Residuals of volume data for NaCl versus density of water (*Experimental data – linear fit*) with temperature shown on a colorbar: (A) Residuals from Equation (11)-(12) & (B) Residuals from Equation (13)-(14)

(C)



(D)

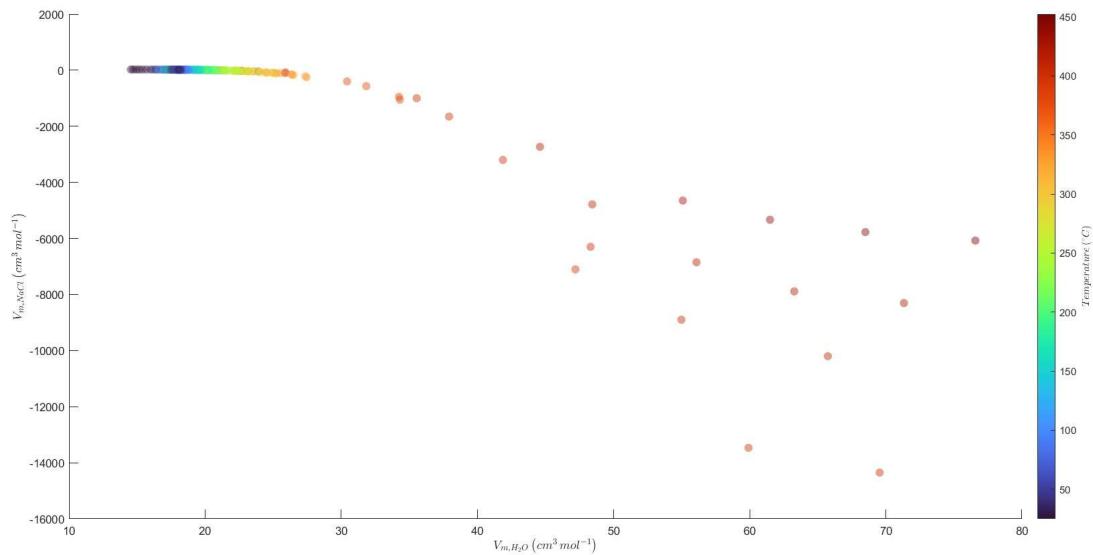


Figure 6.8.: Experimental NaCl data versus volumetri properties of water with temperature shown on a colorbar: (C) Volume data versus density of water; (D) Volume data versus Volume of water

(E)

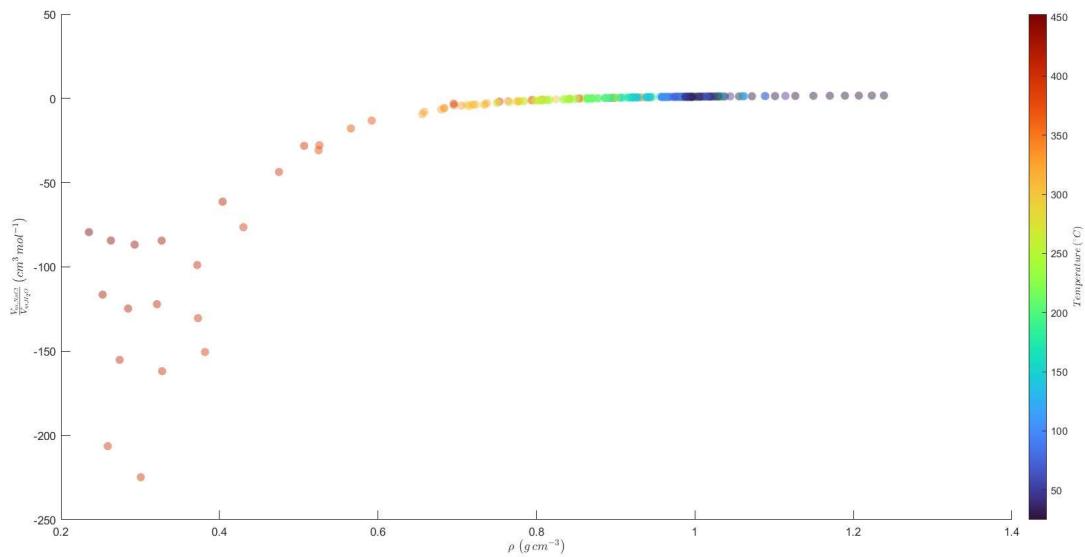
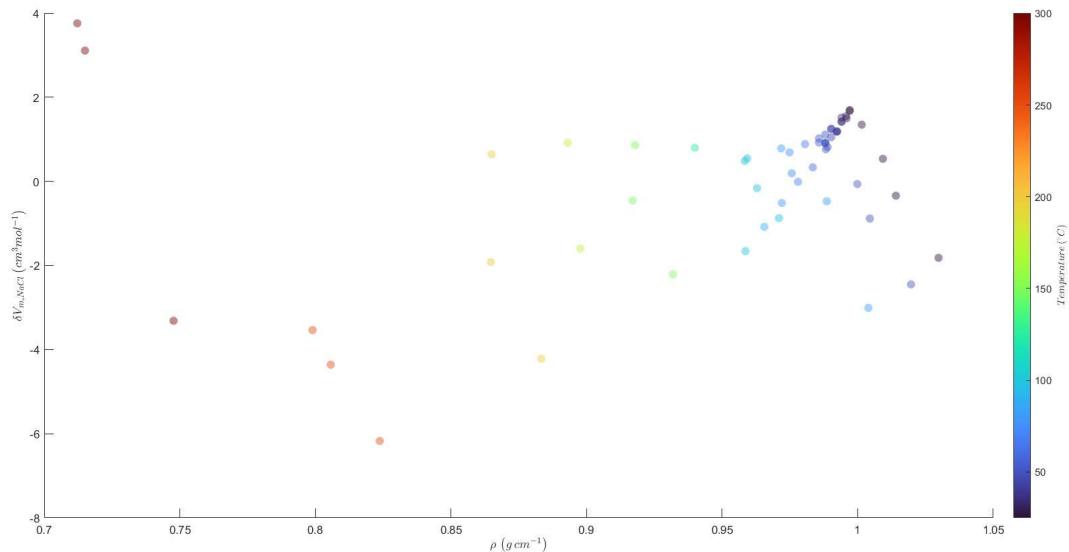


Figure 6.9.: Volume coefficient ( $NaCl$  Experimental data/ $Volume$  of water) versus density of water with temperature variations shown on a colorbar

## HCl Volume Density Plots

(A)



(B)

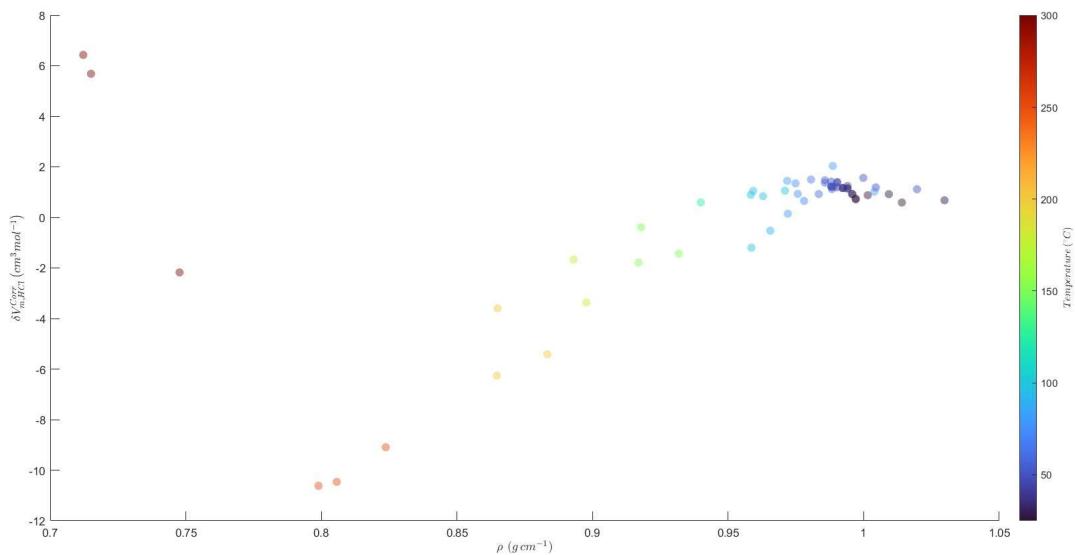
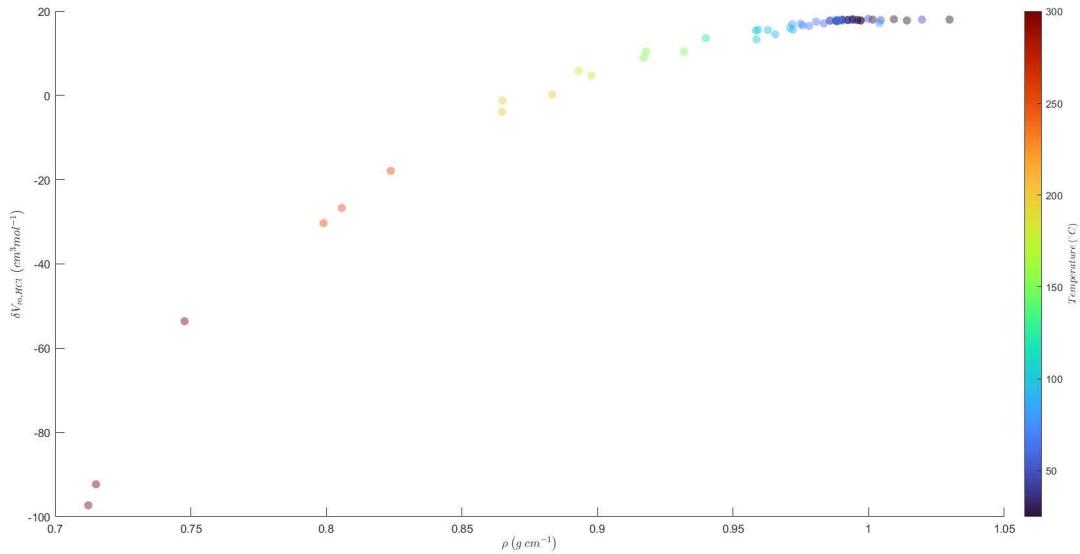


Figure 6.10.: Residuals of volume data for HCl versus density of water (*Experimental data – linear fit*) with temperature shown on a colorbar: (A) Residuals from Equation (11)-(12) &; (B) Residuals from Equation (13)-(14)

(C)



(D)

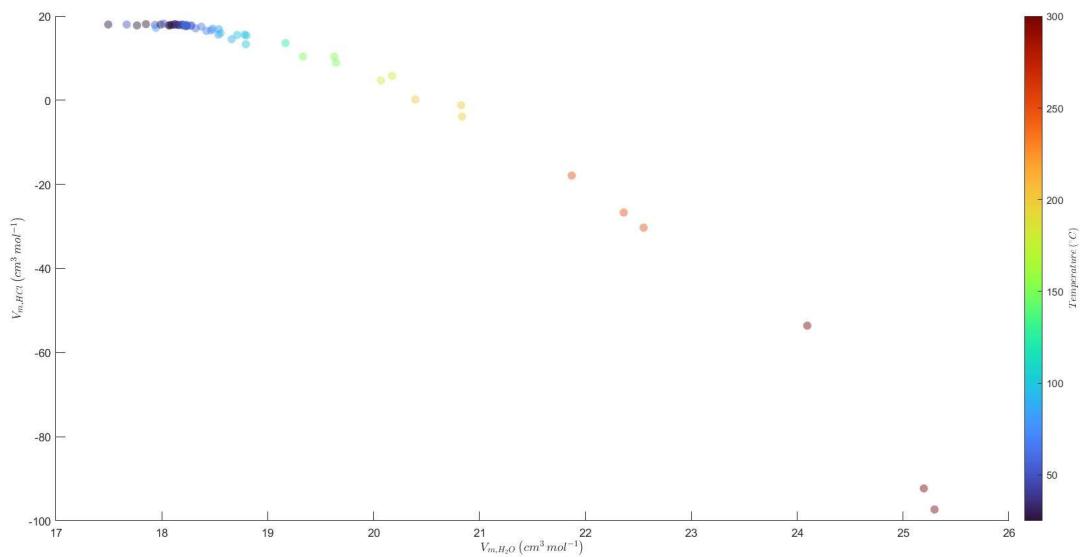


Figure 6.11.: Experimental HCl data versus volumetric properties of water with temperature shown on a colorbar: (C) Volume data versus density of water; (D) Volume data versus Volume of water

# Bibliography

- [1] T. Ackermann, “Aussagen über die Eigendissoziation des Wassers aus Molwärmemessungen gelöster Elektrolyte,” *Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für physikalische Chemie*, vol. 62, no. 4, pp. 411–419, Jun. 1958, ISSN: 0372-8382. DOI: [10.1002/bbpc.19580620406](https://doi.org/10.1002/bbpc.19580620406).
- [2] L. H. Adams, “Equilibrium in binary systems under pressure. I. An experimental and thermodynamic investigation of the system, nacl-h<sub>2</sub>o, at 25°C,” *Journal of the American Chemical Society*, vol. 53, no. 10, pp. 3769–3813, 1931, ISSN: 15205126. DOI: [10.1021/ja01361a020](https://doi.org/10.1021/ja01361a020).
- [3] G. C. Allred and E. M. Woolley, “Heat capacities of aqueous HCl, NaOH, and NaCl at 283.15, 298.15 and 313.15 K: ΔC<sub>rp</sub> for ionization of water,” *The Journal of Chemical Thermodynamics*, vol. 13, no. 2, pp. 147–154, 1981, ISSN: 10963626. DOI: [10.1016/S0021-9614\(81\)80019-5](https://doi.org/10.1016/S0021-9614(81)80019-5).
- [4] D. G. Archer, *Thermodynamic Properties of the NaCl+H<sub>2</sub>O System I. Thermodynamic Properties of NaCl(cr)*, 1992. DOI: [10.1063/1.555913](https://doi.org/10.1063/1.555913).
- [5] N. Bjerrum, “Untersuchungen über Ionenassoziation. I. Der Einfluss der Ionenassoziation auf die Aktivität der Ionen bei mittleren Assoziationsgraden,” *Math. Fys. Medd.*, vol. 7, no. 9, pp. 1–48, 1926.
- [6] Carter Richard W., “APPARENT MOLAR HEAT CAPACITIES AT CONSTANT PRESSURE OF 1:1 AQUEOUS ELECTROLYTES FROM 598 TO

691 K AND 28 TO 38 MPa,” Ph.D. dissertation, University o f Delaware, 1992, p. 134.

- [7] C.-T. Chen, R. T. Emmet, and F. J. Millero, “The apparent molal volumes of aqueous solutions of sodium chloride, potassium chloride, magnesium chloride, sodium sulfate, and magnesium sulfate from 0 to 1000 bars at 0, 25, and 50.degree.C,” *Journal of Chemical & Engineering Data*, vol. 22, no. 2, pp. 201–207, Apr. 1977, ISSN: 0021-9568. DOI: [10.1021/je60073a007](https://doi.org/10.1021/je60073a007).
- [8] Y. S. Choi and O. D. Bonner, “The Partial Molai Volumes of Some Representative Solutes in H<sub>2</sub>O and D<sub>2</sub>O,” vol. 87, no. 4-6, pp. 188–197, 1973. DOI: [doi:10.1524/zpch.1973.87.4-6.188](https://doi.org/10.1524/zpch.1973.87.4-6.188).
- [9] I. Cibulka and V. Majer, “CHAPTER 8. Partial Molar Volumes of Non-Ionic Solutes at Infinite Dilution,” in *Volume Properties: Liquids, Solutions and Vapours*, Cambridge: Royal Society of Chemistry, 2014, pp. 246–272. DOI: [10.1039/9781782627043-00246](https://doi.org/10.1039/9781782627043-00246).
- [10] E. C. W. Clarke and D. N. Glew, “Evaluation of the Thermodynamic Functions for Aqueous Sodium Chloride from Equilibrium and Calorimetric Measurements below 154 řC,” *Journal of Physical and Chemical Reference Data*, vol. 14, no. 2, pp. 489–610, 1985, ISSN: 15297845. DOI: [10.1063/1.555730](https://doi.org/10.1063/1.555730).
- [11] L. M. Connaughton, J. P. Hershey, and F. J. Millero, “PVT properties of concentrated aqueous electrolytes: V. Densities and apparent molal volumes of the four major sea salts from dilute solution to saturation and from 0 to 100řC,” *Journal of Solution Chemistry*, vol. 15, no. 12, pp. 989–1002, 1986, ISSN: 00959782. DOI: [10.1007/BF00645194](https://doi.org/10.1007/BF00645194).
- [12] C. M. Criss and F. J. Millero, “Modeling the Heat Capacities of Aqueous 11 Electrolyte Solutions with Pitzer’s Equations,” *The Journal of Physical Chemistry*, vol. 100, no. 4, pp. 1288–1294, Jan. 1996, ISSN: 0022-3654. DOI: [10.1021/jp9513551](https://doi.org/10.1021/jp9513551).

- [13] C. M. Criss and J. W. Cobble, “The Thermodynamic Properties of High Temperature Aqueous Solutions. I. Standard Partial Molal Heat Capacities of Sodium Chloride and Barium Chloride from 0 to 100° 1,” *Journal of the American Chemical Society*, vol. 83, no. 15, pp. 3223–3228, Aug. 1961, ISSN: 0002-7863. DOI: 10.1021/ja01476a013.
- [14] C. W. Davies, *Ion Association*. Butterworths, Washington, DC, 1962.
- [15] P. Debye and E. Hückel, “The theory of electrolytes. I. Freezing point depression and related phenomena [Zur Theorie der Elektrolyte. I. Gefrierpunktsterniedrigung und verwandte Erscheinungen],” *Physikalische Zeitschrift*, vol. 24, pp. 185–206, 1923.
- [16] G. Dessauges, N. Miljevic, and W. A. Van Hook, “Isotope effects in aqueous systems. 9. Partial molar volumes of sodium chloride/water and sodium chloride/water-d<sub>2</sub> solutions at 15, 30, and 45.degree.C,” *The Journal of Physical Chemistry*, vol. 84, no. 20, pp. 2587–2595, Oct. 1980, ISSN: 0022-3654. DOI: 10.1021/j100457a021.
- [17] E. Djamali, W. G. Chapman, and K. R. Cox, “Prediction of the Standard State Partial Molar Volume of Aqueous Electrolytes to High Temperatures and High Pressures,” *Journal of Chemical & Engineering Data*, vol. 60, no. 12, pp. 3792–3799, Dec. 2015, ISSN: 0021-9568. DOI: 10.1021/acs.jced.5b00722.
- [18] E. Djamali, K. Chen, and J. W. Cobble, “Standard state thermodynamic properties of completely ionized aqueous sodium sulfate using high dilution calorimetry up to 598.15 K,” *Journal of Physical Chemistry B*, vol. 113, no. 34, pp. 11 688–11 695, Aug. 2009, ISSN: 15206106. DOI: 10.1021/jp9049236.
- [19] D. Dolejš and C. E. Manning, “Thermodynamic model for mineral solubility in aqueous fluids: theory, calibration and application to model fluidflow

- systems," *Geofluids*, vol. 10, no. 1-2, pp. 20–40, May 2010, ISSN: 1468-8115. DOI: [10.1111/j.1468-8123.2010.00282.x](https://doi.org/10.1111/j.1468-8123.2010.00282.x).
- [20] I. W. Duedall and P. K. Weyl, "Apparatus for Determining the Partial Equivalent Volumes of Salts in Aqueous Solutions," *Review of Scientific Instruments*, vol. 36, no. 4, pp. 528–531, Apr. 1965, ISSN: 0034-6748. DOI: [10.1063/1.1719614](https://doi.org/10.1063/1.1719614).
- [21] L. A. Dunn, "Apparent molar volumes of electrolytes. Part 3. Some 1-1 and 2-1 electrolytes in aqueous solution at 0, 5, 15, 35, 45, 55 and 65 °C," *Transactions of the Faraday Society*, vol. 64, no. 0, pp. 2951–2961, 1968, ISSN: 0014-7672. DOI: [10.1039/TF9686402951](https://doi.org/10.1039/TF9686402951).
- [22] M. Eigen and E. Wicke, "Ionenhydratation und spezifische Wärme wäSSriger Elektrolytlösungen," *Zeitschrift für Elektrochemie und angewandte physikalische Chemie*, vol. 55, no. 5, pp. 354–363, Jul. 1951, ISSN: 0372-8323. DOI: [10.1002/bbpc.19510550504](https://doi.org/10.1002/bbpc.19510550504).
- [23] A. J. Ellis, "Partial molal volumes of alkali chlorides in aqueous solution to 200°C," *J. Chem. Soc. A*, no. 0, pp. 1579–1584, 1966. DOI: [10.1039/J19660001579](https://doi.org/10.1039/J19660001579).
- [24] A. J. Ellis and I. M. McFadden, "The partial molal volume of hydrochloric acid in high-temperature water," *Chemical Communications (London)*, no. 9, pp. 516–517, 1968, ISSN: 0009-241X. DOI: [10.1039/C19680000516](https://doi.org/10.1039/C19680000516).
- [25] F. Franks and H. T. Smith, "Apparent molal volumes and expansibilities of electrolytes in dilute aqueous solution," *Transactions of the Faraday Society*, vol. 63, no. 2, pp. 2586–2598, 1967, ISSN: 00147672. DOI: [10.1039/tf9676302586](https://doi.org/10.1039/tf9676302586).
- [26] W. L. Gardner, R. E. Mitchell, and J. W. Cobble, "Thermodynamic properties of high-temperature aqueous solutions. XI. Calorimetric determination

- of the standard partial molal heat capacity and entropy of sodium chloride solutions from 100 to 200.deg.,” *The Journal of Physical Chemistry*, vol. 73, no. 6, pp. 2025–2032, Jun. 1969, ISSN: 0022-3654. DOI: 10.1021/j100726a064.
- [27] J. A. Gates, D. M. Tillett, D. E. White, and R. H. Wood, “Apparent molar heat capacities of aqueous NaCl solutions from 0.05 to 3.0 mol<sup>1</sup>kg<sup>1</sup>, 350 to 600 K, and 2 to 18 MPa,” *The Journal of Chemical Thermodynamics*, vol. 19, no. 2, pp. 131–146, Feb. 1987, ISSN: 00219614. DOI: 10.1016/0021-9614(87)90103-0.
- [28] D. F. Grant-Taylor, “Partial molar volumes of sodium chloride solutions at 200 bar, and temperatures from 175 to 350°C,” *Journal of Solution Chemistry*, vol. 10, no. 9, pp. 621–630, 1981, ISSN: 00959782. DOI: 10.1007/BF00650738.
- [29] L. G. Hepler and J. K. Hovey, “Standard state heat capacities of aqueous electrolytes and some related undissociated species,” *Canadian Journal of Chemistry*, vol. 74, no. 5, pp. 639–649, May 1996, ISSN: 0008-4042. DOI: 10.1139/v96-069.
- [30] T. M. Herrington, A. D. Pethybridge, and M. G. Roffey, “Densities of hydrochloric, hydrobromic, hydriodic, and perchloric acids from 25 to 75.degree.C at 1 atm,” *Journal of Chemical & Engineering Data*, vol. 30, no. 3, pp. 264–267, Jul. 1985, ISSN: 0021-9568. DOI: 10.1021/je00041a008.
- [31] R. Hilbert, “PVT-daten von Wasser und von wässrigen Natriumchloridlösungen bis 873 K, 4000 Bar und 25 Gewichtsprozent NaCl,” Ph.D. dissertation, Universität Karlsruhe, 1979, ISBN: 3810720534.
- [32] L. Hndkovský, V. Hynek, V. Majer, and R. H. Wood, “A new version of differential flow heat capacity calorimeter; tests of heat loss corrections and heat capacities of aqueous NaCl from T= 300 K to T= 623 K,” *The Journal*

*of Chemical Thermodynamics*, vol. 34, no. 6, pp. 755–782, Jun. 2002, ISSN: 00219614. DOI: 10.1006/jcht.2001.0949.

- [33] H. Holmes, R. Busey, J. Simonson, R. Mesmer, D. Archer, and R. Wood, “The enthalpy of dilution of HCl(aq) to 648 K and 40 MPa thermodynamic properties,” *The Journal of Chemical Thermodynamics*, vol. 19, no. 8, pp. 863–890, Aug. 1987, ISSN: 00219614. DOI: 10.1016/0021-9614(87)90033-4.
- [34] B. S. Krumgalz, R. Pogorelsky, and K. S. Pitzer, “Volumetric properties of single aqueous electrolytes from zero to saturation concentration at 298.15 řK represented by pitzer’s ion-interaction equations,” *Journal of Physical and Chemical Reference Data*, vol. 25, no. 2, pp. 663–689, 1996, ISSN: 00472689. DOI: 10.1063/1.555981.
- [35] A. Kumar and G. Atkinson, “Thermodynamics of concentrated electrolyte mixtures. 3. Apparent molal volumes, compressibilities, and expansibilities of NaCl-CaCl<sub>2</sub> mixtures from 5 to 35 ŚC,” *Journal of Physical Chemistry*, vol. 87, no. 26, pp. 5504–5507, 1983, ISSN: 00223654. DOI: 10.1021/j150644a039.
- [36] S. Likke and L. A. Bromley, “Heat capacities of aqueous sodium chloride, potassium chloride, magnesium chloride, magnesium sulfate, and sodium sulfate solutions between 80.deg. and 200.deg.,” *Journal of Chemical & Engineering Data*, vol. 18, no. 2, pp. 189–195, Apr. 1973, ISSN: 0021-9568. DOI: 10.1021/je60057a027.
- [37] S. N. LVOV and V. I. ZAREMBO, “ULTIMATE PARTIAL VOLUMES OF DISSOLVED ELECTROLITES UNDER STATE HIGH VARIABLES,” *GEOKHIMIYA*, no. 4, pp. 565–575, 1982, ISSN: 0016-7525.

- [38] Y. Marcus and G. Hefter, “Standard Partial Molar Volumes of Electrolytes and Ions in Nonaqueous Solvents,” *Chemical Reviews*, vol. 104, no. 7, pp. 3405–3452, Jul. 2004, ISSN: 0009-2665. DOI: [10.1021/cr030047d](https://doi.org/10.1021/cr030047d).
- [39] F. J. Millero, “The apparent and partial molal volume of aqueous sodium chloride solutions at various temperatures,” *Journal of Physical Chemistry*, vol. 74, no. 2, pp. 356–362, 1970, ISSN: 00223654. DOI: [10.1021/j100697a022](https://doi.org/10.1021/j100697a022).
- [40] F. J. Millero, “The effect of pressure on the solubility of minerals in water and seawater,” *Geochimica et Cosmochimica Acta*, vol. 46, no. 1, pp. 11–22, 1982, ISSN: 00167037. DOI: [10.1016/0016-7037\(82\)90286-1](https://doi.org/10.1016/0016-7037(82)90286-1).
- [41] F. J. Millero, E. V. Hoff, and L. Kahn, “The effect of pressure on the ionization of water at various temperatures from molal-volume data1,” *Journal of Solution Chemistry*, vol. 1, no. 4, pp. 309–327, 1972, ISSN: 00959782. DOI: [10.1007/BF00715990](https://doi.org/10.1007/BF00715990).
- [42] M. V. Mironenko, G. E. Boitnott, S. A. Grant, and R. S. Sletten, “Experimental Determination of the Volumetric Properties of NaCl Solutions to 253 K,” *The Journal of Physical Chemistry B*, vol. 105, no. 41, pp. 9909–9912, Oct. 2001, ISSN: 1520-6106. DOI: [10.1021/jp011356f](https://doi.org/10.1021/jp011356f).
- [43] M. A. Motin, “Temperature and concentration dependence of apparent molar volumes and viscosities of NaCl, NH<sub>4</sub>Cl, CuCl<sub>2</sub>, CuSO<sub>4</sub>, and MgSO<sub>4</sub> in pure water and water + urea mixtures,” *Journal of Chemical and Engineering Data*, vol. 49, no. 1, pp. 94–98, 2004, ISSN: 00219568. DOI: [10.1021/je0340957](https://doi.org/10.1021/je0340957).
- [44] C. S. Oakes, J. M. Simonson, and R. J. Bodnar, “The System NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O. 2. Densities for Ionic Strengths of 0.1-19.2 molkg<sup>-1</sup>at 298.15 and 308.15 K and at 0.1 MPa,” *Journal of Chemical and Engineering Data*, vol. 35, no. 3, pp. 304–309, 1990, ISSN: 15205134. DOI: [10.1021/je00061a022](https://doi.org/10.1021/je00061a022).

- [45] M. OBSIL, “Propriétés volumiques des solutions aqueuses d’electrolytes 1 : 1,1 :2 et 2 :1 jusqu’au domaine critique de l’eau,” Ph.D. dissertation, 1997, 185 P.
- [46] J. I. Partanen, L. J. Partanen, and K. P. Vahteristo, “Traceable Thermo-dynamic Quantities for Dilute Aqueous Sodium Chloride Solutions at Temperatures from (0 to 80) °C. Part 2. The Quantities Associated with the Partial Molar Heat Capacity,” *Journal of Chemical & Engineering Data*, vol. 62, no. 12, pp. 4215–4227, Dec. 2017, ISSN: 0021-9568. DOI: 10.1021/acs.jced.7b00590.
- [47] G. Perron, J. L. Fortier, and J. E. Desnoyers, “The apparent molar heat capacities and volumes of aqueous NaCl from 0.01 to 3 mol kg<sup>-1</sup> in the temperature range 274.65 to 318.15 K,” *The Journal of Chemical Thermodynamics*, vol. 7, no. 12, pp. 1177–1184, 1975, ISSN: 10963626. DOI: 10.1016/0021-9614(75)90039-7.
- [48] G. Perron, A. Roux, and J. E. Desnoyers, “Heat capacities and volumes of NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, and NiCl<sub>2</sub> up to 6 molal in water,” *Canadian Journal of Chemistry*, vol. 59, no. 21, pp. 3049–3054, 1981, ISSN: 0008-4042. DOI: 10.1139/v81-446.
- [49] K. S. Pitzer, “Thermodynamics of electrolytes. I. Theoretical basis and general equations,” *The Journal of Physical Chemistry*, vol. 77, no. 2, pp. 268–277, Jan. 1973, ISSN: 0022-3654. DOI: 10.1021/j100621a026.
- [50] K. S. Pitzer, J. C. Peiper, and R. H. Busey, “Thermodynamic Properties of Aqueous Sodium Chloride Solutions,” *Journal of Physical and Chemical Reference Data*, vol. 13, no. 1, pp. 1–102, 1984, ISSN: 15297845. DOI: 10.1063/1.555709.
- [51] A. V. Plyasunov, “A novel method for correlating/predicting the thermodynamic properties of aqueous ions at high T and P,” *Chemical Geology*,

vol. 682, p. 122756, 2025, ISSN: 0009-2541. DOI: <https://doi.org/10.1016/j.chemgeo.2025.122756>.

- [52] R. Pogue and G. Atkinson, “Apparent molal volumes and heat capacities of aqueous hydrogen chloride and perchloric acid at 15–55.degree.C,” *Journal of Chemical & Engineering Data*, vol. 33, no. 4, pp. 495–499, Oct. 1988, ISSN: 0021-9568. DOI: [10.1021/je00054a030](https://doi.org/10.1021/je00054a030).
- [53] P. S. Z. Rogers and K. S. Pitzer, “Volumetric Properties of Aqueous Sodium Chloride Solutions,” *Journal of Physical and Chemical Reference Data*, vol. 11, no. 1, pp. 15–81, Jan. 1982, ISSN: 0047-2689. DOI: [10.1063/1.555660](https://doi.org/10.1063/1.555660).
- [54] P. P. S. Saluja, D. J. Jobe, J. C. LeBlanc, R. J. Lemire, and P. M. ( of Canada Limited Whiteshell Laboratories, *Apparent molar heat capacities and volumes of mixed electrolytes: [NaCl(aq)] + CaCl2(aq)], [NaCl(aq) + MgCl2(aq)], and [CaCl2(aq) + MgCl2(aq)]*, Jan. 2025.
- [55] P. P. S. Saluja, K. S. Pitzer, and R. C. Phutela, “High-temperature thermodynamic properties of several 1:1 electrolytes,” *Canadian Journal of Chemistry*, vol. 64, no. 7, pp. 1278–1285, Jul. 1986, ISSN: 0008-4042. DOI: [10.1139/v86-220](https://doi.org/10.1139/v86-220).
- [56] J. Sedlbauer and R. H. Wood, “Thermodynamic properties of dilute NaCl(aq) solutions near the critical point of water,” *Journal of Physical Chemistry B*, vol. 108, no. 31, pp. 11838–11849, 2004, ISSN: 15206106. DOI: [10.1021/jp036775m](https://doi.org/10.1021/jp036775m).
- [57] J. Sedlbauer, E. M. Yezdimer, and R. H. Wood, “Partial molar volumes at infinite dilution in aqueous solutions of NaCl, LiCl, NaBr, and CsBr at temperatures from 550 K to 725 K,” *The Journal of Chemical Thermodynamics*, vol. 30, no. 1, pp. 3–12, 1998, ISSN: 0021-9614. DOI: <https://doi.org/10.1006/jcht.1997.0262>.

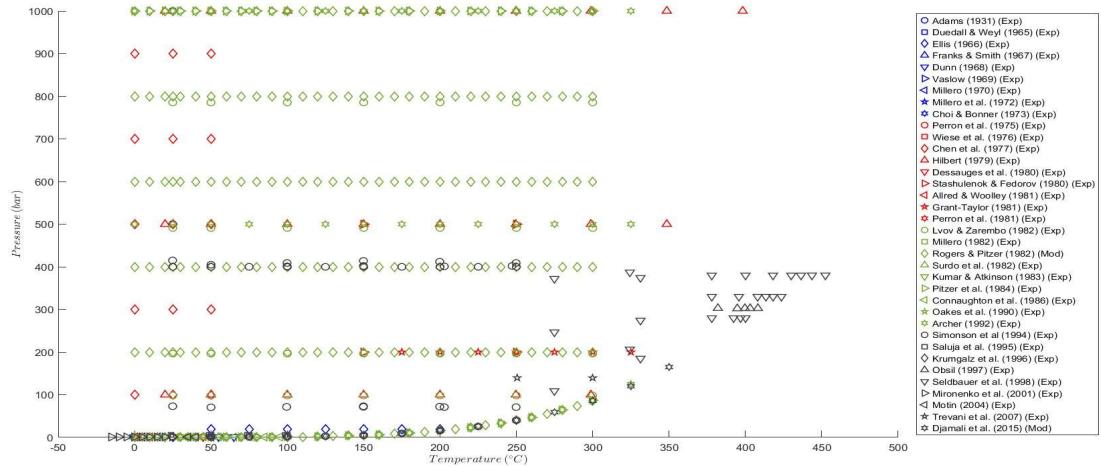
- [58] A. Sharygin, “Experimental investigation and theoretical prediction of the standard thermodynamic properties of aqueous solutions in a wide range of temperatures, pressures and concentrations,” Ph.D.Thesis, Sankt-Peterburg State Mining Institute., 1994.
- [59] A. V. Sharygin and R. H. Wood, “Volumes and heat capacities of aqueous solutions of ammonium chloride from the temperatures 298.15 K to 623 K and pressures to 28 MPa,” *The Journal of Chemical Thermodynamics*, vol. 28, no. 8, pp. 851–872, Aug. 1996, ISSN: 00219614. DOI: [10.1006/jcht.1996.0076](https://doi.org/10.1006/jcht.1996.0076).
- [60] E. L. Shock and H. C. Helgeson, “Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C,” *Geochimica et Cosmochimica Acta*, vol. 52, no. 8, pp. 2009–2036, 1988, ISSN: 0016-7037. DOI: [https://doi.org/10.1016/0016-7037\(88\)90181-0](https://doi.org/10.1016/0016-7037(88)90181-0).
- [61] E. L. Shock, H. C. Helgeson, and D. A. Sverjensky, “Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species,” *Geochimica et Cosmochimica Acta*, vol. 53, no. 9, pp. 2157–2183, 1989, ISSN: 0016-7037. DOI: [https://doi.org/10.1016/0016-7037\(89\)90341-4](https://doi.org/10.1016/0016-7037(89)90341-4).
- [62] J. M. Simonson, C. S. Oakes, and R. J. Bodnar, “Densities of NaCl(aq) to the temperature 523 K at pressures to 40 MPa measured with a new vibrating-tube densitometer,” *The Journal of Chemical Thermodynamics*, vol. 26, no. 4, pp. 345–359, 1994, ISSN: 0021-9614. DOI: <https://doi.org/10.1006/jcht.1994.1044>.

- [63] D. Smith-Magowan and R. H. Wood, “Heat capacity of aqueous sodium chloride from 320 to 600 K measured with a new flow calorimeter,” *The Journal of Chemical Thermodynamics*, vol. 13, no. 11, pp. 1047–1073, 1981, ISSN: 10963626. DOI: 10.1016/0021-9614(81)90004-5.
- [64] V. N. SOBOL, V. N. Gilyarov, and V. I. Zarembo, *EQUATIONS OF STATE FOR AQUEOUS-SOLUTIONS OF SULFURIC AND HYDROCHLORIC ACIDS IN THE 298-353-K TEMPERATURE AND 0.1-100 MPa PRESSURE RANGES*, 1993.
- [65] V. Stashulenok and M. Fedorov, “Limiting partial molar volumes of dissolved aqueous alkali metal halogenides at temperatures 423623 K and pressures up to 150 MPa (in Russian),” *Zh. Prikl. Khim.*, vol. 53, pp. 2330–2332, 1980.
- [66] A. L. Surdo, E. M. Alzola, and F. J. Millero, “The (p, V, T) properties of concentrated aqueous electrolytes I. Densities and apparent molar volumes of NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, and MgSO<sub>4</sub> solutions from 0.1 mol·kg<sup>-1</sup> to saturation and from 273.15 to 323.15 K,” *The Journal of Chemical Thermodynamics*, vol. 14, no. 7, pp. 649–662, 1982, ISSN: 10963626. DOI: 10.1016/0021-9614(82)90080-5.
- [67] D. A. Sverjensky, E. L. Shock, and H. C. Helgeson, “Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb,” *Geochimica et Cosmochimica Acta*, vol. 61, no. 7, pp. 1359–1412, 1997, ISSN: 0016-7037. DOI: [https://doi.org/10.1016/S0016-7037\(97\)00009-4](https://doi.org/10.1016/S0016-7037(97)00009-4).
- [68] J. E. Tanner and F. W. Lamb, “Specific heats of aqueous solutions of NaCl, NaBr, and KCl: Comparisons with related thermal properties,” *Journal of Solution Chemistry*, vol. 7, no. 4, pp. 303–316, 1978, ISSN: 00959782. DOI: 10.1007/BF00644277.

- [69] P. R. Tremaine, K. Sway, and J. A. Barbero, “The apparent molar heat capacity of aqueous hydrochloric acid from 10 to 140°C,” *Journal of Solution Chemistry*, vol. 15, no. 1, pp. 1–22, 1986, ISSN: 00959782. DOI: 10.1007/BF00646308.
- [70] L. N. Trevani, E. C. Balodis, and P. R. Tremaine, “Apparent and Standard Partial Molar Volumes of NaCl, NaOH, and HCl in Water and Heavy Water at T = 523 K and 573 K at p = 14 MPa,” *The Journal of Physical Chemistry B*, vol. 111, no. 8, pp. 2015–2024, Mar. 2007, ISSN: 1520-6106. DOI: 10.1021/jp063824x.
- [71] F. Vaslow, “The apparent molal volumes of the lithium and sodium halides. Critical-type transitions in aqueous solution,” *Journal of Physical Chemistry*, vol. 73, no. 11, pp. 3745–3750, 1969, ISSN: 00223654. DOI: 10.1021/j100845a031.
- [72] W. Wagner *et al.*, “CHAPTER 5 - Density,” in *Measurement of the Thermodynamic Properties of Single Phases*, ser. Experimental Thermodynamics, A. R. H. Goodwin, K. N. Marsh, and W. A. Wakeham, Eds., vol. 6, Elsevier, 2003, pp. 125–235. DOI: [https://doi.org/10.1016/S1874-5644\(03\)80008-5](https://doi.org/10.1016/S1874-5644(03)80008-5).
- [73] G. Wiese, J. Wunsch, and B. Behrens, “Die Bestimmung der Konzentrationsabhängigkeit des scheinbaren Molvolumens mit Hilfe dilatometrischer Verdünnungstitrationen,” *Zeitschrift für Physikalische Chemie*, vol. 100, no. 3-6, pp. 113–118, Mar. 1976, ISSN: 2196-7156. DOI: 10.1524/zpch.1976.100.3-6.113.

# A. Appendix

(A)



(B)

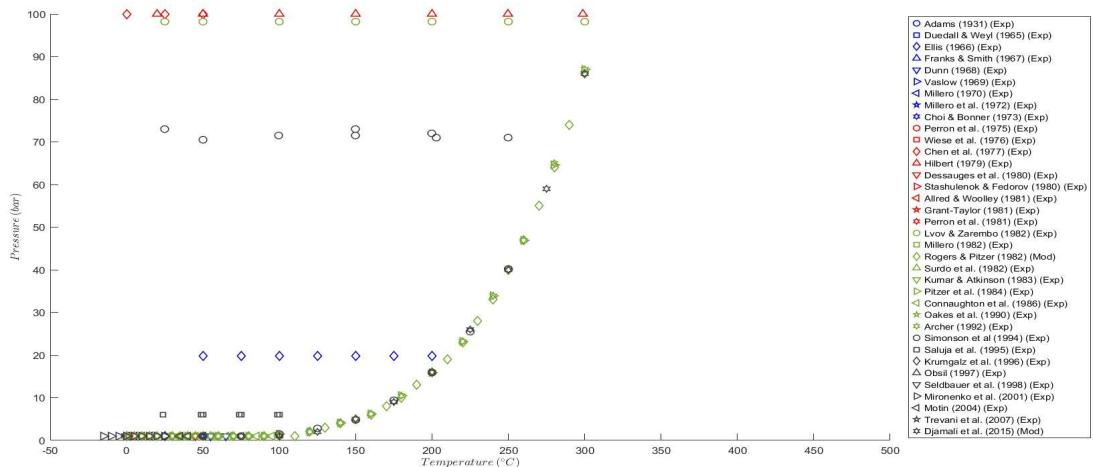


Figure A.1.: Plot showing  $P$ - $T$  conditions of all  $V_{m,NaCl}$  data (Experiments and Models) with limits on y-scale (Pressure) to emphasize data spread.(B) y-scale limit of 1000 bar, (C) y-scale limit of 100 bar

(A)

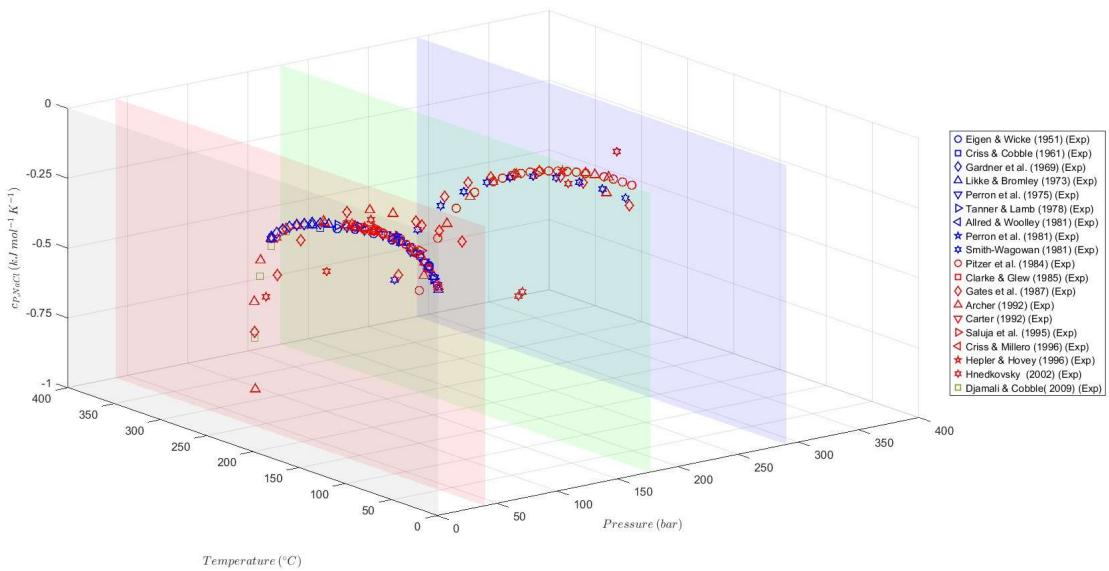
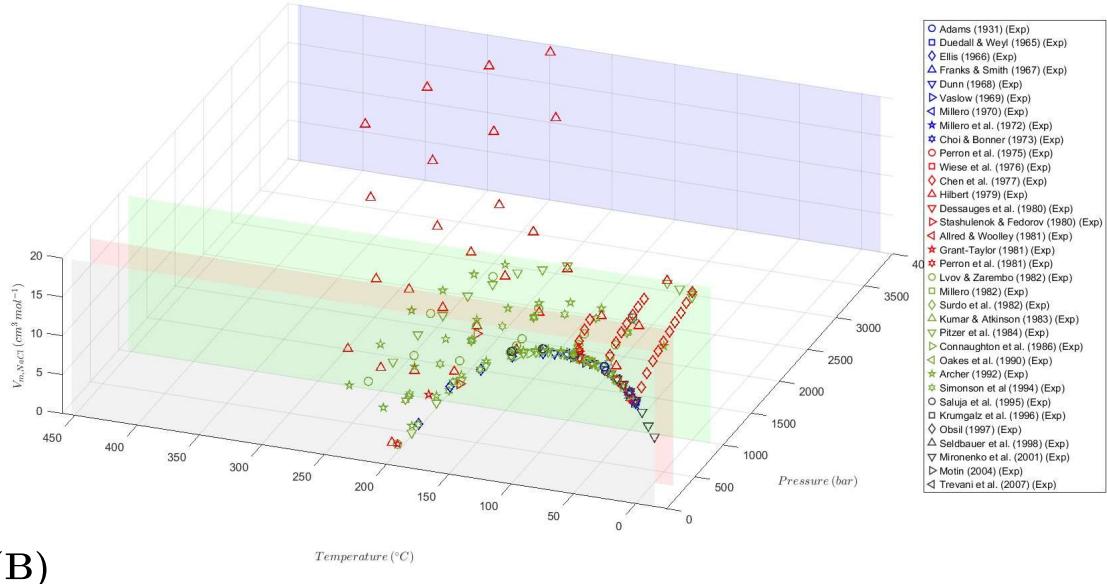


Figure B.3.: Subplot of  $c_{P,NaCl}$  pressure slices (Figure 5.2). (A) Zoomed view of 3D plot to show cluster between 0 and  $-10\ kJ mol^{-1} K^{-1}$ . (B) Pressure slice at 1 bar ( $\pm 0.5$ ).

$V_{m,NaCl}$

(A)



(B)

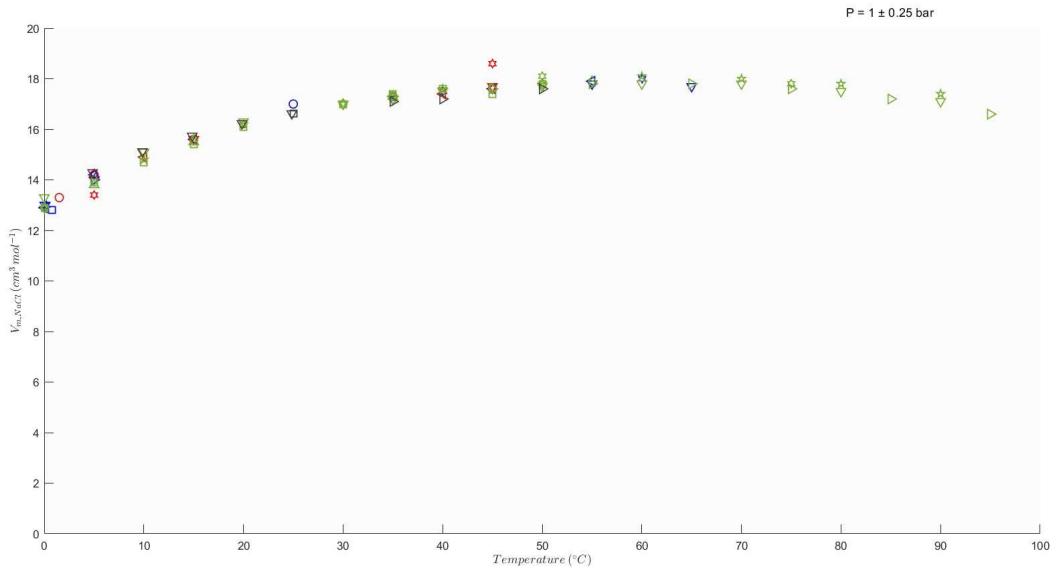


Figure B.8.: 3D plot and 2D subplot of  $V_{m,NaCl}$ . (A) 3D plot showing temperature slices plotted in Figures B.10(J)-??(M). (B) Pressure slice at 1 bar ( $\pm 0.25$ ).