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

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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 (NaCl) and hydrochloric acid (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 Dolej, D. and Manning (2010)[1], the energy that results in the dissolution of a solute in water can be broken down into three energy contributions [1], [2]: (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[1] through Equations (1)-(3),

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

expanding the terms gives,

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

which can be simplified to,

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

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 dissoluton and the volumetric contribution to dissolution, respectively; ΔH and ΔS are the enthalpy and entropy; ρ_{hs} and ρ_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),

$$0 = \Delta_{ds}G + RT \ln K \tag{4}$$

Which can be rewritten explicitly in terms of K as

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

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),

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

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

which measure the change in volume and heat capacity when an infinitessimal 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 ($d\mu_i$)[3]. This leads to further equations for $V_{m,i}$ and $c_{P,i}$ which relate them to their associated Gibbs energies,

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

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

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[2], such as the density of solution (ρ), the density change ($\Delta\rho - \Delta\rho°$) 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 [2], [4], [5]. 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[6], Bjerrum theory[7], Pitzer Equations[8]

and Davies Equations[9]. 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,

$$\log_{10} \gamma\pm \ = \ -Az_j^2 \frac{\sqrt{I}}{1 \ + \ Ba_\circ\sqrt{I}} \tag{10}$$

where:

γ = 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

$Ba_\circ$ = 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 $mol^{-1/2}\,dm^{1/2}$ and 0.3 $mol^{-1/2}\,dm^{1/2}$ respectively at 25 $°C$ and 1 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 emperical 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 ($^\circ C$) and pressure in bar, while all $V_{m,i}$ data has been converted to $cm^3\,mol^{-1}$ and $c_{P,i}$ to $J\,mol^{-1}\,K^{-1}$. The summary of the P-T conditions of the chosen data are shown in Figures 1-4