AN ABSTRACT OF THE THESIS OF

Hubert A. Gasteiger for the degree of Master of Science in Chemical Engineering presented on October 3, 1988

Title: Mechanism and Equilibrium Modeling of Aluminosilicate Scaling in Alkaline Media

Abstract Approved: Redacted for Privacy

Problems with aluminosilicate scales in pulp and paper recycle streams create an interest in the formation mechanism and the chemical equilibrium of aluminosilicates.

Evaluating solubility data from a system containing Na\(^+\), Cl\(^-\), and OH\(^-\) ions as well as aluminium and silicon compounds, allowed to elucidate the characteristics of the aluminosilicate scaling process, especially with regards to the influence of the aluminium and silicon distribution in solution. A chemical model was developed to describe the equilibrium of sodalite and hydroxysodalite over a range of conditions encountered in industrial liquors (OH\(^-\) molality and ionic strength from 1 to 4).

Pitzer's activity coefficient equations were successfully fitted to describe the apparent solubility product (i.e., [Al] \cdot [Si], in molalities) over the whole range of experimental data. Unfortunately, the regressed coefficients are linearly dependent, thus, physically insignificant. Pitzer coefficients will be assessable only if single electrolyte parameters for either the aluminium or the silicon species are made available.

The apparent solubility product is graphically represented as a function of ionic strength and pH. An estimation on technical liquors (like white, green or black liquor) which contain additional anions is outlined.
MECHANISM AND EQUILIBRIUM MODELING OF ALUMINOSILICATE SCALING IN ALKALINE MEDIA

by

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A THESIS

submitted to
Oregon State University

in partial fulfillment of the requirements for the degree of

Master of Science

Completed October 3, 1988
Commencement June 1989
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Date Thesis is Presented: October 3, 1988
Typed By: Meredith J. Cornelius
ACKNOWLEDGEMENT

Well, having concluded my hopefully strictly scientific contemplations and having gotten tired of the words "equilibrium" and "aluminosilicate," the traditional "cleaning up" of all the personal matters entangled with this work is due:

Foremost, I would like to begin with extending my utmost gratitude to Dr. Frederick, my major professor, for his unreserved support in occasional moments of slow progress. In spite of -- maybe even because of -- lacking regular scheduling, our meeting hours never failed in imparting refreshed stimulus to me and often I would leave his office endowed with new ideas. I shall never forget Dr. Frederick's unshattered confidence in all my endeavours, facilitating opportunities which certainly promoted my future development.

Meredith Cornelius, the "diabolical" genius on the word processor was frequently facing an abyss of despair in moments when I persuaded her into the necessity of triple superscripts or the importance of equations, whose lengths could be measured in feet. Hence, a little "thank you" for a big deed and I do hope she will not shun chemical engineers' theses in the future.

My special thanks are extended to the faculty and staff of the Chemical Engineering Department, who is responsible for the personal atmosphere among students and professors, which I have never encountered before. Especially, thanks to Dr. Mrazek and Dr. Levien, as well as Dr. Thomas of the Department of Statistics, who never hesitated to answer my maybe cumbersome questions and inquiries. Dr. Octave Levenspiel will always remain in my memory with his interrogations about the geographical outline of Germany on my first day in the department and with his famous "Whose music is that?" whenever I entered his room.

Approaching the end of my list I would like to mention my friends in Corvallis, who luckily succeeded in preventing me from too deep an immersion into my
Although, I am afraid, their job had not been too difficult, I feel like saying, "thanks."

Last, but not least at all: my great friend "Dr." Nina. Her uncomfortable but constructive criticism in many respects as well as her invaluable help in establishing all my graphs ought to be exclaimed. I guess she has deserved a big "Cmok."
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MECHANISM AND EQUILIBRIUM MODELING OF ALUMINOSILICATE SCALING IN ALKALINE MEDIA

I. INTRODUCTION

The chemical recovery cycle in paper mills employs highly concentrated aqueous electrolyte solutions, known as black, green and white liquors. The main (i.e., the chemically active species) are sodium and hydroxide ions, together with $\text{CO}_3^{2-}$ ions and sulfur compounds in various oxidation states. Non-process elements, viz. aluminium and silicon represent a serious problem to the chemical recycling process, especially in the context of increasing system closures. In contrast to other non-process chemicals (Ca, Mg, Fe, etc.) the above elements are not subject to natural purges (e.g., as grits or dregs) and thus, accumulate to elevated concentrations in the prevalently alkaline liquors. Aluminosilicate scaling ensues on stirrer blades and heated surfaces whose low thermoconductivity and glassy, mechanically resistant nature are vexatious features in the operation of the chemical recovery cycle. Entering through limestone, mill water and wood chips [1], aluminium and silicon cannot be avoided; however, knowledge about their equilibrium distribution will assist in preventing conditions favouring aluminosilicate scaling.

Hitherto, research was focused on the synthesis of aluminosilicates and little data on their solubility is available. Besides Streisel's data [1], which constitutes the body of the present study, only low pH data by Ulmgren [2] and data from the bauxite processing industry [3] are accessible.

Streisel's experimental set-up was pragmatically oriented towards studying the influence of all potential parameters on the aluminosilicate scaling: pH, ionic strength and Al/Si input ratios as well as temperature (the latter one is not considered here). Measurements were taken in a system containing Na⁺, OH⁻, and
Cl ions in interaction with aluminium and silicon compounds, reflecting an environment encountered in industrial liquors. Sodalite, or better, a sodalite structured compound was detected to be the solid phase; amorphous precipitates were found as well. Interesting observations, predominantly with respect to the initial Al/Si ratio were recorded, but no ubiquitous model, incorporating all the parameters could be devised. At this point, the present investigation’s objectives evolve naturally:

- Extraction of the chemically active aluminium and silicon compounds through a combined analysis of solubility data and literature with respect to the two species and aluminosilicates.
- Elucidating the precipitate’s character depending upon the system composition as well as their formation mechanism; also, addressing the basic question concerned with the existence of an aluminosilicate equilibrium.
- Assessing a chemical model presenting the aluminosilicate solubility over the entire range of experimental data.
- Developing a predictive model based on Pitzer’s activity coefficient equations in order to guarantee a quantitative modeling of equilibrium concentrations.
- Finally, composing a concise representation of the above quantifications and devising estimative methods on aluminosilicate solubilities in industrial liquors.
II. EQUILIBRIUM SYSTEM

To investigate the solubility of aluminium and silicon in an highly caustic environment, prevalent in pulp and paper processes, Streisel [1] designed the following system. Aluminium chloride and sodium metasilicate, respectively, were dissolved separately in equal volumes of an aqueous sodium hydroxide/sodium chloride solution (molar ionic strengths ranging from 1 to 4 moles/lit). The two clear mixtures were then combined, resulting in concentrations in the order of $10^{-3}$ with respect to aluminium and silicon. During equilibriation at 95°C over several weeks, concentrations of soluble aluminium and silicon were recorded. X-ray diffraction analysis identified the crystalline precipitate to be sodalite; amorphous material was detected as well.

No equilibrium measurements of Cl⁻, OH⁻ or Na⁺ ions were undertaken. The reverse approach of equilibrium (i.e., the redissolution of precipitate) was not tested. However, the establishment of a steady state was assured by monitoring aluminium and silicon concentrations versus time. These measurements always refer to total concentrations, i.e., no consideration is paid to the actual compounds in solution.

All of Streisel's data used in this work is listed in Appendix A. The experiment numbers are those originally assigned in Streisel's thesis. Molarity measurements were recalculated to a molality scale; the necessary densities are listed following the data table. Values for [Al], [Si] and [Al]-[Si] represent means of three successive measurements, usually taken after runs had equilibriated for at least 20 days. Standard deviations from the mean are mostly around 4 to 6%, with a few exceptions.

For further information on the experimental procedures, please refer to the Ph.D. thesis of Robert Streisel.
III. CHEMISTRY OF INVOLVED SPECIES

III.1. Aluminium Species

Since aluminium is well known for its amphoteric behaviour, its modification in solution strongly depends on the hydroxide ion concentration. At low pH, hydrated Al ions exist, which gradually hydroxylate as a neutral environment is approached, where aluminium hydroxide precipitates. A further pH increase favours its redissolution and above a pH of eight to nine, the predominant species in solution is the aluminate ion, $\text{Al(OH)}_4^-$ (see Fig. 1, [4]), given that no excessive concentrations of aluminium occur. Under the latter circumstances condensation reactions do occur, forming polyaluminate ions, whose structure is analogous to the poly compounds of silicates (see "silicon species").

Geometrically, the aluminate ion is depicted by a regular tetrahedron, with the aluminium atom located in the center and the hydroxide ions forming the corner points (see Fig. 2a).

III.2. Silicon Species

In aqueous solution, silicon exhibits a fourfold coordination to oxygen, forming species generally referred to as silicates. The basic molecular structure is visualized by a tetrahedral geometry, analogous to the previously mentioned aluminate structure (Fig. 2b).

Orthosilicate is understood to be a four protonic, weak acid and according to the causticity of the solution, one or more protons can be released:

$$
\begin{align*}
\text{H}_4\text{SiO}_4 & \rightleftharpoons \text{H}_3\text{SiO}_4^- & \text{H}_2\text{SiO}_3^- & \text{HSiO}_4^- & \text{SiO}_4^{4-} \\
+\text{H}^+ & +\text{H}^+ & +\text{H}^+ & +\text{H}^+ & +\text{H}^+ 
\end{align*}
$$

(1)
Figure 1. Aluminium Species Distribution as a Function of pH
Figure 2. Geometric and Symbolic Representation of: a) Aluminate, and; b) Silicate Anions

Figure 3. Formation of: a) "Infinite Chain" Structures (SiO$_2^-$ units), and; b) Layer Structures (Si$_2$O$_5^-$ units)
Orthosilic acid, however, is subject to polymerization, yielding a variety of different substances. The below mechanism applies to the polymerization reaction of the neutral molecule:

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H} \\
\end{align*}
\]

This can proceed to:

1. Single, "Infinite" Chains: Each silicon tetrahedron shares exactly two oxygen atoms, forming chains with the unit formula \( \text{SiO}_2^- \), which is commonly referred to as metasilicate. Figure 3a depicts the principal structural elements. The "free" (i.e., the unbound) oxygens either retain their acidic character or release a proton to form salt-like ionic bonds with cations from the solution.

2. Sheet or Layer Structures: Sharing three out of four corner oxygens results in two dimensional sheets, with the ideal unit structure \( \text{Si}_2\text{O}_5^- \). Hundreds of those sheets stacked on top of each other, with charge-balancing ions in between the layers form the principal structure for the wide variety of clay minerals (Fig. 3b).

3. Framework Structures: Finally, in the case of all four oxygen atoms participating in the mutual bonding, the three dimensional structure of quartz minerals, \( \text{SiO}_2 \), is established. Since all potential bonds are saturated no
additional ions will be embedded in the crystal.

In more alkaline media, the charges carried by the silicate species retard the mutual reactions [5] and even depolymerization is favoured. This is visualized in the following, hypothetical reaction between two perfectly deprotonized silic acid ions:

\[
\text{H}_2\text{O} + \text{Si}^4- \rightarrow \text{Si}^3- + \text{OH}^-
\]

Thus, with respect to Streisel's experimental design, the assumption of the presence of orthosilic acid only, is chemically justified by extremely high hydroxide concentrations as well as relatively low silicon concentrations in solution.

III.3. Aluminosilicates

Substituting silicon units by tetrahedrally coordinated aluminate ions, yields substances referred to as aluminosilicates. Since each aluminium tetrahedron carries a negative charge, electroneutrality demands the incorporation of cations into the structure, which characterizes the most abundant class of minerals on earth. The ratio of silicon to aluminium in the crystal ranges from infinity (quartz) to one (the upper limit) established by Loewenstein's Rule [6] (to date, only few exceptions were found). Modifying the three dimensional, quartz-like framework structure in the above manner results in tectoaluminosilicates, viz. feldspars, feldspathoids and
zeolites. The latter two especially exhibit outstanding adsorptive and ion exchange properties, caused by an enormous channel network throughout the crystal structure, mostly in all three dimensions. As a matter of fact, the name zeolite is composed of the greek words "zeo" (water) and "lithos" (stone) and indicates the observed "boiling" of the mineral stilbite, i.e., its loss of water under heating is very much like a boiling fluid. Together with an unique molecular sieving effect, tectoaluminosilicates are invaluable components in numerous chemical processes, be it catalysts in the petrochemical industry or molecular filters in purification treatments.

In the present study, sodalite, a feldspathoid, was detected as the crystal phase in the precipitate. Its structure was first investigated Linus Pauling [7]. An octahedral framework of Al and Si tetrahedra forming a "cage" around the centrally located anion (Cl\(^-\)) and the cations (Na\(^+\)), placed in the corner points (see Fig. 4). Its chemical formulation is Na\(_8\)(AlSiO\(_4\))\(_6\)Cl\(_2\).

Embedding a hydroxide ion instead of a chloride ion yields hydroxysodalite without noticeably changing crystallographic properties [8]. A comparison of the x-ray diffraction spectra for synthetic sodalite and synthetic hydroxysodalite do not show any difference [9].
Figure 4. Sodalite Model by Linus Pauling — Tetrahedra centers are alternately occupied by Al and Si atoms; the corner points locate O atoms; the big spheres represent Cl− ions.

Figure 5. Comparison of the Crystal Structures of: a) Sodalite, and; b) Zeolite A
IV. ALUMINOSILICATE SYNTHESES AND FORMATION MECHANISM

In 1862, the precipitation of levynite marked the first aluminosilicate synthesis. Perpetuated by industrial demand, synthesis and classification have since been focused on by chemists and crystallographers in order to supply, as well as to modify artificial aluminosilicates. Research in respect to reaction mechanisms was neglected for a long time and questions concerning equilibria did not arise until recently.

In non-hydrothermal syntheses, the desired zeolites are usually precipitated from solutions with less than 80 mole-% water. Initially, aluminates and silicates will form an amorphous gel, which in the course of reaction disappears in favour of crystalline reaction products.

As an example, Barrer [10] produced zeolite Q in reaction mixtures of a pH above 10 and temperatures between 85° and 110°C, if the initial molar ratio of Al/Si was kept within 4/1 and 1/1. Zeolite Q was assigned the chemical formula Na₂O·Al₂O₃·2SiO₂·4H₂O. Crystallographically, its structure is composed of the same octahedral framework units as sodalite, with just a slight difference in their mutual assemblage (compare Figs. 5a and 5b). Proceeding to lower Al/Si ratios, crystals richer in silicon related to philippsite (Na₂O·Al₂O₃·3.3SiO₂·aq to Na₂O·Al₂O₃·5.3SiO₂·aq) precipitated. Breck [11] then reports the successive recrystallization of zeolite A (identical with zeolite Q) to hydroxsodalite in the presence of anions such as chloride and sulfate and at high NaOH/Al₂O₃ ratios.

The occurrence of sodalite in Streisel's system is in agreement with the above observations (pH > 12, NaOH/Al₂O₃ = 50). Since, however, sodalite was detected together with amorphous material, the question arises, whether the true sodalite equilibrium was measured or, whether a non-equilibrium state prevailed. In order to
answer this, the formation mechanism of aluminosilicates must be considered more closely.

In 1969 Zhdanov [12] investigated the influence of gel and liquid phase composition on crystal growth. He concluded that the crystal phase does not derive from a restructurization of an initially occurring, amorphous gel, but that an equilibrium between liquid phase and the aluminosilicate must exist (Fig. 6). The gel itself is to be viewed as an extremely entangled cluster of arbitrarily bridged silicon and aluminium units (Fig. 7). Furthermore, lowering the pH resulted in silicon-richer precipitates. This is due to the increased activity of silicates with increasing degree of hydroxylation, i.e., with decreasing hydroxide concentration (see Reaction Scheme II in contrast to Scheme III).

The initial precipitation of an amorphous phase, i.e. an aluminosilicate gel, was observed for even dilute systems, reflecting Ostwaldt’s Law, which states the temporary formation of metastable phases, if they exhibit a structure of higher simplicity. A gel of almost constant composition precipitates instantaneously from caustic solutions (pH above 13) at temperatures ranging from 25° to 90°C and for initial charges of aluminium chloride and sodium metasilicate in ratios of Al/Si between 4/1 and 1/4 [13]. The total amounts of aluminium and silicon were designed to yield solutions of 0.1 moles/lit in respect to both substances; these quantities compare within a factor of 2.5 with Streisel's design. Thus, the establishment of an amorphous gel, at least initially, seems a realistic assumption and all three steps in Fig. 6 (a to c) should be expected to apply to the system under investigation. The fact that amorphous material was found in the X-ray diffraction analysis hints that we might interrupt the process at a condition depicted in Fig. 6b. True equilibrium will only be measured then, if the redissolution of the gel proceeds at a slower rate than the formation of sodalite from the liquid phase.
Figure 6. General Formation Mechanism of Aluminosilicate Precipitates -- a) Initial Gel Formation; b) Gel Redissolution and Precipitation of the Crystalline Phase, and; c) Final Presence of Aluminosilicate Crystals

Figure 7. Schematic Composition of the Aluminosilicate Gel
reactants. At 95°C and at a hydroxide concentration of 0.5, Zhdanov finds an apparent gel solubility product (defined as: [Al]-[Si]) in the order of 5·10⁻⁴. This is roughly two magnitudes higher than products recorded by Streisel at even higher hydroxide concentrations.

In equilibria studies on aluminosilicate scaling in a similar system (at 120° to 150°C and an ionic strength range of 3 to 7 moles/lit) Ulmgren [2] observed the precipitation of cancrinite, whose chemical formula (Na₅(AlSiO₄)₃CO₃) is almost identical with sodalite. The hydroxide concentration extended from 1 to 0.03 moles/lit and, an additional contrast, the background matrix was composed of sodium acetate instead of sodium chloride. Equilibrium was approached from two sides, i.e., by crystallization or redissolution of cancrinite and, thus, a state of equilibrium was confirmed.

Breuer and coworkers [3] did sodalite equilibrium studies also on a similar system (CO₃²⁻ being the anion instead of Cl⁻); again, equilibrium was approached from two sides. The research was focused on the bauxite digestion in the Bayer process, where high concentrations in respect to aluminium do occur. Hence, their data is located above Al/Si equilibrium ratios of 50. A comparison of Streisel’s results with respective data from Breuer’s work at his lowest Al/Si ratio is summarized in Table 1.

Table 1. Data Comparison Among Streisel’s and Breuer’s Investigations

<table>
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<tr>
<th>Author</th>
<th>Temp</th>
<th>[OH] = 0.99 ± 7%</th>
<th>[Na⁺] = 1.1 ± 10%</th>
<th>[OH] = 3.8 ± 2%</th>
<th>[Na⁺] = 4.4 ± 7%</th>
</tr>
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<tr>
<td>Breuer</td>
<td>75°C</td>
<td>70.0; [Al]/[Si] = 142</td>
<td></td>
<td>702.; [Al]/[Si] = 217</td>
<td></td>
</tr>
<tr>
<td>Steisel</td>
<td>95°C</td>
<td>123.; [Al]/[Si] = 1.1</td>
<td></td>
<td>887.; [Al]/[Si] = 103</td>
<td></td>
</tr>
<tr>
<td>Breuer</td>
<td>150°C</td>
<td>160.; [Al]/[Si] = 50</td>
<td></td>
<td>1130.; [Al]/[Si] = 1.4</td>
<td></td>
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Streisel's products of [Al]-[Si] at 95°C are bracketed between Breuer's values at 150° and 70°C, as it should be expected and model predictions, based on Streisel's data should be accurate up to Al/Si ratios in the order of 50. Proceeding to higher Al/Si ratios, however, displays a contrary behaviour, viz. the increase of the silicon concentration with increasing amounts of aluminium in solution. This must be related to the formation of polyaluminate species, as they were proposed by Raizman [14], who investigated the character of aluminium in the bauxite leaching process.

The fact that equilibrium was reached under these so similar conditions, together with Zhdanov's measurements on gel solubilities, strongly supports the theory of a slow gel redissolution. Hence, aluminium and silicon concentrations in Streisel's experiments are expected to be subject to a crystalline aluminosilicate equilibrium.
V. SOLUBILITY DATA EVALUATION

Analogous to previous synthesis efforts, Streisel gathered data for a wide range of different input ratios of Al/Si for a more dilute system (93 to 95 mole-% water). If governed by the sodalite equilibrium (a 1/1 precipitate with respect to Al and Si; Scheme IV), the plot of [Al][Si] in a linear or logarithmic scale is apt to yield a zero-slope straight line at constant ionic strength and pH, independent of the [Al]/[Si] ratio measured at equilibrium (see Eq. 1).

\[
\ldots + \{\text{Al}\} + \{\text{Si}\} + \ldots \Leftrightarrow \text{sodalite} \quad (\text{IV})
\]

\[
K_{\text{app}} = [\text{Al}][\text{Si}] = \text{constant, for all } [\text{Al}], [\text{Si}] \quad (1)
\]

{Al} and {Si} refer to any kind of active species in solution.

In viewing Fig. 8, as originally published, an obvious discrepancy is realized. Above an equilibrium ratio (Al/Si) of roughly 1/13 (corresponding to initial ratios above 1/1.4), the expectation of a straight line of zero slope is fairly well-satisfied. A discontinuity, however, is observed at the above ratio; its reproducability was tested positive.

To elucidate the underlying physical relationship, the findings of former synthesis efforts must be reconsidered. As reported, crystals rich in silicon evolve from solutions which are relatively high in silicon as compared to aluminium. Following Loewenstein's Rule, the maximum Al/Si ratio in crystalline aluminosilicates is limited to 1/1, identical to the composition found in sodalite. Hence, a more flexible formulation of a potential equilibrium equation would be:

\[
K_{\text{app}} = [\text{Al}]^a[\text{Si}]^s \quad (2)
\]

according to: \ldots + a\{\text{Al}\} + b\{\text{Si}\} \Leftrightarrow \{\ldots\text{Al}_a\text{Si}_b\}_{\text{crystal}}

subject to: \ a \leq s \ (\text{Loewenstein's Rule})
Figure 8. Impact of the Al/Si Equilibrium Ratio on the Apparent Solubility Product ([Al] · [Si]) at Constant Ionic Strength and pH

Log ([Al]/[Si]) (mole/kg H₂O)

Log([Al]/[Si])
arithmetically equivalent to:

\[ \log([Al]/[Si]) = s+a \cdot \log ([Al]/[Si]) + \text{constant} \]  \hspace{1cm} (3)

Thus, in reexamining Fig. 8 three distinct regions are recognized:

1. To the right of the "breakpoint", the equilibrium must be determined by a 1/1 precipitate. Even up to excessively large ratios of Al/Si in solution, the solid never seems to incorporate more aluminium than silicon, as predicted by Loewenstein's Rule.

2. A definitely positive slope in the region to the left, indicates silicon richer precipitates to be determining the equilibrium \(((s-a)/(s+a) = 0.2, \text{i.e.}, s > a)\).

3. The breakpoint marks the transition from the existence of the stable sodalite phase into precipitation of metastable, silica richer solids, analogous to the philippsite-like phases observed by Barrer.

Following the reaction path by means of a mass balance, the major amount of precipitates is formed in the sodalite region (according to initial input ratios, Al/Si, being above 1/3 in all cases, with one exception). Since x-ray diffraction analysis requires at least 10% of a crystal phase to be present in the sample powder to assess a significant signal, it is no surprise that no other phase than sodalite was detected.

At this point the necessity of carefully selecting the data which will be utilized in modeling the sodalite equilibrium does not need any further explanation. Measurements, taken at the breakpoint as well as data to its left must be excluded. Since there is not enough data to clarify the nature of the silica-rich precipitate(s), it is not possible to include them into the fit for the activity model. Nevertheless, the
region covered by the sodalite equilibrium fully represents the environment encountered in recycle processes in paper mills. As reported by Ulmgren [15], the Al/Si ratio in pulp and paper chemical cycles is in the order of 1/3 at already low concentrations. Any potential precipitation will not markedly change this ratio and the seemingly critical breakpoint composition is not likely to be approached.
VI. MODEL ASSESSMENT

In developing an equilibrium model, the first problem to be tackled is to
determine the chemical species in the system. As previously outlined, aluminium is
most likely to occur as aluminate ion, Al(OH)$^-$$_4$. Silicon, especially considering the
highly caustic environment is expected to prevail in the form of its monomeric acid
(see Reaction Scheme I). Under this assumption, five silicon species are eligible to
occur and a further specification will have to be made by additional data evaluation.

VI.1. Mass Balances

Since no equilibrium measurements on Cl', OH', and Na' were taken, an
estimate of those concentrations must be developed.

Aluminium is added in the form of aluminium chloride, whose reaction in the
caucistic environment follows:

$$\text{AlCl}_3 + 4\text{OH}^- \rightarrow \text{Al(OH)}^-$$_4 + 3\text{Cl}^-$$  \hspace{1cm} (V)

Given a 100% yield in sodalite which would show in a 1/1 disappearance ratio
of aluminium to sodalite, the reaction scheme will allow a mass balance on the
undetermined ionic species.

$$2\text{OH}^- + \text{AlCl}_3 + \text{Na}_2\text{SiO}_3 \rightarrow \frac{1}{6}\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2 + \frac{2}{3}\text{Na}^+ + \frac{8}{3}\text{Cl}^- + \text{H}_2\text{O}$$  \hspace{1cm} (VI)

The data compilation in Appendix A, however, shows that 1/1 disappearance
ratios do not occur exactly, confirmed by the finding of amorphous precipitates. This
signals two important features. First, exact mass balances can not be carried out
and, second, hydroxide balances on experiments with high absolute aluminium input
(#33 and #34) as well as on low pH systems (#22) are a vain effort, especially if
the above ratio deviates largely from one. Uncertainties, most pronounced in
data-set #22, of more than 100% do occur and no predictions without a final
analysis can be made. For example, Ulmgren's investigation [2] at low hydroxide
concentrations was accompanied by final analyses of the respective anions.

Hence, approximate balances derived from Reaction Schemes V and VI are:

\[
\begin{align*}
\text{OH}^-_{\text{eq}} &= \text{OH}^-_{\text{o}} - 4 \cdot [\text{Al}] - 2 \cdot \Delta \text{Al} \\
\text{Na}^+_{\text{eq}} &= \text{Na}^+_{\text{o}} - 4/3 \cdot \Delta \text{Al} \\
\end{align*}
\]

with: \(\Delta \text{Al} = \text{Al}_o - [\text{Al}]\)

where eq denotes final concentrations and o denotes initial concentrations.

Since a chloride balance is extremely problematic (mainly with respect to a
potential hydroxysodalite formation), it was omitted. The resulting error, however, is
small for two reasons: 1) chloride does only enter the equilibrium equations in an
additive term with hydroxide (this will be outlined in the following), and; 2) the
activity coefficient estimation depends insignificantly on small absolute changes in
the chloride ion. Relative changes, occurring on account of the above mass balances
are up to 12% for the hydroxide concentration (except #22) and in the order of 4%
for sodium.

VI.2. Hydroxide Ion Influence

Figure 9 elucidates which form of silic acid is predominant under reaction
conditions. A slope of 3.5 in a logarithmic plot of [Al]-[Si] vs. \(\text{OH}^- (1.0 < \text{OH}^- < 4.0,\)
adjusted by the previous mass balances) indicates either one of the Reaction
Schemes below:
Figure 9. Apparent Solubility Product Versus OH⁻ Concentration at Constant Ionic Strength

slope = 3.5 ± 0.5  \( 1 \leq [OH^-] \leq 4 \)
\[
\begin{align*}
4/3\text{Na}^+ + 1/3\text{Cl}^- + \text{Al(OH)}_4^- + \text{HSiO}_3^- & \Leftrightarrow \\
1/6\{\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2\} + 3\text{OH}^- + \text{H}_2\text{O} & \quad \text{(VIIa)}
\end{align*}
\]

\[
\begin{align*}
4/3\text{Na}^+ + 1/3\text{Cl}^- + \text{Al(OH)}_4^- + \text{SiO}_4^- & \Leftrightarrow \\
1/6\{\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2\} + 4\text{OH}^- & \quad \text{(VIIb)}
\end{align*}
\]

mathematically expressed as (at constant Na\(^+\) concentration):

\[
\begin{align*}
[\text{Al}] \cdot [\text{Si}] & \propto \frac{1}{[\text{OH}]^3} \quad \text{(6a)}
\end{align*}
\]

\[
\begin{align*}
[\text{Al}] \cdot [\text{Si}] & \propto \frac{1}{[\text{OH}]^4} \quad \text{(6b)}
\end{align*}
\]

The gradual decrease of the slope with decreasing pH, marks a shift to \(\text{H}_2\text{SiO}_3^-\) (slope of -2 in Fig. 9) or even \(\text{H}_2\text{SiO}_4^-\) (slope of -1), reflecting the usual behaviour of weak acids.

Published dissociation constants at 25°C together with free enthalpy data and Cp values [16] allow to evaluate dissociation constants at 95°C, if a \(\Delta \text{Cp}_{\text{reaction}}\) at 25°C is believed to be constant (see Appendix B). An approximate orthosilicic acid distribution at 95°C, under the assumption of similar activity coefficients for the silicon species is then calculated:

Equilibrium equation of a multiprotonic acid:

\[
\begin{align*}
\frac{[\text{H}_{(n+1)}\text{SiO}_4^-][\text{H}_2\text{O}]}{K_n} = [\text{H}_{(n+1)}\text{SiO}_4^{(1-n)}][\text{OH}] & \quad n = 1, \ldots, 4
\end{align*}
\]

(7)

Arithmetical manipulation yields the following terms for the percentage distribution:

\[
\begin{align*}
\%[\text{H}_4\text{SiO}_4] = [1 + \frac{K_1}{R} + \frac{K_1K_2}{R^2} + \frac{K_1K_2K_3}{R^3} + \frac{K_1K_2K_3K_4}{R^4}]^{-1} \cdot 100%, \quad \text{(8a)}
\end{align*}
\]
where:

\[
\begin{align*}
[H_2O] \\
R = [OH] \\
\end{align*}
\]

\[
%[H_{(s-n)}SiO^{n-}] = \frac{\prod_{i=1}^{n} K_i}{R^n} \cdot [%H_4SiO_4] 
\quad (8b)
\]

These equations result in Fig. 10.

According to Fig. 10, all the data, except one measurement at the lowest hydroxide concentration (this point will be excluded, for reasons mentioned before) fall into a region where more than 90% of the silic acid prevail as HSiO$_3^-$ . This, together with the previous assessment of a slope of 3.5 in Fig. 9, subject to an error of ±0.5, does lead to the conclusion of HSiO$_3^-$ prevailing as the major silicon species in Streisel’s system.

The mass balance on the hydroxide ion (Eq. 4) must then be adjusted by considering the reaction of metasilicate with the caustic solution:

\[
Na_2SiO_3 + OH^- \rightarrow 2Na^+ + HSiO_3^- \quad (VIII)
\]

The final hydroxide balance yields:

\[
OH^-_{\text{eq}} = OH^-_{o} - 4[Al] - [Si] - 2 \cdot \Delta Al 
\quad (9)
\]

VI.3. Ionic Strength Dependency

In reference to reaction scheme VIIa, a plot of [Al]-[Si] versus 1/[Na]$^{4+}$-[Cl]$^{13}$ should result in a straight line if activity coefficients do not change too drastically (see Fig. 11a). Data at an ionic strength of one (filled symbols) clearly mismatch the
Figure 10. Assessment of the Mono Silic Acid Species Distribution as a Function of OH Activity
Figure 11. Apparent Solubility Product Versus Major Species' Concentration Terms:
a) for Pure Sodalite Formation, and; b) for Sodalite and Hydroxsodalite Precipitation
model predictions, where extremely low chloride concentrations provoke a tremendous step in the positive x-direction. Recalling the ideas presented in the chapter about formation mechanisms, the difference between sodalite and hydroxysodalite is irrelevant in a crystallographic view and is also expected to be negligible as far as solubility is concerned. Therefore, any available mono-valent anion (or, more precisely, anions of similar radius) must be eligible to participate in the equilibrium reaction:

$$4/3 Na^+ + 1/3 X^- + Al(OH)_4^- + HSiO_3^- \leftrightarrow $$

$$1/6 Na_8(AlSiO_4)_6X_2) + 3OH^- + H_2O$$

(IX)

with: $X^- = Cl^-, OH$.

or:

$$[Al][Si] \propto 1/([Na^+])^{4/3} [X^-]^{1/3}$$

(10)

Readjusting the equilibrium equation according to Scheme IX, indeed, results in a disappearance of the anomaly at an ionic strength of one (Fig. 11b).

A similar procedure was adopted by Ulmgren [2]. Additional justification is given by his results which show no significant difference in cancrinite solubility, with different anions in the solution matrix. A similar insensitivity of the precipitate towards the anion in solution was observed by Schwarz [13].

VI.4. Final Model Selection

In summarizing the information gained up until now, the final form of the sodalite, or better sodalite/hydroxysodalite, equilibrium can be proposed, considering that:
1. Reliable measurements only cover a hydroxide range of 1.0 to 4.0 moles/lit;  
high uncertainties in the mass balance do not advise the use of dataset #22.

2. Hydroxysodalite and sodalite are thought to be chemically and  
   crystallographically "identical".

Hence:

\[
\begin{align*}
E_{K_{sl}} &= \frac{[Na^{+}]^{4} [X^{-}]^{2} [Al(OH)_{4}^{3-}] [HSiO_{4}^{3-}]}{[OH^{-}]^{3} [H_{2}O]} \quad ; \quad X^{-} = Cl^{-}, OH^{-} \quad (11a)

K_i &= \frac{[SiO_{4}^{4-}] [H_{2}O]}{[HSiO_{4}^{4-}] [OH^{-}]} \quad (11b)
\end{align*}
\]

In a first modelling attempt, the existance of silicon species other than HSiO\(^{3-}\), will  
be neglected, as evidenced by the orthosilic dissociation constants. Thus, the  
determining equilibrium relationship will be Eq. 11a only.

The number of available data points to fit the equilibrium equations is, after the  
outlined selection procedures, reduced to 13. They are indicated by an asterisk in  
Appendix A.
VII. NUMERICAL TREATMENT OF MODEL BEHAVIOR

VII.1. Activity Coefficient Equations

In modeling the sodalite equilibrium at the high levels of ionic strength prevailing in the system, the concentration dependency of activity coefficients is of prime importance. Various empirically and/or theoretically based activity coefficient models are available; an excellent review of the ones most commonly applied is given in the "Handbook of Aqueous Electrolyte Thermodynamics" [17].

The Pitzer model, a virial expansion of the excess free energy, with a Debye-Hueckel term, was selected for its good agreement with many mixed electrolyte data-sets [17] and its ease to calculate single-ion activity coefficients (valid, if they are applied to solubility equations [18]). The principal idea is to utilize single-electrolyte ion-interaction parameters $\beta^0_{mX}$, $\beta^1_{mX}$, and $C_{mX}$ ($M$=cation, $X$=anion) to estimate the behaviour of mixed electrolyte solutions. To account for higher ionic strengths, interaction parameters for equally charged ions, $\theta_{XX}$, and mixed ion interaction parameters, $\psi_{XXX}$, are added. This full set of parameters, together with the Debye-Hueckel parameter, $A^\theta$, yield an arithmetic expression, which satisfactorily describes numerous multi-ion electrolytes. In the case of highly unsymmetrical electrolyte solutions, i.e., 1-3, 1-4 etc. cation/cation or anion/anion combinations, unsymmetrical mixing terms become important.

The single ion activity coefficient expressions (as adapted from Harvie and Weare [19]) are:

$$
\ln \gamma_a = z^2_m F + \sum_a m_a (2B_{ma} + ZC_{ma}) \\
+ \sum_c m_c (2\Phi_{mc} + \sum_a m_a \psi_{mca}) \\
+ \sum_{a<a'} m_a m_{a'} \psi_{aa'M}
$$
\[ \ln \gamma_x = z^2 x F + \sum_c m_c (2B_{cx} + ZC_{cx}) \]
\[ + \sum_a m_a (2\phi_{xa} + \sum_c m_c \psi_{xac}) \]
\[ + \sum_{c < c'} m_c m_{c'} \psi_{ocx} \]
\[ + |z_x| \sum_c \sum_a m_c m_a C_{ca} \]

the osmotic coefficient for the solvent is:

\[ (\phi - 1) = \frac{2}{(\sum m_i)} \left\{ -\frac{A^4_{s}^{32}}{1 + b l^{1/2}} \right\} \]
\[ + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \]
\[ + \sum_{c < c'} \sum m_c m_{c'} (\phi_{oc} + \sum_a m_a \psi_{ocx}) \]
\[ + \sum_{a < a'} \sum m_a m_{a'} (\phi_{a'} + \sum_{c} m_c \psi_{a'c}) \right\} \]

with:

\[ F = -A^4 \left[ \frac{l}{1 + b l} + \frac{2}{b \ln(1 + b l)} \right] \]
\[ + \sum_c \sum_a m_c m_a B_{ca}^\phi + \sum_{c < c'} \sum m_c m_{c'} \phi_{oc} \]
\[ + \sum_{a < a'} \sum m_a m_{a'} \phi_{a'} ; b = 1.2 \]
\[ B_{mx}^{\beta} = \beta_{mx}^{(0)} + \beta_{mx}^{(1)} \alpha^{1/2} \]

\[ B_{mx} = \beta_{mx}^{(0)} + \beta_{mx}^{(1)} g(\alpha^{1/2}) \]

\[ B'_{mx} = \beta_{mx}^{(1)} g'(\alpha^{1/2})/l \quad ; \quad \alpha = 2.0 \]

The ionic strength terms, \( g(\alpha \cdot l^{1/2}) \) are:

\[ g(x) = 2[1 - (1 + xe^x)/x^2] \]

\[ g'(x) = -2[1 - (1 + x + 1/2x^2)e^x]/x^2 \]

\[ \phi_i^\beta = \theta_i + \epsilon \theta_i(l) + l \phi_i'(l) \]

\[ \phi_i = \theta_i + \epsilon \theta_i(l) \]

\[ \phi_i' = \epsilon \theta_i'(l) \]

where:

\( z \) = ionic charge

\( l \) = ionic strength = \( 1/2 \cdot \sum m_i \cdot z_i^2 \)

\( m_i \) = molalities in moles/kg H₂O

\( a \) = all anions

\( c \) = all cations

\( Z = \sum m_a \cdot |z_a| = \sum m_c \cdot z_c \)

An excellent outline of the Pitzer equations is given in [19,21].
VII.2. Parameter Selection

The limited amount of available solubility measurements, advise an economical handling of variables, in order not to overparameterize the model. As mentioned before, one silic acid species is expected to sufficiently describe the data. The potential species, then, are \( \text{Na}^+, \text{Cl}^-, \text{OH}^-, \text{Al(OH)}_4^-, \) and \( \text{HSiO}_3^- \).

Four sets of single electrolyte coefficients will be necessary, viz. for \( \text{NaCl} \), \( \text{NaOH} \), \( \text{Na[Al(OH)}_4 \) and \( \text{Na}_3\text{HSiO}_4 \).

Fortunately, \( \text{NaCl} \) parameters are available for 95°C [20]. 25°C values, together with temperature gradients at 25°C are tabulated for both \( \text{NaCl} \) and \( \text{NaOH} \) [17]. Accuracy of the linear extrapolation was tested by a comparison of \( \text{NaCl} \) measurements at 95°C with the linear estimate. Results are summarized in Table 2. The Debye-Hückel parameter for the temperature of interest was taken from the same source.

<table>
<thead>
<tr>
<th>Table 2. Contrast of the Differences among Measured and Linearly Extrapolated Values for Single Electrolyte Pitzer Coefficients at 95°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
</tr>
<tr>
<td>measured</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>( \beta^0 )</td>
</tr>
<tr>
<td>( \beta^1 )</td>
</tr>
<tr>
<td>( C^0 )</td>
</tr>
</tbody>
</table>

As outlined by Harvie and Weare, the single-electrolyte third virial coefficients, \( C_{ux} \), as well as the mixed electrolyte coefficients, \( \theta_{xx}' \) and \( \gamma_{mx}' \) are not very significant up to an approximate ionic strength of four, which marks the upper limit
in the present study. The only exception is introduced by the $E_{\theta}$ terms, deriving from the interaction between $HSiO_3^-$ and $OH^-$ or $Cl^-$, respectively, revealed by an order of magnitude analysis:

$$E_{\theta_{1,3}} = O(10^0) \quad \text{(see Fig. 12)}$$

$$\theta_{1,3} = O(10^{-1}) \quad \text{(for example, see [21])}$$

where $O$ is order of magnitude.

Thus,

$$O(1_{1,3}) = E_{\theta_{1,3}} + \theta_{1,3} = E_{\theta_{1,3}} = O(10^0)$$

Terms involving $1_{1,3}$ are:

$$T(1_{1,3}) = O(m_{OH} \cdot 1_{1,3}) = O(10^0)$$

Summarizing the above, five variables are retained to be determined by a least square estimate:

$$\beta^2_{NaAl(OH)_4}$$
$$\beta^1_{NaAl(OH)_4}$$
$$\beta^0_{Na_3HSiO_4}$$
$$\beta^1_{Na_3HSiO_4}$$, and the sodalite equilibrium constant $EK_{SL}$

The interaction parameters $\theta$ and $\psi$ for the major species ($Na^+$, $Cl^-$, and $OH^-$) are set to their $25^\circ C$ values. The full array of parameters is tabulated in Table 3.
Figure 12. Ionic Strength Dependency of the Unsymmetrical Mixing Terms $E_{\phi}$ and $E_{\phi}'$ for a 1/3 Ion Combination
Table 3. Utilized Pitzer Coefficients from the Literature ([17],[20]) and Regression Parameters

<table>
<thead>
<tr>
<th></th>
<th>$\beta^0$</th>
<th>$\beta^1$</th>
<th>C</th>
<th>Additional Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.1008</td>
<td>0.3207</td>
<td>-0.0034</td>
<td>$\theta_{\text{Cl}^-\text{OH}^-} = -0.05$</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.1354</td>
<td>0.2624</td>
<td>-0.0089</td>
<td>$\psi_{\text{Na}^+\text{Cl}^-\text{OH}^-} = -0.006$</td>
</tr>
<tr>
<td>Na$_3$HSiO$_4$</td>
<td>P</td>
<td>P</td>
<td>---</td>
<td>$A^\Phi = 0.455$</td>
</tr>
<tr>
<td>NaAl(OH)$_4$</td>
<td>P</td>
<td>P</td>
<td>---</td>
<td>$E_{KSL} = P$</td>
</tr>
</tbody>
</table>

*note: P = model parameter*

VII.3. Unsymmetrical Mixing Terms

These terms do arise in the presence of either two anions or two cations, respectively, whose charges differ in magnitude. $E_\Phi$ depends solely on the total ionic strength of the solution and the Debye-Hückel parameter.

For $i$ and $j$ denoting two differently charged ions of equal sign, the following equations describe the unsymmetrical mixing term parameter:

\[
X_{ij} = 6 \cdot z_i \cdot z_j \cdot A^0 \cdot I^{1/2} \tag{12a}
\]

\[
E_{\theta_{ij}} = z_i z_j / 4 \cdot (J_0(x_i) - 1/2J_0(x_i) - 1/2J_0(x_j)) \tag{12b}
\]

\[
J_0(x) = 1/4x - 1 + 1/x \int_0^{\infty} [1 - \exp(x/y \cdot e^{-y})] \cdot y^2 dy \tag{12c}
\]

To evaluate $E_\Phi$ at various levels of ionic strength, the integral of Eq. 12c has to be solved numerically. This was achieved by employing the IMSL (International Statistics and Math Library) subroutine DCADRE. Special care was taken to sufficiently approach lower and upper limits of the integral (zero, the lower limit...
yields an indefinite expression); a relative difference of $10^{-7}\%$ in the integral evaluations was set as a convergence criteria.

For the region of interest ( $1.0 < x < 70.0$ ), the function $J_0(x)$ was expressed by scaled Chebyshev series, truncated, when the first element was less than $10^{-6}$. The most economical fit (i.e., the one involving the least amount of parameters) was achieved by dividing the $x$-region into two intervals.

The file, containing the Chebyshev constants for $J_0(x)$ is listed in Appendix A, together with the respective program.

VII.4. Program Description

The core element of the sodalite modeling program, DOPT5, is IMSL subroutine ZXSSQ. In minimizing an user-supplied residual vector, a finite-difference Levenberg-Marquardt algorithm is employed. DOPT5 (see Appendix D) is composed of several subroutine blocks, easing the perception of the calculation procedures. A brief overview is given below by means of a structurized block diagram:
VII.4.1. Residual Vector

The residual vector, $F(j)^*$, contains the arithmetic difference between model prediction for each data point and its expectation; $F(j)^*$ is derived from the equilibrium relationship, Eq. 11a.

$$
F(j)^* = EK_{sL} \cdot \frac{(m_{Na} \cdot \gamma_{Na})^{y_2} \cdot (m_{Cl} \cdot \gamma_{Cl} + m_{OH} \cdot \gamma_{OH})^{y_3} \cdot (m_{AIOH_4} \cdot \gamma_{AIOH_4})^{y_4} \cdot (m_{HSO_4} \cdot \gamma_{HSO_4})^{y_5}}{(m_{OH} \cdot \gamma_{OH})^z \cdot (a_{H_2O})} \quad (13)
$$

where $(m_{Cl} \cdot \gamma_{Cl} + m_{OH} \cdot \gamma_{OH})$ corresponds to $[X]$ in Eq. 11a and $a_{H_2O}$ refers to the water activity.

Since the Pitzer model parameters are linear in respect to the logarithm of the activity coefficients, the residual vector elements can easily be rewritten to yield a nearly linear functional relationship in the regression variables. The logarithm of the equilibrium constant, instead of the constant itself, must then be substituted as a variable (avoiding negative values for $EK_{sL}$ during the iterations is an additional advantage of the logarithmic expression). The applied, reformulated residual is:

$$
F(j) = \log(m_{Na}^{y_2} \cdot m_{AIOH_4} \cdot m_{HSO_4}/m_{OH}^{y_3}) + \log(m_{Cl} \cdot \gamma_{Cl} + m_{OH} \cdot \gamma_{OH})
+ 4/3 \cdot \log(y_{Na}) + \log(y_{AIOH_4}) + \log(y_{HSO_4}) - 3\log(y_{OH}) - \log(EK_{sL}) \quad (14)
$$

The final least-square objective function to be minimized in the form of:

$$
Q_z = \sum_{j=1}^{N} F^2(j) \quad N = \text{number of data points} \quad (15)
$$

VII.4.2 Scaling

A two magnitude difference between $\log(EK_{sL})$ and the Pitzer parameters does advise to scale the variables. This was found to be of utmost importance, if
conjugate gradient methods are employed. However, in the present study, the Marquardt-Levenberg algorithm is of superior efficiency.

VII.4.3 Penalties

Penalties, $\Omega_i$, in the form of a bracket operator are assigned to excessive values of $\log(y_i)$. The mathematical formulation is:

$$\Omega_i = <P - |\ln y_i|>^2 \quad <X> = 0, \text{ if } X > 0$$

$$<X> = X_0, \text{ if } X < 0$$

where $P$ is the assigned penalty boundary.
VIII. RESULTS AND DISCUSSION

VIII.1 Numerical Fit

In trying to fit the developed model to the solubility data, an important feature of the Pitzer equations had to be recognized: The $\beta^o$ parameters, as well as the $\beta^i$ parameters for the two electrolyte species, NaAl(OH)$_4$ and Na$_3$HSiO$_4$ are linearly dependent, if combined in the residual equations 14. Therefore, an infinite amount of solutions to the least-square fit is encountered, with the restriction:

$$
\beta^o_{\text{NaAl(OH)}_4} + \beta^o_{\text{Na}_3\text{HSiO}_4} = \text{constant} \tag{17a}
$$

$$
\beta^i_{\text{NaAl(OH)}_4} + \beta^i_{\text{Na}_3\text{HSiO}_4} = \text{constant} \tag{17b}
$$

The evaluated equilibrium constant, the residual vector (Eq. 14) and the constants of the above equation do converge to the same numerical values for different initial parameter guesses.

Although the determination of physically significant activity coefficients was not possible, the model predictions in respect to solute concentrations are still valid. If activity coefficient measurements on either NaAl(OH)$_4$ or Na$_3$HSiO$_4$ were available, the parameters for the other species could be assessed accurately (within the experimental error). Fixing the parameters for either species does result in unambiguous, non-multiple solutions; no penalties are needed in this case, to avoid convergence to infinite boundaries.

The summarized results of three runs with different penalty boundaries on single ion activity coefficients reveal the effect of linear dependency (the input file, STREISEL.DAT, is given in Appendix D):
Table 4. Least-Square Minimization Results for Different Penalties

<table>
<thead>
<tr>
<th>Penalty</th>
<th>$\gamma_{\text{NaAl(OH)}_4}^*$</th>
<th>$\gamma_{\text{Na}_3\text{HSiO}_4}^*$</th>
<th>$E_{\text{KL}}$</th>
<th>$Q$ (See Eq. 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>\ln(\gamma)</td>
<td>&lt; 4.0$</td>
<td>0.12 - 0.15</td>
<td>0.27 - 0.39</td>
</tr>
<tr>
<td>$</td>
<td>\ln(\gamma)</td>
<td>&lt; 5.0$</td>
<td>0.18</td>
<td>0.24</td>
</tr>
<tr>
<td>$</td>
<td>\ln(\gamma)</td>
<td>&lt; 6.0$</td>
<td>0.12 - 0.15</td>
<td>0.27 - 0.39</td>
</tr>
</tbody>
</table>

whereas:

$$
\gamma_{\mu_0}^{*} \gamma_{\lambda_0} = (\gamma_{\mu}^* \cdot \gamma_{\lambda}^*)^{1/\max}
$$

Clearly, the values of both, the least-squares function (see Eq. 15) and the equilibrium constant are unaffected by the change in the mean activity coefficients of the minor species $\gamma_{\text{NaAl(OH)}_4}^*$ and $\gamma_{\text{Na}_3\text{HSiO}_4}^*$. The activities of the major species (Cl$^-$, Na$^+$, and OH$^-$) are virtually unaffected by the minor species' activities.

The above results are based on 12 data-points, corresponding to 7 degrees of freedom. Data #19 was excluded as an outlier, which is conceivable by reviewing Fig. 11b.

Quintessentially, any of the parameter sets in the output of the above least-square minimizations can be chosen arbitrarily to predict sodalite solubilities in the covered range:

$$
3/1 \leq [\text{Al}]/[\text{Si}] \leq 1/13
$$

$$
1.0 \leq \text{ionic strength (mole/lit)} \leq 4.0
$$

$$
0.9 \leq \text{OH (mole/lit)} \leq 3.8
$$
Moreover, comparison with Breuer's solubility measurements does support the extension of the Al/Si range up to 50.

The full output file of one of the optimization runs, SLFIT.V5, is listed in Appendix D. The applied termination criteria was a relative change in the iteration parameters of less than four figures. The final Euclidian norm of the gradient, $\sum (\partial Q/\partial X)^2$ is in the order of $10^4$; its expectation, given a perfect fit, is zero.

Figure 13 compares predicted and measured equilibrium products [Al]-[Si], for the 12 measurements of Al/Si, which were utilized in the least-square approximation.

VIII.2. Error Analysis

In Appendix A the percent standard deviations (coefficients of variation in %) about the mean of three consecutive measurements of aluminium and silicon are tabulated for each experiment. These deviations are usually within 6%, but a few measurements do exceed 10%.

If these fluctuations are assigned to errors in the sample analysis, an overall relative standard error of the analysis can be evaluated under the following assumptions:
- the error distribution is normal
- the standard deviations of the relative errors are identical

A pooled coefficient variation can then be calculated. For equal replications as in the present case one finds [22]:

$$S = \left( \frac{N}{\sum S_i^2} \right)^{1/2}$$

(19)
Figure 13. Measured Versus Predicted Values of the Apparent Solubility Product and Statistically Determined Error Boundaries
where:

\( N \) = number of data sets \\
\( S \) = pooled coefficient of variation \\
\( S_i \) = relative standard error of one run \\

This yields a relative standard error of roughly 7% in the analysis of aluminium and 5% for silicon measurements.

The coefficient of variation for the terms \([\text{Al}] - [\text{Si}]\) and \([\text{Al}]/[\text{Si}]\) is determined to be 8.8%, according to the law of error propagation [23]:

\[
S_{\text{Al}/\text{Si}} = S_{\text{Al}/\text{Si}} = \left( (S_{\text{Al}})^2 + (S_{\text{Si}})^2 \right)^{1/2}
\]

Hence, the dotted line in Fig. 13 represents the measurement error in the solubility products. The model predictions do fall within these margins in almost all cases.

VIII.3 Theoretical Equilibrium Constant Evaluation

The attempt to extract the sodalite equilibrium constant from published chemical potentials (see Appendix B), free enthalpies and heat capacities did fail.

Evaluation at 25°C yields a sodalite solubility constant of \(2.56 \times 10^2\) according to reaction Scheme VIIa; assuming \(\Delta C_P\) to be constant, a value of \(8.61 \times 10^0\) is attained at a temperature of 95°C. Both numbers are far off any realistic value, since they would indicate an extreme solubility of the mineral sodalite.

The obvious discrepancy cannot be resolved and must be based on large errors of one or more of the chemical potentials.
VIII.4. Graphical Representation

At first sight, the apparent solubility product (molality product of alumiminium and silicon) can only be solved for, if both, the molalities of the major species (Na⁺, Cl⁻ and OH⁻) and either the equilibrium ratio of Al/Si (minor species) or the concentration of one of the minor species are known. Consequently, predictions of the aluminosilicate equilibrium do require an iterative process including mass and electroneutrality balances.

Fortunately, however, the absolute concentrations of the minor species do remain below an order of magnitude of 10⁻¹ for the investigated system, given an Al/Si equilibrium ratio between, roughly, 10⁻¹ and 10⁻¹. This limit fully represents the conditions encountered in pulp and paper recycle streams. Together with the understanding that minor species' activities do not significantly depend on their concentrations (a fact, also reflected in the Pitzer equations) but are governed by the background matrix, the apparent solubility product may be assessed fairly accurately without prior knowledge of the silicon and aluminium equilibrium distribution.

Hence, the numerical model predictions of [Al][Si] for three different equilibrium ratios Al/Si (10, 1, 0.1) do yield values which deviate only up to 3 percent around their mean for a OH⁻ molality less than 2.5 and up to 6 percent for the highest pH investigated here. In the latter case, the minor species' molalities approach 0.1 moles/kg H₂O.

As a result, the apparent solubility product for the system under study may be found as the ordinate value in Fig. 14, if ionic strength and hydroxide molality are known. The ionic strength is approximated to be either the sodium ion molality or the sum of the molalities of Cl⁻ and OH⁻. The ordinate value then, allows to
Figure 14. Graphical Representation of the Apparent Solubility Product as a Function of Ionic Strength and pH for the Regimes Covered by Streisel's Data

\[ [Al] \cdot [Si] = \left( \frac{\text{ordinate}}{A_{eq}} \right)^2 \]

\[ A_{eq} = C + \sqrt{C^2 + \text{ordinate}} \]

\[ S_{eq} = \frac{\text{ordinate}}{A_{eq}} \]

\[ C = \frac{1}{2} \cdot (A_{0} - S_{0}) \]
evaluate the equilibrium molalities of aluminium and silicon, according to the mass balance equations in Fig. 14. Their initial loadings must be known.

Predictions from Fig. 14 are valid (within the above limitations on accuracy) as long as the minor species' molalities do not largely exceed 0.1 moles/kg H₂O.

VIII.5. Application to Technical Pulp Liquours

The presented modeling of aluminosilicate formation is restricted to chemical systems, containing Na⁺, Cl⁻, and OH⁻ solely (besides aluminium and silicon). Technical liquors differ in the additional presence of organic compounds and anions other than the above (CO₃²⁻ and SO₄²⁻); sodium remains to represent the major cationic species (only white liquor might show an increased calcium content) [24].

Anions like CO₃²⁻ and SO₄²⁻ contribute largely to the background matrix and activity coefficients will certainly be different from those found in Streisel's simplified system. Nevertheless, considering that aluminosilicates are easily eligible of incorporating a wide range of anions, the nature of the precipitate will be similar. Thus, an order of magnitude estimation of the apparent solubility product based on Fig. 14 seems reasonable, given the following adjustment: according to the modelling equation (see Eq. 13), the contribution of the cation concentration does outweigh the anion influence (X'), because it enters with a power of 4/3 in contrast to 1/3; also, the hydroxide term in X' does buffer the influence of other anions.

Hence, if ionic strength in Fig. 14 is exchanged for the actual sodium molality, an approximation of the magnitude of the sodalite solubility in pulp liquors should be guaranteed.

Ulmgren [15] reports an [Al]·[Si] product of 2.5 · 10⁻³ in technical green liquor with the following composition in mole/lit: 1.0 NaOH, 1.2 Na₂CO₃, and 0.5 NaHS. This results in a sodium concentration of 3.9 mole/lit. Neglecting small changes if
converted into a molality scale, Fig. 14 predicts an apparent solubility product of $1.3 \cdot 10^5$. Keeping in mind the extreme simplifications which led to achieving this result, a deviation of 100% is not unacceptable.
IX. CONCLUSION

Evaluating Streisel's aluminosilicate data succeeded in elucidating the characteristics of aluminosilicate scaling. The investigated equilibrium system contained Na⁺, OH⁻, and Cl⁻ (major species, i.e., present in high concentration) as well as aluminium and silicon compounds (minor species). The hydroxide molality varied from 1 to 4 and the ionic strength covered the same range.

Initiating from different input ratios of Al/Si resulted in a discontinuity in the apparent solubility product ([Al][Si]) at an Al/Si equilibrium ratio of roughly 1/13. It derives from the metastable growth of silicon-rich precipitates from solutions with a low Al/Si ratio. Recycle streams in pulp and paper processes are run in the regime of stable sodalite precipitates (above Al/Si of 1/13); their formation thermodynamics was modeled effectively over the whole range of pH and ionic strength. The chemical model is based on aluminium and silicon compounds, whose nature was inferred to by extensive data and literature evaluation.

The successive numerical modeling is based on Pitzer's activity coefficient equations, whereas the necessary number of parameters was kept at a minimum. This resulted in a fit with 7 degrees of freedom. A linear dependency among the Pitzer coefficients for the minor species was observed; the equilibrium constant was unaffected by this phenomenon. Although the estimated Pitzer coefficients do lack physical significance, the model predictions are replicable and do yield unique solutions for Streisel's system, which lie within the statistically determined experimental error. The linear dependency could be resolved, if single electrolyte data for either of the minor species were available.

A graphical representation was developed, which pictures the dependency of the apparent solubility product for the whole range of hydroxide molality and ionic strength (see Fig. 14); the Al/Si ratios may vary from roughly $10^1$ to $10^{-1}$. An
estimation method on aluminium and silicon concentrations in technical liquors is presented. Its predictive accuracy is believed to be within a few hundred percent; one comparison with real mill data on green liquor is given.

Future research in the equilibrium of aluminosilicate scaling should be oriented towards the incorporation of anions like $\text{CO}_3^{2-}$ and $\text{SO}_4^{2-}$, allowing more ubiquitous predictions, especially in regard to technical liquors. The gathering of single electrolyte data for at least one of the minor species is desirable in order to attain physically significant Pitzer parameters. Finally, in any future investigations, special emphasis ought to be put on closing the mass balances in the equilibrium systems, i.e., a final chemical analysis of all species must be carried out to increase the model's accuracy.
BIBLIOGRAPHY


APPENDICES
### Table 5. Streisel's Experimental Data, Used in the Present Study

Varying Initial Ratios $\text{Al}_i/\text{Si}_o$

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Al/Si</th>
<th>$\text{Al}_010^3$</th>
<th>$\text{Al}_{eq}10^3$</th>
<th>$\text{Si}_{eq}10^3$</th>
<th>$[\text{Al}:\text{Si}]_{eq}10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>10/1</td>
<td>74.1</td>
<td>$43.6 \pm 1.9%$</td>
<td>$.169 \pm 12%$</td>
<td>$7.38 \pm 14%$</td>
</tr>
<tr>
<td>34</td>
<td>3/1</td>
<td>134.0</td>
<td>$33.2 \pm 5.4%$</td>
<td>$.311 \pm 18%$</td>
<td>$9.77 \pm 21%$</td>
</tr>
<tr>
<td>23*</td>
<td>1/1</td>
<td>44.5</td>
<td>$4.38 \pm 1.1%$</td>
<td>$1.46 \pm 3.7%$</td>
<td>$6.42 \pm 3.7%$</td>
</tr>
<tr>
<td>24*</td>
<td>1/1</td>
<td>44.5</td>
<td>$4.56 \pm 1.1%$</td>
<td>$1.44 \pm 5.6%$</td>
<td>$6.58 \pm 4.6%$</td>
</tr>
<tr>
<td>25*</td>
<td>1/1</td>
<td>44.5</td>
<td>$3.16 \pm 5.6%$</td>
<td>$2.10 \pm 12%$</td>
<td>$6.66 \pm 17%$</td>
</tr>
<tr>
<td>20*</td>
<td>1/1.3</td>
<td>34.2</td>
<td>$.648 \pm 4.2%$</td>
<td>$9.04 \pm 2.9%$</td>
<td>$5.86 \pm 3.7%$</td>
</tr>
<tr>
<td>21*</td>
<td>1/1.3</td>
<td>34.2</td>
<td>$.673 \pm 19%$</td>
<td>$8.84 \pm 1.9%$</td>
<td>$5.96 \pm 21%$</td>
</tr>
<tr>
<td>39</td>
<td>1/1.4</td>
<td>31.8</td>
<td>$.754 \pm 11%$</td>
<td>$11.0 \pm 2.9%$</td>
<td>$8.32 \pm 14%$</td>
</tr>
<tr>
<td>36</td>
<td>1/1.5</td>
<td>29.7</td>
<td>$1.16 \pm 11%$</td>
<td>$13.2 \pm 3.5%$</td>
<td>$15.3 \pm 18%$</td>
</tr>
<tr>
<td>37</td>
<td>1/2</td>
<td>22.2</td>
<td>$.808 \pm 16%$</td>
<td>$20.1 \pm 0.5%$</td>
<td>$16.3 \pm 15%$</td>
</tr>
<tr>
<td>38</td>
<td>1/2.5</td>
<td>17.8</td>
<td>$.663 \pm 19%$</td>
<td>$24.5 \pm 1.3%$</td>
<td>$16.2 \pm 21%$</td>
</tr>
<tr>
<td>29</td>
<td>1/3</td>
<td>14.8</td>
<td>$.416 \pm 7.8%$</td>
<td>$27.2 \pm 3.8%$</td>
<td>$11.3 \pm 4.2%$</td>
</tr>
<tr>
<td>30</td>
<td>1/3</td>
<td>14.8</td>
<td>$.585 \pm 16%$</td>
<td>$26.5 \pm 4.5%$</td>
<td>$15.6 \pm 21%$</td>
</tr>
<tr>
<td>35</td>
<td>1/10</td>
<td>49.8</td>
<td>$.254 \pm 7.4%$</td>
<td>$47.7 \pm 2.2%$</td>
<td>$12.1 \pm 5.8%$</td>
</tr>
</tbody>
</table>

- all values without dimension are based on moles/kg water
- $o$ designates initial concentrations
- $eq$ designates equilibrium concentrations
- $I = 4.0$ moles/lit
  - $\text{OH}^- = 1.0$ moles/lit
  - $\text{NaOH}_o = 1.06$ moles/kg water
  - $\text{NaCl}_o = 3.18$ moles/kg water
- solution density = 1.160 kg/lit
<table>
<thead>
<tr>
<th>Exp. #</th>
<th>NaOH</th>
<th>NaCl</th>
<th>$A_10^3$</th>
<th>$A_{\text{eq}}10^3$</th>
<th>$S_{\text{eq}}10^3$</th>
<th>$[\text{Al-Si}]_{\text{eq}} \cdot 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>.108</td>
<td>4.21</td>
<td>45.4</td>
<td>2.98 ± 1.4%</td>
<td>.312 ± 4.4%</td>
<td>.930 ± 3.7%</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1.06</td>
<td>3.18</td>
<td>see above table</td>
<td></td>
<td></td>
<td>6.55 (mean)</td>
</tr>
<tr>
<td>26*</td>
<td>2.09</td>
<td>2.09</td>
<td>43.8</td>
<td>8.43 ± 6.4%</td>
<td>8.87 ± 4.6%</td>
<td>74.6 ± 2.7%</td>
</tr>
<tr>
<td>27*</td>
<td>4.04</td>
<td>0.00</td>
<td>42.4</td>
<td>35.1 ± 6.0%</td>
<td>25.2 ± 5.0%</td>
<td>887. ± 11%</td>
</tr>
</tbody>
</table>

- $A_1/S_{\text{eq}} = 1/1$
- $I = 4.0$ moles/lit
- solution densities =
  - #22: 1.158 kg/lit
  - #26: 1.155 kg/lit
  - #27: 1.150 kg/lit
Table 5. Continued.

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>NaOH°</th>
<th>NaCl°</th>
<th>Al°10³</th>
<th>Al°10³</th>
<th>Si°10³</th>
<th>[Al-Si]°10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>14*</td>
<td>.988</td>
<td>0.00</td>
<td>41.5</td>
<td>11.7 ± 5.9%</td>
<td>10.5 ± 2.0%</td>
<td>123. ± 7.6%</td>
</tr>
<tr>
<td>15*</td>
<td>1.01</td>
<td>1.01</td>
<td>42.3</td>
<td>8.74 ± 7.2%</td>
<td>6.77 ± 2.8%</td>
<td>59.3 ± 10%</td>
</tr>
<tr>
<td>16*</td>
<td>1.03</td>
<td>2.07</td>
<td>43.4</td>
<td>5.66 ± 6.3%</td>
<td>3.97 ± 5.2%</td>
<td>22.5 ± 6.9%</td>
</tr>
<tr>
<td>22,23,24</td>
<td>see above table</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17*</td>
<td>.988</td>
<td>0.00</td>
<td>31.9</td>
<td>9.47 ± 1.3%</td>
<td>12.2 ± 2.5%</td>
<td>116. ± 3.4%</td>
</tr>
<tr>
<td>18*</td>
<td>1.01</td>
<td>1.01</td>
<td>21.5</td>
<td>7.10 ± 2.5%</td>
<td>10.3 ± 1.7%</td>
<td>72.9 ± 3.7%</td>
</tr>
<tr>
<td>19</td>
<td>1.03</td>
<td>2.07</td>
<td>33.4</td>
<td>5.25 ± 6.3%</td>
<td>9.26 ± 3.0%</td>
<td>48.6 ± 5.2%</td>
</tr>
</tbody>
</table>

- OH° = 1.0 moles/lit
- solution densities =
  #14,17: 1.052 kg/lit
  #15,18: 1.091 kg/lit
  #16,19: 1.124 kg/lit

Varying Ionic Strengths

Al°/Si° = 1/1

Al°/Si° = 1/1.3
Table 6. Thermodynamic Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH°\textsubscript{25°C} [kJ/mole]</th>
<th>S°\textsubscript{25°C} [J/(moleK)]</th>
<th>ΔG°\textsubscript{25°C} [kJ/moleK]</th>
<th>Cp°\textsubscript{25°C} [J/(moleK)]</th>
<th>ΔCp°\textsubscript{25°C} [J/(moleK)]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsuperscript{+}</td>
<td>-240.5</td>
<td>+59.0</td>
<td>-262.2</td>
<td>+46.4</td>
<td>+18.2</td>
<td>[16]</td>
</tr>
<tr>
<td>Cl\textsuperscript{−}</td>
<td>-167.2</td>
<td>+56.5</td>
<td>-131.3</td>
<td>-136.0</td>
<td>-153.0</td>
<td>[16]</td>
</tr>
<tr>
<td>OH\textsuperscript{−}</td>
<td>-230.0</td>
<td>-10.8</td>
<td>-157.3</td>
<td>-149.0</td>
<td>-178.0</td>
<td>[16]</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>-285.8</td>
<td>+70.0</td>
<td>-237.1</td>
<td>+75.3</td>
<td>+31.7</td>
<td>[16]</td>
</tr>
<tr>
<td>Al(OH)\textsubscript{4}</td>
<td>-1490.3</td>
<td>+144.0</td>
<td>-1305.4</td>
<td>+12.8*</td>
<td>-126.0</td>
<td>[16], [14]</td>
</tr>
<tr>
<td>H\textsubscript{4}SiO\textsubscript{4}</td>
<td>-1460.7</td>
<td>+179.0</td>
<td>-1308.4</td>
<td>+215.0</td>
<td>+98.7</td>
<td>[16]</td>
</tr>
<tr>
<td>H\textsubscript{3}SiO\textsubscript{4}</td>
<td>-1424.9</td>
<td>+113.0</td>
<td>-1252.6</td>
<td>-72.4</td>
<td>-174.0</td>
<td>[16]</td>
</tr>
<tr>
<td>H\textsubscript{2}SiO\textsubscript{2}\textsuperscript{−}</td>
<td>-1395.5</td>
<td>-13.0</td>
<td>-1186.1</td>
<td>-280.0</td>
<td>-368.0</td>
<td>[16]</td>
</tr>
<tr>
<td>HSiO\textsuperscript{3}\textsuperscript{−}</td>
<td>-1362.8\textsuperscript{1}</td>
<td>---</td>
<td>-1117.7\textsuperscript{2}</td>
<td>-535.0\textsuperscript{3}</td>
<td>-608.0</td>
<td>[16]</td>
</tr>
<tr>
<td>SiO\textsuperscript{4}\textsuperscript{−}</td>
<td>-1330.9</td>
<td>-402.0</td>
<td>-1027.5</td>
<td>-777.0\textsuperscript{3}</td>
<td>-836.0</td>
<td>[16]</td>
</tr>
<tr>
<td>Na\textsubscript{8}[AlSiO\textsubscript{6}]Cl\textsubscript{2}</td>
<td>-13307.0</td>
<td>884.0</td>
<td>-12562.0\textsuperscript{4}</td>
<td>+726.0</td>
<td>-358.0</td>
<td>[25]</td>
</tr>
</tbody>
</table>

S° and C°\textsubscript{e} values for the elements at 25°C are taken from Robie et. al [26].

\textsuperscript{1}linear regression of ΔH° on charge; \( r^2 = 0.9996 \)

\textsuperscript{2}linear regression of ΔG° on charge; \( r^2 = 0.9991 \)

\textsuperscript{3}linear regression of ΔH° on charge; \( r^2 = 0.9994 \)

\textsuperscript{4}\( ΔG° = ΔH° - T \cdot ΔS° \); \( ΔS° = S°\textsubscript{SL} - \Sigma S°\textsubscript{elements} \)
Table 6. Continued.

Orthosilic Acid Dissociation Constants

Dissociation constants according to Reaction Scheme I are:

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$K_1^{diss}$</th>
<th>$K_2^{diss}$</th>
<th>$K_3^{diss}$</th>
<th>$K_4^{diss}$</th>
<th>$K_{water}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>$1.7 \cdot 10^{-10}$</td>
<td>$2.0 \cdot 10^{-12}$</td>
<td>$1.0 \cdot 10^{-12}$</td>
<td>$1.58 \cdot 10^{-12}$</td>
<td>$1.01 \cdot 10^{-14}$</td>
</tr>
<tr>
<td>95°C</td>
<td>$1.3 \cdot 10^{-9}$</td>
<td>$1.1 \cdot 10^{-11}$</td>
<td>$6.5 \cdot 10^{-12}$</td>
<td>$1.00 \cdot 10^{-15}$</td>
<td>$4.51 \cdot 10^{-13}$</td>
</tr>
</tbody>
</table>

To attain $K_n$ in Eq. 7:

$$K_n = \frac{K_n^{diss}}{K_{water}}$$

Values at 95°C were evaluated under the assumption of constant $\Delta C_{p}^{\circ}_{\text{reaction}}$:

$$\ln K_n^{(T)} = \ln K_n^{(T_o)} - \frac{\Delta H^{\circ}_o}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_o}\right) - \Delta C_{p}^{\circ} \cdot \left[\ln\left(\frac{T}{T_o}\right) - \frac{T_o}{T} + 1\right]$$

where:

$T_o =$ reference temperature of 298.15K
APPENDIX C

CHEBYSHEV EXPANSION PROGRAM

PROGRAM MAIN

CHEBYSHEV FOR evaluates the Chebyshev series constants for the
unsymmetrical mixing term \( J_0(x) \). The series' upper and lower
limits are to be entered, together with a midpoint in the
series evaluations. IMSL subroutine DCDREK is employed to cal-
culate the integral in \( J_0(x) \). The results are written in the
output file CHEBJS.P1T

COMMON II

EXTERNAL PSUB

Chebyshev's bounds: lower bound=AA, upper bound=BB
WRITE(*,*) 'Enter the lower and the upper bounds for the Chebyshev
function evaluation'
READ(*,*) AA, BB
WRITE(*,*) 'Enter the separation point for the interval division'
READ(*,*) SP

error limitations on the DCDRE integral evaluation:
WRITE(*,*) 'Enter the absolute and relative error limits to find t
the integral'
READ(*,*) ERRR, ERRR

number of series elements to be evaluated:
WRITE(*,*) 'Enter the number of series elements in the Chebyshev se
ries'
READ(*,*) M
M=number of points; M-1=degree of the polynomial

evaluation of PI:
PI=2.0D0*DASIN(1.0D0)
evaluate the Chebyshev divisors $I(k)$ and the $X(k)$ values:

```fortran
DO 111 ISTIP=1,2

C
C
evaluate the function at $X(k)$'s using DCADRE

C
C
DO 35 K=1,N

C
C
reinitialization of the variables:

K=1

C
C
lower and upper bounds for the integral evaluation in DCADRE:

LB=1.0D0
UB=10.0D0

C
C
IF(X(K).EQ.0.0D0) P(K)=0.0D0
IF(X(K).EQ.0.0D0) GOTO 35

II=II

C
C
moving the lower bound as close as possible to zero:
24 IF(HN.EQ.2) GOTO 20
LB=LB/2.0D0
GOTO 32

C
C
increasing the upper bound of the integral (infinity):
26 UB=UB+2.5D0

C
C
F(K)=DCADRE(PSUB,LB,UB,ABER,ERRR,ERROR,IER)

C
F(K)=F(K)/II/II/4.0D0-1.0D0
IF(LB.EQ.0.5D0) GOTO 34

C
C
calculation for the next $X(k)$ value:
34 POLD=F(K)
GOTO 24
```

C
C
C
calculation for the next $X(k)$ value:
find Chebyshev constants $a(k)'s:

computation of Chebyshev functions $T(j,x(k))$:

```
DO 45 K=1,N  
  T(1,X)=1.0D0  
  T(2,X)=X  
DO 40 J=3,N  
  JM0=J-1  
  JMT=J-2  
  T(J,X)=2.0D0*T(K)*T(JM0,X)-T(JMT,X)  
CONTINUE
40 CONTINUE
50 CONTINUE

DO 65 J=1,N  
  A(J)=0.0D0  
60 CONTINUE
65 CONTINUE

DO 60 J=1,N  
  DO 65 K=1,N  
  CONST=1.0D0  
  IF(X.EQ.1) CONST=0.5D0  
  IF(X.EQ.N) CONST=0.5D0  
  A(J)=A(J)+P(K)*T(J,X)*CONST  
CONTINUE
70 CONTINUE
80 CONTINUE
```

write the evaluated constants into file CHEBIJ0.FIT

```
IF(ISTEP.EQ.1) THEN
  OPEN (5, FILE='CHEBIJ0.FIT', STATUS='NEW')
  WRITE(5,*)'Filename: CHEBIJ0.FIT'
  WRITE(5,70) N, AA, SP
ENDIF
IF(ISTEP.EQ.2) WRITE(9,70) N, SP, BB

70 FORMAT///,2, 'Chebyshev constants of Jo(x) for ',F6.1, ' <= x <= '  
     ,F6.1,//)
11=-2
2ND=INT((N+2)/3)
DO 72 J=1,2ND  
  II=J
  IL=J+1
  IN=J+2
  WRITE(9,*)(A(J), J=IL,IN)
72 CONTINUE
```
CONTINUE

END

DOUBLE PRECISION FUNCTION PSUB(X)
DOUBLE PRECISION X, XX
COMMON XX
PSUB=(1.0D0-DEXP(-XX/X*DEXP(-X)))*XX**2.0D0
RETURN
END
15 Chebyshev constants of $J_0(x)$ for $1.0 \leq x \leq 10.0$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$J_0(x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.11627397</td>
<td>0.01920782359258E-001</td>
</tr>
<tr>
<td>-7.63863981</td>
<td>2.293987042058E-003</td>
</tr>
<tr>
<td>2.633175534308E-004</td>
<td>-9.644853956008E-005</td>
</tr>
<tr>
<td>-1.43331726</td>
<td>5.7453293691323E-006</td>
</tr>
<tr>
<td>9.17652424</td>
<td>-4.1485623556524E-007</td>
</tr>
</tbody>
</table>

15 Chebyshev constants of $J_0(x)$ for $10.0 \leq x \leq 70.0$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$J_0(x)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.767210</td>
<td>7.36997872624E000</td>
</tr>
<tr>
<td>-1.05429866</td>
<td>3.4102159579647E003</td>
</tr>
<tr>
<td>4.26238416</td>
<td>-1.5710448512936E004</td>
</tr>
<tr>
<td>-2.25534083</td>
<td>8.7244111409657E006</td>
</tr>
<tr>
<td>1.34655227</td>
<td>-5.3597470869370E007</td>
</tr>
</tbody>
</table>
APPENDIX D

PROGRAM FOR THE LEAST-SQUARES MINIMIZATION
DOPT5.FOR, INPUT AND OUTPUT FILES

PROGRAM MAIN

******************************************************************************
C
C  Program DOPT5.FOR utilizes the data provided in the input file
C  STREISKL.DAT. It carries out a mass balance, evaluates the non-
C  symmetrical mixing term and regresses the data on the chemical
C  model for the sodalite/hydroxysodalite solubility. Penalties to
C  excessive activities are assigned. The regression results are
C  written into output file SLFIT.V5.
C
******************************************************************************
C  PARAMETER (IDATAP=20, NVAR=5, IWORK=80, IJAC=15)
C          IDATAP = maximum number of data points to be used
C          NVAR  = number of optimization variables
C          IWORK = WORK vector: 5*NVAR+2*IDATAP+(NVAR+1)*NVAR/2
C          IJAC  = WORK vector: (NVAR+1)*NVAR/2
C
C  DOUBLE PRECISION ALIMIT(20), AMO(2,15),
C                         AWATER(20), BETA05(5), BETA11(5), CPH112,
C                         CPH113, DPHUC, DELTAL, DELTAOPT, ESSL, EPS,
C                         F(IDATAP), GAMMA(5,20), GRADNORM, M(5,20),
C                         NACL(20), NAOH(20), OBJECT,
C                         OMEGA(20), PARMAQ, PARMOPT(4), PENVAR,
C                         PS1123, SLIMIT(20),
C                         THETA(5,5),
C                         WORKOPT(IWORK), X(NVAR), IJAC(IDATAP,NVAR),
C                         IJAC(IJAC), ISCALE(10), ISTEP(10), Z(5)
C
C  REAL DUMP
C
C  INTEGER I, IENSIGOPT, INROPT, IMIX, INPFR, INFOGAM, IOPT, ITER,
C         ITMAX, IJAC, J, NDATA, NPSF, NDASSET, NSIGOPT
C
C  COMMON /CALCPC/ NDASSET, AWATER, GAMMA, N
C  COMMON /CONVAR/ BETA05, BETA11, PS1123, THETA
C  COMMON /EQUILIB/ ESSL
C  COMMON /PHUC/ DPHUC
C  COMMON /PMAQOPT/ DELTAOPT, EPS, GRADNORM, IEPSIGOPT, INPFR,
C                    INPFR, IOPT, ITER, MAXPS, MYPD, NSIGOPT,
C                    OBJECT, PARMAQ, PARMOPT
C  COMMON /MAINPC/ CPH112, CPH113, IMIX, INFOGAM, NDATA, I
C  COMMON /NIDAT/ AO
C  COMMON /PENULT/ PENVAR, OMEGA
C  COMMON /PRECISE/ ISCALE
C
C  EXTERNAL CALCPC


C
INFO=0
INFORAD=0
INFOGAM=0

C
C
WRITE(*,'(A,A)') 'Enter the number of data points to be fitted'
READ(*,*) NDATA

C
C
WRITE(*,'(A,A)') 'Enter the penalty term factor'
READ(*,*) PKPAR

C
C
WRITE(*,'(A,A)') 'To consider unsymmetrical mixing enter 1, if not 0'
READ(*,*) MIX

C
C
WRITE(*,'(A,A)') 'ENTER THE SCALING FACTORS FOR I(1) TO I(N)'
READ(*,*) (ISCALE(I),I=1,NVAR)

C
C
C
Initialization of the data arrays
C
DO 1 I=1,5
  BETA(I)=0.0D0
  BETALL(I)=0.0D0
 1 CONTINUE
DO 3 I=1,5
  DO 2 J=1,5
    THETA(I,J)=0.0D0
 2 CONTINUE
3 CONTINUE

C******** Reading of the input files *********************************
C
C
Reading file STIESEL.DAT, containing Pitzer parameter values
and estimates as well as the solubility data
C
OPEN(UNIT=9, FILE='STIESEL.DAT', STATUS='OLD')
READ(9,10)
10 FORMAT(//)
  READ(9,*) (BETA(I),I=2,5)
  READ(9,11)
11 FORMAT(//)
  READ(9,*) (BETALL(I),I=2,5)
  READ(9,12)
12 FORMAT(//)
  READ(9,*) (THETA(I),I=3,5)
  READ(9,13)
13 FORMAT(//)
  READ(9,*) (THETA(I),I=4,5)
  READ(9,14)
14 FORMAT(//)
READ(9,*) CP112, CP113, PSI123, IRWNUC
READ(9,15)
15 FORMAT(/)
DO 16 J=1,N3DATA
READ(9,*) DUMP,JASON(J),HACL(J),M(4,J),M(5,J),ALINITL(J),SIINITL(J)
16 CONTINUE
READ(9,17)
17 FORMAT(/)
READ(9,*) (I(1),I=1,5)
READ(9,18)
18 FORMAT(/)
READ(9,*) EXSL
C
C IF(IMII.EQ.1) THEN
C
C Reading the file for the Chebyshev fit of Jo(x):
C
C File CHARTJS.FIT
C
OPEN(UNIT=10, FILE='CHARTJS.FIT', STATUS='OLD')
READ(10,20)
20 FORMAT(/)
READ(10,*) (AJ1(1,J), J=1,15)
READ(10,22)
22 FORMAT(/)
READ(10,*) (AJ1(2,J), J=1,15)
C
EXSLF
C
C******** End of the input routines ******************************
C
C
C***************************************************************
C
C Calculation of the equilibrium molalities
C
40 DO 100 J=1,N3DATA
C
Disappearance of Al and Si during a reaction
DELTA3=ALINITL(J)-M(4,J)
C
C Calculation of the equilibrium sodium moliity
M(1,J)=JASON(J)+HACL(J)+2.0D0*SIINITL(J)-(4.0D0/3.0D0)*DELTA3
Calculation of the chloride concentration (consumption by soda-
lime formation is neglected)
\[ N(2,J) = NaCL(J) + 3.8D9*ALIVITL(J) \]

Calculation of the equilibrium hydroxide molality
\[ N(3,J) = NaOH(J) - 4.8D9*M(4,J) - M(5,J) - 2.8D9*DELTALL \]

Aluminium equilibrium concentration: \( M(4,J) \)

Silica species concentration: \( M(5,J) \)

100 CONTINUE

CALL CON(NVAR,X)

Initiation of the IXSSQ parameters

\[ \text{DELTAPQ} = 0.8D0 \]
\[ \text{EPS} = 0.8D0 \]
\[ \text{MAXP} = 5000 \]
\[ \text{NSIGOPT} = 3 \]
\[ \text{IOPY} = 2 \]
\[ \text{IIJAC} = \text{MDATA} \]

IF (IOPY.EQ.2) THEN
  PARMOPT(1) = 0.05D0
  PARMOPT(2) = 1.3D0
  PARMOPT(3) = 1.0D3
  PARMOPT(4) = 1.0D0
END IF

CALL IXSSQ(CALCFX,NDATA,NVAR,NSIGOPT,EPS,DELTAPQ,MAXP,1OPY,}
  PARMOPT,X,OBJECT,P,IIJAC,IIJAC,IR1,WORKOPT,INTER,IRKOPT)
ITER = IDINT(WORKOPT(5))
NPNLC = IDINT(WORKOPT(2))
INSIGOPT = IDINT(WORKOPT(3))
GRADNORM = WORKOPT(1)
PARMARQU = WORKOPT(4)

Writing the results in the output file STREISEL.SIO
CALL OUTPUT(MVAR,P)

WRITE(*,*) 'The Jacobian at the optimum solution is: '
DO 500 J=1,MDATA
WRITE(*,300)(JAC(J,1),I=1,5)
300   FORMAT(5(E9.4,1X))
500 CONTINUE

End of the main program
END

************************************************************************

SUBROUTINE CON(MVAR,X)
Conversion of the optimization variables into an X-matrix

DOUBLE PRECISION BETA0(5), BETA1(5), BESL,
       PSI123, THETA(5,5), X(MVAR), XSCALE(10)

INTEGER MVAR

COMMON /CONVAR/ BETA0, BETAL, PSI123, THETA
COMMON /EQUILIB/ BESL
COMMON /PRECISE/ ISCALE

I(1)=BETA0(4)*ISCALE(1)
I(2) = BETA1(5) / ISCALE(2)
I(3) = BETA1(4) / ISCALE(3)
I(4) = BETA1(4) / ISCALE(4)
I(5) = BETA1(5) / ISCALE(5)

SUB RETURN
End of subroutine CON

END

******************************************************************************

SUBROUTINE CONV(NVAR, I)

Conversion of the I-matrix into the optimization variables

DOUBLE PRECISION BETA1(5), BETA1(5), BESL,
PSI12, TA(5,5), I(NVAR), ISCALE(I)

INTEGER NVAR

COMMON /CONVAR/ BETA1, BETA1, PSI12, THETA
COMMON /EQUILIB/ BESL
COMMON /PRECISE/ ISCALE

Backtransformation of the I-matrix

BETA1(4) = I(1) / ISCALE(1)
BETA1(5) = I(2) / ISCALE(2)
BETA1(4) = I(3) / ISCALE(3)
BETA1(5) = I(4) / ISCALE(4)
BESL = I(5) / ISCALE(5)

RETURN
End of subroutine COMINV

END

*******************************************************************************

SUBROUTINE CALCPL(I,NDATA,NVAR,F)

Function, organizing the calculation of activity
coefficients ( subroutine PCN) and the evaluation of the ob-
jective function, including a penalty term ( subroutine PEN).

DOUBLE PRECISION AVATER(20), RXSL, F(20),
   GAMMA(5,20), LNAVATER(20), LNGAMMA(5,20), W(5,20)
   OMEGA(20), PENPAR,
   I(NVAR), ISCALE(10)

INTEGER I, IEE, J, NVAR, NDATA, HDATASET

COMMON /CALCFCR/ HDATASET, AVATER, GAMMA, W
COMMON /EQUILIB/ RXSL
COMMON /OBJFCR/ LNAVATER, LNGAMMA
COMMON /PENCR/ PENPAR, OMEGA
COMMON /PRECISE/ ISCALE

Conversion of the I-matrix into original optimization variables
CALL COMINV(NVAR,I)

JJI=JJJ+1
WRITE(*,8)'Function evaluation J=',JJJ

Evaluation of the activity coefficients for each composition

DO 100 J=1,NDATA
   Data-set counter

100 CONTINUE

*******************************************************************************
Sodalite equilibrium equations:

\[
P(J) = \left( \frac{1.008}{3.006} \right) \log\left( \frac{W(1,J)^2}{W(2,J) + W(3,J) \Gamma(3,J)} \right) + \log\left( \frac{W(4,J)}{W(3,J)} \right) + \log\left( \frac{W(5,J)}{W(3,J)} \right) + \log\left( \frac{W(1,J)}{W(3,J)} \right) + \frac{4.008}{3.006} \left( \log\left( \frac{\Gamma(1,J)}{\Gamma(3,J)} \right) + \log\left( \frac{\Gamma(5,J)}{\Gamma(3,J)} \right) - 3.006 \Gamma(3,J) - \Gamma(J) \right)
\]

Repeat for the next composition j

Output of the first set of activity coefficients

\[
\text{IF(INFOGAM.EQ.1) GOTO 500}
\]

\[
\text{WRITE(*,*) 'The gammas 1 to 5 for all data points and awater are:'
WRITE(*,*) ' '}
\text{DO 300 J=1,NDATA}
\text{WRITE(*,250) (GAMMA(I,J), I=1,5), AAWATER(J)}
\text{300 FORMAT(6(I1,11.5))}
\text{CONTINUE}
\]

\[
\text{WRITE(*,*) ' '}
\text{WRITE(*,*) 'The initial equilibrium equation deviations are:'}
\text{WRITE(*,*)'P(J): ',(F(J),J=1,NDATA)}
\]

\[
\text{IF(PEXPAQ.EQ.0.000) GOTO 1000}
\]
Evaluate the penalty term

CALL PEN(LNGAMMA, NDATA, OMEGA)

The penalized objective function is then:

$$\begin{align*}
\text{DO } & \text{ J=1, NDATA} \\
\text{IF}(F(J) .LT. 0.0) & F(J) = F(J) + OMEGA(J) \cdot PENPAR \\
\text{IF}(F(J) .LT. 0.0) & F(J) = F(J) - OMEGA(J) \cdot PENPAR \\
\text{IF}(F(J) .EQ. 0.0) & F(J) = OMEGA(J) \cdot PENPAR
\end{align*}$$

CONTINUE

Transformation into the I-matrix

CALL CON(NVAR, I)

IF POIN=1

RETURN

End of the subroutine CALCFI

END

SUBROUTINE FCQ

Evaluation of the activity coefficients

DOUBLE PRECISION WATER(20), B1(5), B2(5), BPM(5),
BETA1(5), BETA2(5), C1, C2, C3, C4, CHARGE,
CONST1, CONST2, CONST3, CPW112, CPW113,
RHNHC, R(3,3), RSI, RSI,
Definition of the j-variable, i.e., of the data-set in work
j=HDATASET

Activity coefficients:

general terms:

IONICS=0.8D0
SUMNOL=0.8D0
CHARGE=0.8D0
DO 30 I=1,5
IONICS=IONICS+H(I,J)*X(I)*2.8D0
SUMNOL=SUMNOL+H(I,J)
CHARGE=CHARGE+H(I,J)*DABS(X(I))

CONTINUE
IONICS=IONICS/2.8D0
ROOT=DSQRT(IONICS)
CONST1=DEEP(-2.8D0*ROOT)
CONST2=1.8D0-(1.8D0+2.8D0*ROOT)*CONST1
CONST3=1.8D0+(1.8D0+2.8D0*ROOT+2.8D0*IONICS)*CONST1
FPHI=-DEBUC*ROOT/(1.8D0+1.2D0*ROOT)
FGAMMA=FPHI-DEBUC*2.8D0/1.2D0*LOG(1.8D0+1.2D0*ROOT)
DO 35 I=1,5
B1(I)=BETA11(I)+BETA11(I)/(2.8D0*IONICS)*CONST2
B2(I)=BETA11(I)/(2.8D0*IONICS)*CONST3
B3(I)=BETA11(I)+BETA11(I)*CONST1

CONTINUE

Unsymmetric mixing: since no mass balances are included in the present calculations, the ionic strength is fixed. Thus, the
unsymmetrical mixing parameter needs to be calculated only once

IF(INPGM.EQ.0) THEN

IF(INII.EQ.0) THEN
  DO 45 I=1,3
  DO 44 L=1,3
  H(I,L)=0.0D0
  CONTINUE
  CONTINUE
  GOTO 50
ENDIF

retrieving H, EPRIME from subroutine CHRY
CALL CHRY(H,1ONICS)

evaluate PHI(i,j) values; i,j must be ions of the same sign;

DO 64 I=2,4
  LL=I+1
  DO 63 L=LL,5
  PHI(I,L)=I(H(I))
  PHI(L,I)=I(H(L))
  PHI(I,L)=THETA(I,L)*H(R,I,L)
  creating a symmetric PHI matrix
  PHI(L,I)=PHI(I,L)
  CONTINUE
  CONTINUE
ENDIF

calculation of the PFIT2-term; see Harvie & Weare, 1980, pg. 504

T1=0.0D0
T2=0.0D0
DO 66 I=2,5
  T1=T1*M(1,J)*BPI(I)
  CONTINUE
  PPITI=PGAMMA*M(1,J)**T1

Sodium ion activity coefficient for jth composition:

T1=0.0D0
DO 70 J=2,5
  T1=T1*M(1,J)*2.0D0*BI(J)
  CONTINUE
  LUGAMMA(I,J)=(PPITI+T1*H(2,J)*M(3,J)*PSI12)
  GAMMA(I,J)=DEXP(LUGAMMA(I,J))
Activity coefficients for anion \( k \) (\( k=2,5 \)), for \( j \)th composition:

\[
\begin{align*}
\text{DO 90 } & \text{ } k=2,5 \\
 & \\
C1=0.000 \\
T2=0.000 \\
\text{DO } 88 \ & \text{ } i=2,5 \\
C2=0.000 \\
\text{IF (K.EQ.1) GOTO 86} \\
\text{IF (K.EQ.2) GOTO 74} \\
\text{IF (K.EQ.3) GOTO 76} \\
\text{GOTO 78} \\
\text{IF (L.EQ.1) } & \text{ } C1=H(1,J)\ast PS1123 \\
\text{IF (L.EQ.2) } & \text{ } C2=H(1,J)\ast PS1123 \\
78 & \text{ } T2=T2+H(1,J)\ast (2.000*PHI(K,1)+C2) \\
88 & \text{ } \text{CONTINUE} \\
\text{IF (K.EQ.2) } & \text{ } C1=H(1,J)\ast CPH112 \\
\text{IF (K.EQ.3) } & \text{ } C1=H(1,J)\ast CPH113 \\
\text{LJGAMMA}(E,J)= & \text{ } (E(I)\ast 2.000\ast PSI2+H(1,J)\ast (2.000\ast B1(E)\ast C1)+T2) \\
\text{CONTINUE} \\
\text{GAMMA}(E,J)= & \text{ } \text{DEXP} \text{LJGAMMA}(E,J) \\
98 & \text{ } \text{CONTINUE} \\
\end{align*}
\]

Water activity for the \( j \)th composition:

\[
\begin{align*}
\text{T1=0.000} \\
\text{DO 92 } & \text{ } i=2,5 \\
C3=0.000 \\
\text{IF (L.EQ.3) } & \text{ } C3=H(1,J)\ast CPH112 \\
\text{IF (L.EQ.3) } & \text{ } C3=H(1,J)\ast CPH113 \\
92 & \text{ } \text{CONTINUE} \\
T2=0.000 \\
\text{DO 96 } & \text{ } i=2,4 \\
\text{LL=1+1} \\
\text{DO 96 } & \text{ } L=LL,5 \\
C4=0.000 \\
\text{IF (L.EQ.2) GOTO 95} \\
\text{IF (L.EQ.3) } & \text{ } C4=H(1,J)\ast PS1123 \\
95 & \text{ } T2=T2+H(1,J)\ast (PHI(L,J)+C4) \\
96 & \text{ } \text{CONTINUE} \\
94 & \text{ } \text{CONTINUE} \\
\text{OSMOTIC}= & \text{ } 2.000\text{SUMI}(\text{IONICS}\ast PHI(H(1,J)\ast T1+T2)+1.000) \\
\text{LWATER}= & \text{ } (18.029\ast \text{CHARGE}\ast \text{OSMOTIC}/1000.000) \\
\text{AWATER}= & \text{ } \text{DEXP} \text{LWATER}(J) \\
\end{align*}
\]
RETURN

End of subroutine FCH

END

*******************************************************************************

**SUBROUTINE PEN(LGAMMA,NDATA,OMEGA)**

**PEN assigns a bracket operator penalty on excessive activity coefficient values; the penalty is returned as OMEGA**

**DOUBLE PRECISION BETAIL(5), BETALL(5), LGAMMA(5,20),**
**OMEGA(20), PSI1223, THETA(5,5), UNEQU(2)**

**INTEGER NDATA**

**COMMON /CONVAR/ BETAIL, BETALL, PSI1223, THETA**

**Initialization of the penalty term**

**DO 1 J=1, NDATA**
OMEGA(J)=0.0D0
CONTINUE

**DO 1000 J=1, NDATA**
UNEQU(1 to 2)=5.0-ABSOLUTE OF LOG(GAMMA(4 to 5),J) >= 0.0
UNEQU(1)=5.0D0-DABS(LGAMMA(4, J))
UNEQU(2)=5.0D0-DABS(LGAMMA(5, J))

**DO 100 I=1,2**
Calculate < UNEQU(i,j) > (Bracket operator!)
IF(UNEQU(1),GR.0.0D0) UNEQU(1)=0.0D0

**Calculation of the penalty term OMEGA**
\[
\Omega(j) = (\omega \cos(1) \times 2.088) \times \Omega(j)
\]

CONTINUE

CONTINUE

RETURN

End of subroutine PEN

END

*******************************************************************************

SUBROUTINE CHEBY(R,IONICS)

Subroutine Cheby approximates the unsymmetrical mixing parameter by Chebyshev series

DOUBLE PRECISION A0(2,15), CH1, CH2, CONST,
|   B(3,3), IONICS,
|   J0(3), J1(3), T(3), X(3), SCALE

INTEGER I, J, LEVEL, ECH1, ECH2, IMAI, IMAIM, IMIN

COMMON /PCHNIX/ B(3,3)
COMMON /MIIBAT/ A0

smallest absolute charge
IMIN=1

largest absolute charge
IMAI=3

IMAII=IMAII-1

note: rank of R: IMAI by IMAI
x-values of the unsymmetrical mixing terms

\[ \begin{align*}
X(1) &= \text{CH1} \ast \text{CH2} \ast \text{DENNUC} \ast 6.0D0 \ast \text{DSQRT} (\text{IONICS}) \\
X(2) &= \text{CH1} \ast 2.0D0 \ast \text{DENNUC} \ast 6.0D0 \ast \text{DSQRT} (\text{IONICS}) \\
X(3) &= \text{CH2} \ast 2.0D0 \ast \text{DENNUC} \ast 6.0D0 \ast \text{DSQRT} (\text{IONICS})
\end{align*} \]

scaling of the x-values to the correspondent intervals

\[ \begin{align*}
\text{DO 100 I=1,3} \\
\text{IF (X(I).GT.10.0D0) GOTO 39} \\
\text{LEVEL=1} \\
\text{ISCALE=(2.0D0*X(I)-11.0D0)/9.0D0} \\
\text{GOTO 40}
\end{align*} \]

\[ \begin{align*}
\text{DO 100 I=3,13} \\
\text{LEVEL=2} \\
\text{ISCALE=(2.0D0*X(I)-88.0D0)/60.0D0}
\end{align*} \]

calculation of the Chebyshev functions \( T_i(x) \):

\[ \begin{align*}
T(1) &= 1.0D0 \\
T(2) &= \text{ISCALE} \\
\text{DO 50 J=3,15} \\
J11 &= J-1 \\
J12 &= J-2 \\
T(J) &= 2.0D0 \ast \text{ISCALE} \ast T(JM1)-T(JM2)
\end{align*} \]

evaluation of \( J_0(x) \), using 15 Chebyshev constants:

\[ \begin{align*}
J0(1) &= 0.0D0 \\
\text{CONST} &= 0.5D0 \\
\text{DO 60 J=1,15} \\
\text{IF (J.GT.1) CONST=1.0D0} \\
J0(J) &= J0(1)+J0(LEVEL,J) \ast T(J) \ast \text{CONST}
\end{align*} \]

\[ \text{DO 60 CONTINUE} \]

\[ \text{DO 100 CONTINUE} \]
evaluation of unsymmetric mixing terms K and KPrime

\[ K(BCH1, BCH2) = \text{CH1}^2 \text{CH2}/(1001\text{CH}^4) \times (J(1) - 0.500^4 (J(2) + J(3))) \]

symmetric in the K matrix:

\[ K(BCH2, BCH1) = K(BCH1, BCH2) \]

increase BCH1 by one

200 CONTINUE

increase BCH2 by one

300 CONTINUE

assure diagonal elements of K to be zero

DO 500 I=1,IMAX
   K(I,I) = 0.000
500 CONTINUE

RETURN

End of subroutine CHEBY

END

SUBROUTINE OUTPUT(SVAR,F)

Writing of the output file SLF1T.95

DOUBLE PRECISION ALIMIT(10), AMATER(20),
  \[ \text{BETA1}(5), \text{BETA11}(5), \text{CPH112}, \text{CPH113}, \text{DEHNUC}, \]
  \[ \text{DELTAPT}, \text{DISTRH}, \text{EXSL}, \text{EPS}, F^*, \]
  \[ \text{GAMMA}(5,20), \text{GHAL}, \text{GHAL1}, \text{GHAL2}, \text{GHI}, \]
  \[ \text{GRADMON}, \text{H}(5,20), \text{OBJECT}, \text{OMEGA}(20), \]
  \[ \text{PARMADV}, \text{PAROPT}(4), \text{PENPAR}, \text{PINTSM}, \text{PSI123}, \]
  \[ \text{S1LMT}(20), \text{THETA}(5,5), \text{ISCALE}(10), \text{Z}(5) \]
INTEGER IHSIGOPT, INFOGAM, I, J, II, J,
! NDATA, NDATASEL, HSIGOPT
C
C COMMON /CALCPC/ NDATASEL, AVATER, GAMMA, N
COMMON /CONVAR/ DELTA1, DELTA2, PSI123, THETA
COMMON /EQUILIB/ KSL
COMMON /OBNII/ DEBBUC
COMMON /INSIGOPT/ DELTAOPT, EPS, GRADWORN, IHSIGOPT, IXOPT,
! INFIX, IOPT, ITERS, MAXIP, NFUNC, NSIGOPT,
! OBJECT, PARMAQU, PARMOPT
COMMON /MAINPC/ CPNII2, CPNII3, II, IINFOGAM, NDATA, I
COMMON /PENALT/ PENPAR, OMEGA
COMMON /PRECI/ XSCALE
C
C OPEN(UNIT=12, FILE='SLPIT.V5', STATUS='NEW')
WRITE(12,50) PENPAR
50 FORMAT('Program DOPT5 with penalty parameter being: ',E11.5)
WRITE(12,55) NDATA, EPS, DELTAOPT, MAXIP, IOPT, NSIGOPT
55 FORMAT('Data points: ',I2,2X,'EPS=',E7.1,2X,
! 'DELTAOPT=',E7.1,2X,'MAXIP=',I5,2X,'IOPT=',I2,2X,'NSIGOPT=',I2)
IF(IOPT.EQ.2) THEN
WRITE(12,60) (PARMOPT(I),I=1,4)
60 FORMAT('PARMOPT 1 to 4 are: ',4(I2,8X),//)
ENDP
WRITE(12,90) 'Pitzer coefficients beta-(1,2) to beta-(1,5):'
WRITE(12,92) (BETAL(I1), I=1,5)
92 FORMAT(5(I2,8X),//)
WRITE(12,94) 'Pitzer coefficients betal-(1,2) to betal-(1,5):'
WRITE(12,94) (BETAL(I1), I=1,5)
94 FORMAT(5(I2,8X),//)
WRITE(12,96) 'Pitzer coefficients theta-(2,3) to theta(2,5):'
WRITE(12,96) (THETA(2,1), I=3,5)
96 FORMAT(4(I2,8X),//)
WRITE(12,98) 'Pitzer coefficients theta-(3,4) to theta(3,5):'
WRITE(12,98) (THETA(3,1), I=4,5)
98 FORMAT(3(I2,8X),//)
WRITE(12,99) 'Pitzer coefficients Cphi-(1,2), Cphi-(1,3), Psi123, a
and Debye-W coeff.:'
WRITE(12,99) CPNII2, CPNII3, PSI123, DEBBUC
99 FORMAT(4(I2,8X),//)
WRITE(12,100) KSL
100 FORMAT('KSL=',E11.4,//)
WRITE(12,102) 'Mean activity coefficients and water activity:'
WRITE(12,102) '
WRITE(12,104) 'Mean activity coefficients and water activity:'
WRITE(12,105) '
WRITE(12,105) DO 100 J=1,NDATA
CHAO=(GAMMA(1,J)*GAMMA(3,J))**0.5D0
CHACL=(GAMMA(1,J)*GAMMA(2,J))**0.5D0
CHUAL=(GAMMA(1,J)*GAMMA(4,J))**0.5D0
C
CHASI=(GAMMA(1, J)*3.0D0*GAMMA(5, J))*0.25D0
WRITE(12, 99) CHREAL, CHIRC, CHWL, CHASI, AVATER(J)
99 FORMAT(5X,9.3,4(4X,9.3))
100 CONTINUE
WRITE(12, 102) ITER, OBJECT
102 FORMAT(/,5X,'Number of iterations was: ',13.5X,
#   'Objective function is: ',X11.5,/) WRITE(12, 103)(SCALE(I), I=1,5)
103 FORMAT(5X,9.3,4(4X,9.3),/)
PENTERM=0.0D0
DO 105 J=1,NDATA
PENTERM=OMEGA(J)*PENTERM
105 CONTINUE
PENTERM=PENTERM*PENPAR
WRITE(12, 106) PENTERM
106 FORMAT(5X,'The given penalty was: ',X9.3,/) WRITE(12, 108) INROPT, INFER, MFUNC, IMNSIGOPT
108 FORMAT('INROPT=',13.2X,'INFER=',11.2X,'MFUNC=',14,2X,
#   'IMNSIGOPT=',12)
WRITE(12, 110) GRADNORM, PARMARQU
110 FORMAT('GRADNORM=',8.1,5X,'PARMARQU=',8.1)
WRITE(12, *) 'F 1 to NDATA: ', (F(I), I=1,NDATA)
C C C
C Closing the output file
C CLOSE(UNIT=12)
C C C
C RETURN
C C
C End of the file writing subroutine OUTPUT
C
END
Pitzer coefficients $\beta_{(1,2)}$ to $\beta_{(1,5)}$:
\[
\begin{array}{llll}
1.0000D-1 & 1.354D-1 & 1.000D-1 & 5.0000D-1 \\
\end{array}
\]

Pitzer coefficients $\beta_{(1,2)}$ to $\beta_{(1,5)}$:
\[
\begin{array}{llll}
3.207D-1 & 2.624D-1 & 2.000D-1 & 1.300D+1 \\
\end{array}
\]

Pitzer coefficients $\theta_{(2,3)}$ to $\theta_{(2,5)}$:
\[
\begin{array}{llll}
-5.0000D-2 & 0.0000D0 & 0.0000D0 \\
\end{array}
\]

Pitzer coefficients $\theta_{(3,4)}$ to $\theta_{(3,5)}$:
\[
\begin{array}{llll}
0.0000D0 & 0.0000D0 \\
\end{array}
\]

Pitzer coefficients $C_{\text{phi}(1,2)}$, $C_{\text{phi}(1,3)}$, $\Psi_{123}$, and Debye-$W$ coeff.:
\[
\begin{array}{llll}
-3.000D-3 & -8.080D-3 & -6.000D-3 & 4.500D-1 \\
\end{array}
\]

Data fitting points and initial values [moles/kg water]:

<table>
<thead>
<tr>
<th>Ref.</th>
<th>[OH]$^-\times$N</th>
<th>[Cl]$^-\times$N</th>
<th>$[\text{Al(OH)}_4]^-$</th>
<th>$[\text{Si}]_{\text{total}}</th>
<th>[\text{Al}]_{\text{limit}}</th>
<th>[\text{Si}]_{\text{lim}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>1.000D0</td>
<td>3.100D0</td>
<td>4.30D-3</td>
<td>1.46D-3</td>
<td>4.45D-2</td>
<td>4.45D-2</td>
</tr>
<tr>
<td>24</td>
<td>1.000D0</td>
<td>3.100D0</td>
<td>4.50D-3</td>
<td>1.44D-3</td>
<td>4.45D-2</td>
<td>4.45D-2</td>
</tr>
<tr>
<td>25</td>
<td>1.000D0</td>
<td>3.100D0</td>
<td>3.16D-3</td>
<td>2.10D-3</td>
<td>4.45D-2</td>
<td>4.45D-2</td>
</tr>
<tr>
<td>20</td>
<td>1.000D0</td>
<td>3.10D0</td>
<td>6.40D-3</td>
<td>9.04D-3</td>
<td>3.42D-2</td>
<td>4.45D-2</td>
</tr>
<tr>
<td>21</td>
<td>1.000D0</td>
<td>3.10D0</td>
<td>6.70D-3</td>
<td>9.04D-3</td>
<td>3.42D-2</td>
<td>4.45D-2</td>
</tr>
<tr>
<td>14</td>
<td>9.000D0</td>
<td>6.000D0</td>
<td>11.70D-3</td>
<td>10.50D-3</td>
<td>4.15D-2</td>
<td>4.15D-2</td>
</tr>
<tr>
<td>15</td>
<td>1.01D0</td>
<td>1.01D0</td>
<td>0.74D-3</td>
<td>6.77D-3</td>
<td>4.23D-2</td>
<td>4.23D-2</td>
</tr>
<tr>
<td>16</td>
<td>1.03D0</td>
<td>2.07D0</td>
<td>5.66D-3</td>
<td>3.97D-3</td>
<td>4.34D-2</td>
<td>4.34D-2</td>
</tr>
<tr>
<td>26</td>
<td>2.09D0</td>
<td>2.09D0</td>
<td>8.43D-3</td>
<td>8.87D-3</td>
<td>4.38D-2</td>
<td>4.38D-2</td>
</tr>
<tr>
<td>27</td>
<td>4.04D0</td>
<td>6.08D0</td>
<td>35.10D-3</td>
<td>25.20D-3</td>
<td>4.24D-2</td>
<td>4.24D-2</td>
</tr>
<tr>
<td>17</td>
<td>9.08D0</td>
<td>6.08D0</td>
<td>9.47D-3</td>
<td>12.20D-3</td>
<td>4.35D-2</td>
<td>4.35D-2</td>
</tr>
<tr>
<td>18</td>
<td>1.01D0</td>
<td>1.01D0</td>
<td>7.10D-3</td>
<td>10.30D-3</td>
<td>3.25D-2</td>
<td>4.23D-2</td>
</tr>
</tbody>
</table>

Ionic charges for species 1 to 5:

<table>
<thead>
<tr>
<th>Na</th>
<th>Cl</th>
<th>[OH]$^-\times$N</th>
<th>Al(OH)$_4^-$</th>
<th>Si</th>
<th>SiO$_4$</th>
</tr>
</thead>
</table>
| .10D+01 | -.10D+01 | -.10D+01 | -.10D+01 | -.30D+01 |}

Equilibrium constant:

\[ \text{LOG(EKSL)} \]
\[ -9.000D0 \]
Program DOPTS with penalty parameter being: .50000E+00

**I**O**S**Q specifications:

Data points: 12

DELTAOPT = .0E+00
MA1PH = 5.000
IOPT = 2
SIGOPT = 4

**P**ARMOFT 1 to 4 are: .50E-01 .10E+01 .10E+04 .10E+01

Pitzer coefficients beta(1,2) to beta(1,5):

.100E+00 .115E+00 .129E+00 .9611E+00

Pitzer coefficients beta(1,2) to beta(1,5):

.200E+00 .262E+00 -.389E+01 .4747E+01

Pitzer coefficients theA(2,3) to theA(2,5):

-.500E+01 .100E+00 .100E+00

Pitzer coefficients theA(3,4) to theA(3,5):

.100E+00 .100E+00

Pitzer coefficients Cphi(1,2), Cphi(1,3), Psi123 and Debye-W. coeff.:

-.300E+02 -.100E+02 -.600E+02 .4545E+00

**X**ESL = -.1531E+02

Mean activity coefficients and water activity:

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>NaOH</th>
<th>NaH(0H)**4</th>
<th>Na3SO4</th>
<th>H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.662E+00</td>
<td>.715E+00</td>
<td>.105E+00</td>
<td>.315E+00</td>
<td>.115E+01</td>
</tr>
<tr>
<td>2</td>
<td>.662E+00</td>
<td>.715E+00</td>
<td>.105E+00</td>
<td>.315E+00</td>
<td>.115E+01</td>
</tr>
<tr>
<td>3</td>
<td>.662E+00</td>
<td>.715E+00</td>
<td>.105E+00</td>
<td>.315E+00</td>
<td>.115E+01</td>
</tr>
<tr>
<td>4</td>
<td>.664E+00</td>
<td>.715E+00</td>
<td>.105E+00</td>
<td>.315E+00</td>
<td>.115E+01</td>
</tr>
<tr>
<td>5</td>
<td>.664E+00</td>
<td>.715E+00</td>
<td>.105E+00</td>
<td>.315E+00</td>
<td>.115E+01</td>
</tr>
</tbody>
</table>

Number of iterations was: 24
Objective function is: .50576E-01

The scaling factors for variables 1 to 5 were:

.50E+01 .50E+01 .10E+01 .10E+01 .10E+00

The given penalty was: .100E+00

**I**E**O**OPT = 0 **I**NFLR = 1 **HF**UNC = 122 **I**MSI**G**OPT = 4

**G**RAD**W**NRM = .3E-03 **P**ARM**ARU** = .3E-01

F(1), the residual vector:

-6.1536430103438E-002 -4.609504659454E-002 5.9294634421655E-002