KP8108 Advanced Thermodynamics:
Applications to Phase and Reaction Equilibria
Project report

The Modified Quasichemical Model:
Applications to molten salts

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Abstract

This report is written as a requirement to the course KP8108 Advanced Thermodynamics: Applications to Phase and Reaction Equilibria and treats the theoretical background for the modified quasichemical model. The theory is derived for a binary molten salt system exhibiting strong ordering around some composition. The quasichemical model is implemented in Matlab and is tested on a KCl-MgCl$_2$ system, using only two free parameters to obtain satisfactory results.
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1 Motivation and objective

KP8108 treats advanced topics in thermodynamics, with emphasis on theoretical issues and implementation of thermodynamic theory. In addition to the theoretical part, an individual project work is required in order to pass the course. This report presents the results of this individual assignment.

According to Callen [1], “thermodynamics is the study of the restrictions on the possible properties of matter that follow from the symmetry properties of the fundamental laws of physics”. Furthermore, “Whether we are physicists, chemists, biologists or engineers, our primary interface with nature is through the properties of macroscopic matter”. Needless to say, the field of thermodynamics has implications and applications in all branches of modern science. However, as stated by Rubí [2], “Thermodynamics is one of the most widely misunderstood branches of physics. Laypeople and scientists alike regularly use concepts such as temperature, pressure and energy without knowing their rigorous meaning and subtleties.” In order to clarify some of the possible misunderstandings, a brief review of thermodynamic theory based on the postulatory formulation of Callen [1] and lecture notes from the course is given in the first sections of this report.

The course is taken as a part of an ongoing PhD research project, which goal is to “increase the fundamental knowledge of mass and momentum transport in the Hall-Héroult process”. The Hall-Héroult process is the main procedure for industrial production of primary aluminium and is named after its inventors who, independently of each other, in 1886 developed and patented an electrolytic process by which alumina (Al₂O₃) is dissolved in an electrolyte consisting mainly of liquid cryolite (Na₃AlF₆) (Thonstad et al. [3]). A Hall-Héroult cell is a vastly complicated system to study in a holistic manner, due to the dynamical, multiscale and -physics nature of the process. In addition, an inherent coupling between phenomena is present, adding an additional degree of complexity to the problem. The coupling of various phenomena is shown schematically in figure 1.

![Figure 1: Coupling of phenomena in Hall-Héroult cells. The figure sketches the coupling between chemical reactions (CR), electromagnetism (EM), boundaries (BC), thermodynamics (TD) and hydrodynamics (HD) for the Hall-Héroult cell. It should be noted that diagonally opposite systems (i.e. TD-EM and CH-BC) are coupled via the Joule effect (Ohmic heating) and chemical reactions, respectively.](image-url)
As seen from figure 1, thermodynamics play a major role in the process and knowledge on the fundamental level is thus crucial for further developments. As the thermodynamic aspects of the Hall-Héroult process are exceedingly large, such a treatment is well beyond the scope of the present work. Instead, attention is given to modelling of the decoupled thermodynamic system, i.e. the electrolytic solution.

Following the section on fundamental theory an introduction to the thermodynamic treatment of solutions is given. The classical treatment of solutions serves as a framework for the final theory section of the present work, namely the modified quasichemical model (MQCM). The MQCM has been extensively used to study molten solutions, alloys and slags [4] as well complicated solutions relevant to the Hall-Héroult process [5]. The success of the MQCM has resulted in commercial software packages such as FactSage [6], where the MQCM serves as a backbone for thermodynamic properties in applicable systems. As FactSage is widely adopted in industries relevant to the ongoing PhD, the research on this topic is further motivated.

Although the cryolite system (with additives) is of the primary interest for the aluminium industry, the theory given in the present work will be applied to a simpler system, KCl-MgCl₂. This is due to the fact that the behaviour of the NaF-AlF₃ (cryolite) system is far from ideality (Solheim [8]), yielding some subtle modifications in the theory. The background work on the MQCM is however similar, and the results of the present work are thus believed to be useful for future applications.
2 Thermodynamic basics

Following Callen [1], thermodynamics can be expressed in a postulatory formulation. In the following section, the four postulates as of Callen [1] are presented, followed by a section defining the concepts introduced by the postulates.

2.1 The thermodynamic postulates

Postulate I. There exists states (equilibrium states) that, macroscopically, are characterized completely by the specification of the internal energy \( U \) and a set of extensive parameters \( S, X_1, X_2, \ldots, X_t \).

Postulate II. There exists a function (the entropy, denoted by \( S \)) of extensive parameters, defined for all equilibrium states, having the following property: The values assumed by the extensive parameter in absence of a constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

Postulate III. The entropy of a composite system is additive over constituent subsystems. The entropy of each constituent subsystem is thus a first order function of the extensive parameters. The entropy is continuous and differentiable and is a monotonically increasing function of energy.

Postulate IV. The entropy of any system vanishes in the state for which

\[
\left( \frac{\partial U}{\partial S} \right)_{X_1, X_2, \ldots} = 0.
\]

That is, at zero temperature.

2.2 Definitions of postulatory concepts

Properties (or state variables) can either be extensive or intensive. Extensive properties (such as volume, particle numbers and energy) scale according to the system size, whereas intensive properties (such as pressure, chemical potential and temperature) are invariant under the same scaling.

Considering postulate I for a simple system, the fundamental equation for the energy can be expressed as

\[
U = U(S, V, N_1, \ldots, N_r) = U(S, V, N),
\]

that is, a function of the extensive properties \( S \) (entropy), \( V \) (volume) and \( N_1, \ldots, N_r \) (particle numbers of the \( r \) species present). Taking the first differential of the fundamental equation one obtains

\[
dU = \left( \frac{\partial U}{\partial S} \right)_{V, N} dS + \left( \frac{\partial U}{\partial V} \right)_{S, N} dV + \sum_{i=1}^{r} \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_j \neq i} dN_i.
\]

The partial derivatives represent the intensive properties (shown in section 2.2.2) and are defined as

\[
\left( \frac{\partial U}{\partial S} \right)_{V, N} = T \quad \text{(Temperature)}
\]

\[
\left( \frac{\partial U}{\partial V} \right)_{S, N} = \pi \quad \text{(Negative pressure)}
\]

\[
\left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_j \neq i} = \mu_i \quad \text{(Chemical potential)}.
\]
Using the above definitions, the first differential of the fundamental equation can be expressed as

\[ dU = TdS + \pi dV + \sum \mu_j dN_j. \]  

(2.6)

Noting that all terms in the above expression have units of energy, equation 2.6 can be re-written in terms of the familiar first law of thermodynamics, i.e.

\[ dU = dQ + dW_m + dW_c, \]  

(2.7)

where \( dQ \) represents the quasistatic heat flow, \( dW_m \) and \( dW_c \) represent quasistatic mechanical and chemical work, respectively.

### 2.2.1 Equations of state

The intensive parameters defined in the above paragraph are functions of the extensive parameters, i.e.

\[
T = T(S, V, N) \quad (2.8) \\
\pi = \pi(S, V, N) \quad (2.9) \\
\mu_j = \mu_j(S, V, N). \quad (2.10)
\]

Such expressions, yielding the intensive parameters as functions of the extensive, are called equations of state. Knowledge of all equation of state is equivalent to knowing the fundamental equation of the system (Callen [1]). As mentioned previously, intensive parameters are invariant under scaling of the system, that is to say, they are homogeneous of zeroth order. This is shown further in the following.

### 2.2.2 Euler homogeneous functions

Following Warberg [7], Euler homogeneity is defined by

**Definition I.** A function \( F \) is Euler homogenous of degree \( k \) in the variables \( x_1, \ldots, x_n \) if it satisfies

\[ F = f(x_1, \ldots, x_2, \xi_{n+1}, \ldots, \xi_m) = \lambda^k f(x_1, \ldots, x_2, \xi_{n+1}, \ldots, \xi_m) \quad (2.11) \]

where

\[ X_i = \lambda x_i. \quad (2.12) \]

Taking the first differential of the function \( f \), one obtains

\[
dF = \frac{\partial f}{\partial X} dX + \frac{\partial f}{\partial \xi} d\xi = \frac{\partial f}{\partial X} x d\lambda + \frac{\partial f}{\partial \xi} \lambda dx + \frac{\partial f}{\partial \xi} d\xi = k \lambda^{k-1} f d\lambda + \lambda^k \frac{\partial f}{\partial x} dx + \lambda^k \frac{\partial f}{\partial \xi} d\xi, \quad (2.13)\]

where the second equality follows from the first differential of \( X \). Assuming linear independence of the variables, the pairs of differentials are compared.

\[
\frac{\partial f}{\partial X} x d\lambda = k \lambda^{k-1} f d\lambda \\
\Rightarrow \lambda \frac{\partial f}{\partial X} x = k \lambda^k f = kF \Rightarrow \frac{\partial f}{\partial X} X = kF. \quad (2.14)
\]
Relation 2.14 (Euler’s first theorem) yields a useful property for 1st order homogeneous functions such as the thermodynamic potentials (described in section 2.3) and the entropy, as it yields the integral of the first differential. Considering equation 2.6, the integral is easily identified as

\[ U = TS + \pi V + \sum_j \mu_j N_j. \] (2.15)

Considering the \( dx \) differential, one obtains

\[ \frac{\partial f}{\partial X} \lambda dx = \lambda^k \frac{\partial f}{\partial x} dx \]
\[ \Rightarrow \frac{\partial f}{\partial X} = \lambda^{k-1} \frac{\partial f}{\partial x}. \] (2.16)

In other words, differentiation with respect to (the extensive parameter) \( X \) reduces the order by one.

Again considering the first order function \( U \),

\[ \left( \frac{\partial U}{\partial V} \right)_{S,N} = \pi, \] (2.17)

shows that the intensive parameter \( \pi \) is a zeroth order function.

The final differential yields

\[ \frac{\partial f}{\partial \xi} = \lambda^k \frac{\partial f}{\partial \xi}, \] (2.18)

i.e., differentiation with respect to (the intensive parameter) \( \xi \) does not alter the order. Again, considering \( U \)

\[ \frac{\partial U}{\partial T} = S, \] (2.19)

that is, differentiation of a first order function (the energy \( U \)) with respect to a zeroth order function (the temperature \( T \)) yields a first order function (the entropy \( S \)).

### 2.3 Thermodynamical potentials

In previous sections, the thermodynamic properties are derived from the fundamental relation for energy. However, not all extensive properties are easy to measure or control (such as for instance entropy) and a formalism is sought where a chosen set of intensive parameters form the independent variables. This is possible by means of a Legendre transforms of the energy \( U \), yielding the thermodynamical potentials.

The theory derived in future sections is based on the Gibbs-potential details are given only for this potential in the present work. Details on the derivation of other potentials are found in textbooks such as ([1] or [7]).

The Gibbs potential \( G \) is the Legendre transform of \( U \), simultaneously replacing entropy by temperature and volume by pressure, i.e.

\[ U = U(S,V,N), \] (2.20)

with the definitions

\[ \frac{\partial U}{\partial S} = T \quad \text{and} \quad \frac{\partial U}{\partial V} = \pi \] (2.21)

yields the Legendre transform

\[ G = U - TS - \pi V, \] (2.22)
elimination yielding

\[ G = G(T, \pi, N). \]  

(2.23)

The first differential of 2.23 yields

\[ dG = -SdT - Vd\pi + \sum_j \mu_j dN_j. \]  

(2.24)

Thus, at constant temperature and pressure (conditions which are readily met), the first differential of the Gibbs potential reduces to a differential in particle numbers. The form of equation 2.22 suggests an alternative form of the Gibbs potential

\[ G = H - TS, \]  

(2.25)

where \( H \) is the enthalpy. This form of the Gibbs potential is useful for the treatment of solutions, as it yields a simple way of differing between various solution models as discussed in section 3.

2.3.1 The extremum principle for the Gibbs potential

Postulate II is formulated in an entropic basis, and requires that the entropy is maximized for some extensive parameter if the system is to be in equilibrium. The extremum principle can also be defined in Legendre transformed representations. As shown in chapter 6 in Callen [1], the Gibbs extremum principle can be formulated as “The equilibrium value of any unconstrained parameter in contact with a thermal and pressure reservoir minimizes the Gibbs potential at constant temperature and pressure, equal to those of the respective reservoirs”.

In other words we require

\[ \left( \frac{\partial G}{\partial X_1} \right)_{X_2, X_3, \ldots} = 0 \quad \text{and} \quad \left( \frac{\partial^2 G}{\partial X_1^2} \right)_{X_2, X_3, \ldots} \geq 0, \]  

(2.26)

in order to obtain the equilibrium distribution for the parameter \( X_1 \).

3 Theory of solutions

According to Zumdahl [9], a solution is a homogeneous mixture of two or more components. Such a mixture constitutes of a solute which is dissolved in a solvent. The formation of a mixture introduces a Gibbs potential of mixing, expressed as

\[ \Delta G = \Delta H - T\Delta S, \]  

(3.1)

where \( \Delta G \) signifies the difference in Gibbs potential when particles are in the solution and when in their reference state. The treatment of “mixture potentials” is what differences the various models presented in the following.

Solutions come in various forms, ranging from dilute solutions to molten salts and alloys. Dilute solutions have been studied extensively, both because of practical importance and the somewhat simple formalism arising from the idea that interactions between solute components can be disregarded. This approximation is however not valid in the opposite extreme, as inter ionic forces could contribute significantly. This is for instance the case for molten salts.

The term “Molten salt” is rather self descriptive, it is a salt which is melted. For the Hall-Héroult cell, the main salt of interest is cryolite. The melting point of pure cryolite is 1284K, above which it
becomes liquid and thus a molten salt. The molten salt thus behaves like a fluid, but has a significant microstructure due to the disassociated ions constituting the melt. The thermodynamic properties of molten salts are somewhat more complicated than other solutions, due to the fact that there is no solvent.

The molten salt can be visualized as an array of positively and negatively charged cations and anions, similar to that found in solid crystals, though the structure can be significantly different. Due to the strong Coulomb repulsion between charges of same sign (and attractive if opposite) a cation will preferably have an anion as its nearest neighbour. As discussed in Grjotheim and Kvande [10], for a compound like NaCl, the energy required to transfer an anion from its preferred site to a site where it is surrounded by only anions requires an energy of about 800kJ, approximately 30 times larger than the heat of melting of the compound. It is thus reasonable to assume that there are only two kinds of positions in a molten salt, one kind for cations and one kind for anions. This tendency towards ordering differs from ideal solutions, treated in the following.

3.1 Raoultian ideal solutions

Ideal solutions are characterized by negligible interactions between particles. As shown in chapter 9 in Gaskell [11], a consequence of non-interacting particles is Raoult’s law

\[ a_i = X_i, \] (3.2)

stating that the activity\(^1\) of the \(i\)-th component is equal to its mole fraction. The partial mixing Gibbs potential (of the \(i\)-th component) is thus given by

\[ \Delta G_i = RT \ln a_i = RT \ln X_i. \] (3.3)

Hence, for an ideal binary A-B solution, the Gibbs energy of mixing can be expressed as

\[ \Delta G^{id} = RT \left( X_A \ln X_A + X_B \ln X_B \right). \] (3.4)

The assumption of non-interacting particles implies that they should be distributed randomly in the solution. Hence, the entropy of mixing for a binary A-B solution can be expressed as

\[ \Delta S' = k \frac{(N_A + N_B)!}{N_A!N_B!}. \] (3.5)

Using Stirling’s approximation and division with the total mole number, the following expression is obtained

\[ \Delta S = -R \left( X_A \ln X_A + X_B \ln X_B \right). \] (3.6)

Comparison with equation 3.1 shows that the enthalpy of mixing, \(\Delta H\), is zero for ideal solutions.

Due to the simple mathematical relations for ideal solutions, models based on this assumption are widely used and constitute the basics for the so called Temkin activity model [13]. According to Grjotheim and Kvande [10], this formalism has proved to be very useful in approximate calculations of thermodynamic properties of molten salts.

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\(^1\)The activity is defined as the ratio of the fugacity of the substance to its fugacity in its standard state. For ideal solutions this ratio reduces to a ratio in pressures.
3.1.1 Deviation from ideality

Following Gaskell [11], a nonideal solution is one in which the activities of the components are not equal to their mole fractions. However, as substantial work has been done on ideal models, it is useful to model nonideality as a modification of ideality. This is done by introducing the activity coefficient, defined by

\[ \gamma_i = \frac{a_i}{X_i} . \]  

(3.7)

For ideal solutions, \( \gamma_i \) is unity yielding Raoult’s law. Solutions with \( \gamma_i > 1 \) are said to have a positive deviation from Raoult’s law, while \( \gamma_i < 1 \) signifies a negative deviation. The Gibbs energy of mixing for a nonideal binary solution can thus be expressed as

\[ \Delta G = RT \left( X_A \ln a_A + X_B \ln a_B \right) = RT \left( X_A \ln \gamma_A + X_B \ln \gamma_B + X_A \ln X_A + X_B \ln X_B \right) \]

\[ = \Delta G^{xs} + \Delta G^{id} , \]  

(3.8)

where \( \Delta G^{xs} \) is the excess Gibbs potential, incorporating the entire nonideal behaviour. If the activity coefficient is allowed to be temperature dependent, it is readily observed from the Gibbs-Helmholtz equation that nonzero enthalpies of mixing are possible, as

\[ \frac{\partial \Delta G_i / T}{\partial T} = \frac{\partial R \ln \gamma_i}{\partial T} = -\frac{\Delta H_i}{T^2} , \]  

(3.9)

where \( \partial R \ln \gamma_i / \partial T \neq 0 \).

3.2 Regular solutions

Hildebrand [12] defines a regular solution as one where

\[ \Delta H_i \neq 0 \quad \text{and} \quad \Delta S_i = \Delta S_i^{id} = -R \ln X_i . \]  

(3.10)

The excess Gibbs potential is thus related to the enthalpy of mixing in a straightforward manner

\[ \Delta G^{xs} = \Delta H . \]  

(3.11)

Expanding the activity coefficient up to second order in mole fractions, Hildebrand [12] found the following relation for activity coefficients in binary systems

\[ RT \ln \gamma_B = \alpha X_A^2 \]  

(3.12)

\[ RT \ln \gamma_A = \alpha X_B^2 , \]  

(3.13)

where \( \alpha \) is a constant. Using the regular expansion model, the excess Gibbs potential (and thus the enthalpy of mixing) reduces to

\[ \Delta G^{xs} = \Delta H = \alpha X_A X_B , \]  

(3.14)

where the mass balance \( X_A + X_B = 1 \) has been used. Equation 3.13 shows that the excess Gibbs potential and enthalpy of mixing is temperature independent for the regular model.

Regular solution models assume a random distribution of atoms even though the enthalpy of mixing is nonzero. In reality, a random solution is expected only if interactions between particles is negligible or at so high temperatures that the entropy term overwhelms any tendency for ordering of atoms.
3.3 Subregular solutions

The subregular model is a further extension of the regular model, allowing $\alpha$ to be composition dependent and $\Delta G^{xs}$ to depend on temperature. Following Gaskell [11]

$$\alpha = \alpha_0 + \alpha_1 X_B$$

(3.15)

and

$$\Delta G^{xs} = (\alpha_0 + \alpha_1 X_B)X_A X_B \left(1 - \frac{T}{\tau}\right),$$

(3.16)

yielding

$$\Delta S^{xs} = \frac{(\alpha_0 + \alpha_1 X_B)X_A X_B}{\tau} \equiv (s_0 + s_1 X_B)X_A X_B$$

(3.17)

and

$$\Delta H = \Delta G^{xs} + \Delta S^{xs} = (\alpha_0 + \alpha_1 X_B)X_A X_B \equiv (h_0 + h_1 X_B)X_A X_B.$$  

(3.18)

3.4 Summary

Ideal solutions are characterized by zero enthalpy of mixing and random entropy of mixing. Deviations from ideality can be treated by regular or subregular expansions, writing properties of interest as polynomials in mole fractions. Regular type models keep the random entropy of mixing but allow for non-zero enthalpy of mixing through a power series expansion

$$\Delta H = X_A X_B \left(h_0 + h_1 X_B + h_2 X_B^2 + \ldots\right).$$

(3.19)

Subregular type models extend the regular models, allowing for non-zero excess entropy through a power series expansion

$$S^{xs} = X_A X_B \left(s_0 + s_1 X_B + s_2 X_B^2 + \ldots\right),$$

(3.20)

where coefficients $h_i$ and $s_i$ are related through a temperature coefficient $\tau$. The coefficients in the expansions are empirical and need to be determined from experiment.

As pointed out by Pelton and Blander [14], the above approaches fail for a system which exhibits strong structural ordering around some certain composition, even if a large number of terms are included. Pelton and Blander [14] introduce a physical model for calculation of thermodynamic properties of ordered systems, based on the quasichemical model of Guggenheim [15]. The modified quasichemical model is treated in detail in the following section.

The four main approaches to the modelling of solutions are summarized in the following table

<table>
<thead>
<tr>
<th>Model</th>
<th>$\Delta S^{\text{M}}$</th>
<th>$\Delta H^{\text{M}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal</td>
<td>Random</td>
<td>0</td>
</tr>
<tr>
<td>Regular</td>
<td>Random</td>
<td>$\neq$ 0</td>
</tr>
<tr>
<td>Subregular</td>
<td>Non-random</td>
<td>$\neq$ 0</td>
</tr>
<tr>
<td>Quasichemical</td>
<td>Non-random</td>
<td>$\neq$ 0</td>
</tr>
</tbody>
</table>
4 Modified Quasichemical Model for binary solutions

The following presentation of the Modified Quasichemical Model for binary solutions is based on the papers by Pelton and Blander [4], [14], [16].

4.1 Introduction

As discussed in Pelton and Blander [14], the formalism based polynomial expansions has been highly successful and phase diagrams and thermodynamic properties have been computed for a wide class of solutions using relatively few coefficients. Furthermore, the analytical representation permits for data to be inter- and extrapolated. However, a difficulty arises when a system exhibits a strong structural ordering about a certain composition. In such a system, the enthalpy of mixing tends to exhibit a negative V-shaped peak close to the composition of maximum order, whereas the entropy of mixing tends to take the shape of an M, having a minimum close to the ordered composition. These curves are not well represented by means of polynomial expansions, even when a large number of terms are included. Pelton and Blander [14] thus suggest a set of equations based upon the quasichemical model of Guggenheim [15] which accounts for the ordering in a manner which gives the required characteristic shapes of $\Delta H^M$ and $\Delta S^M$.

4.2 Derivation of the model

In the modified quasichemical model for binary solutions, particles (anions) $A$ and $B$ are distributed on a quasilattice. Considering a particle occupying an unspecified site, its nearest neighbours can be either $A$’s, $B$’s or a combination. In all cases, the following pair exchange reaction is considered

$$(AA) + (BB) \rightleftharpoons 2(AB); \Delta g_{AB}, (4.1)$$

where $(ij)$ represents a nearest neighbour pair. The above reaction thus states that an $(AA)$ and $(BB)$ pair can be splitted, forming two $(AB)$ pairs, and vice versa. The Gibbs free energy associated with the formation of two $(AB)$ pairs is given by $\Delta g_{AB}$. The magnitude and sign of $\Delta g_{AB}$ determines whether the formation of $(AB)$ pairs is thermodynamically favourable or not. Large and negative value suggests that $(AB)$ pairs are favourable (ordered solution), whereas clustering of $(AA)$ and $(BB)$ pairs (immiscible solution) occurs in the opposite case. In the limit $\Delta g_{AB} \rightarrow -\infty$ the solution tends towards a state where only $(AB)$ pairs are present. If $\Delta g_{AB} = 0$, the solution is ideal, meaning that particles are chemically identical, having no interaction.

Denoting the number of moles of species $A$ and $B$ by $n_A$ and $n_B$, respectively, and the number of moles of $(ij)$ pairs by $n_{ij}$, the following mass balance is obtained

$$Z_A n_A = 2n_{AA} + n_{AB} \quad (4.2)$$
$$Z_B n_B = 2n_{BB} + n_{AB} \quad (4.3)$$

where $Z_A$ and $Z_B$ are the coordination numbers of species $A$ and $B$. The factor 2 arises as an $n_{ii}$ pair consists of two $i$ particles.

The mole fraction of particle $A$ is defined by

$$X_A = \frac{n_A}{n_A + n_B} = 1 - X_B. \quad (4.4)$$

---

2The cations are assumed to be negligible in the present work, and the pair exchange is thus considered for anion nearest-neighbour pairs

3The coordination number is the total number of neighbours of a particle, i.e., each “A” particle is bonded to $Z_A$ neighbours. In a solid, the coordination number is necessarily the same for all species.
In addition, it is useful to introduce coordination equivalent fractions
\[ Y_A = \frac{Z_A n_A}{Z_A n_A + Z_B n_B} = \frac{Z_A X_A}{Z_A X_A + Z_B X_B} = 1 - Y_B. \] (4.5)

The pair fraction \( X_{ij} \) is defined by
\[ X_{ij} = \frac{n_{ij}}{n_{AA} + n_{BB} + n_{AB}}. \] (4.6)

Using relations 4.2 and 4.3, the pair fraction can be re-written as
\[ X_{ij} = \frac{2n_{ij}}{Z_A n_A + Z_B n_B}, \] (4.7)
yielding
\[ 2Y_A = 2X_{AA} + X_{AB}, \] (4.8)
\[ 2Y_B = 2X_{BB} + X_{AB}, \] (4.9)
for equations 4.2 and 4.3.

The Gibbs energy of mixing at a given temperature \( T \) is assumed to be given by
\[ \Delta G' = \frac{n_{AB}}{2} \Delta g_{AB} - T \Delta S' \] (4.10)
where \( \Delta S \) is the entropy of mixing and the factor 1/2 occurs as \( \Delta g_{AB} \) is the Gibbs free energy resulting from the formation of two \((AB)\) pairs. Comparing to equation 3.1, it is observed that the first term plays the role of the enthalpy of mixing.

In order to obtain an expression for the entropy of mixing, the multiplicity of a solution containing \( n_{ij} \) moles of \((ij)\) pairs must be determined. As shown by Pelton and Blander [14], this is equivalent to the Ising model in three dimensions. A simple model, suggested by Guggenheim [15], distributes the pairs randomly over the lattice sites, yielding
\[ \Delta S_{AB}' = -\frac{R}{2} \left( n_{AA} \ln X_{AA} + n_{BB} \ln X_{BB} + n_{AB} \ln X_{AB} \right). \] (4.11)

The above expression however over counts the number of possible configurations (cf. Pelton et. al [4]). A correction factor is computed from the fact that if the solution where ideal, the entropy contribution from the \((ij)\) pairs should be zero. As shown in Pelton et. al [4], the following holds for an ideal solution
\[ X_{AA} = Y_A^2; \quad X_{BB} = Y_B^2; \quad X_{AB} = 2Y_A Y_B. \] (4.12)
The approximated, non-ideal, entropy of mixing is thus given by
\[ \Delta S_{AB}' = -R \left( n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right), \] (4.13)
and the Gibbs energy of mixing is thus given by
\[ \Delta G' = \frac{n_{AB}}{2} \Delta g_{AB} + RT \left( n_A \ln X_A + n_B \ln X_B \right) + RT \left( n_{AA} \ln \frac{X_{AA}}{Y_A^2} + n_{BB} \ln \frac{X_{BB}}{Y_B^2} + n_{AB} \ln \frac{X_{AB}}{2Y_A Y_B} \right). \] (4.14)
It is readily observed that the ideal (Raoltian) Gibbs energy (cf. section 3.1) is obtained when $\Delta g_{AB} = 0$, i.e.

$$\Delta G' = RT (n_A \ln X_A + n_B \ln X_B) = \Delta G'^{id}. \quad (4.15)$$

As discussed in section 2.3.1, the equilibrium distribution of pairs is obtained by

$$\left( \frac{\partial \Delta G'}{\partial n_{AB}} \right)_{n_A,n_B} = 0. \quad (4.16)$$

After some algebra (details provided in appendix A), the following requirement on the equilibrium distribution is obtained

$$\frac{X_{AB}^2}{X_{AA}X_{BB}} = 4 \exp \left( -\frac{\Delta g_{AB}}{RT} \right). \quad (4.17)$$

The above expression describes the “equilibrium constant” of the quasichemical reaction given by the balance equation 4.1. For a given value of $\Delta g_{AB}$, the solution of equation 4.17 together with equations 4.2, 4.3 and 4.6 yields the Gibbs free energy and entropy of the solution at a given temperature. Figures 2 and 3 respectively show the enthalpy and entropy of mixing for constant values of $\Delta g_{AB}$. As seen from the figures, the sought shapes of the curves are obtained when $\Delta g_{AB}$ is large and negative, as expected.

**Figure 2:** Molar enthalpy of mixing for a AB system computed at 1273.15K with $Z_A = Z_B = 2$ and $\Delta g_{AB} = -21$, -42 and -85 kJ.
Figure 3: Molar entropy of mixing for a AB system computed at 1273.15K with $Z_A = Z_B = 2$ and $\Delta g_{AB} = 0$ (ideal solution), -21, -42 and -85 kJ.
In order to advance further, some assumption must be made on the form of $\Delta g_{AB}$. Following Pelton and Blander [14], the pair formation energy is expressed as a polynomial in the coordination equivalent fractions, i.e.

$$\Delta g_{AB} = \sum_{i+j \geq 0} g_{AB}^{ij} Y_A^i Y_B^j, \quad i \geq 0, \quad j \geq 0,$$

$$= \sum_{k \geq 0} g_k Y_k^k$$

(4.18)

where $g_k Y_k^k$ are free parameters to be determined from experimental data. Interpreting $\Delta g_{AB}$ as the enthalpy of mixing, the power series of equation 4.18 corresponds to a regular like model. In principle, given the Gibbs free energy and the equilibrium distribution of bonds, other interesting properties can now be computed. Those used in the present work are shown in the following section.

### 4.3 Computing properties of interest

Following the details given in appendix B, the excess GFE can be expressed as

$$\Delta G_{\text{XS}} = \frac{RT}{2} \left( Z_A n_A + Z_B n_B \right) \left[ Y_A \ln \frac{\xi - 1 + 2 Y_A}{(\xi + 1) Y_A} + Y_B \ln \frac{\xi - 1 + 2 Y_B}{(\xi + 1) Y_B} \right].$$

(4.19)

The partial excess GFE is related to the activity coefficients in the solution by

$$\Delta G_{\text{XS}}^{X_i} = \left( \frac{\partial \Delta G_{\text{XS}}^{X_i}}{\partial n_i} \right)_{n_j \neq n_i} = RT \ln \gamma_i.$$

(4.20)

The details of deriving the partial excess GFE are given in appendix B, resulting in

$$RT \ln \gamma_A = \Delta G_{\text{XS}}^{X_A} = \frac{RT}{2} \left[ Z_A \ln \frac{\xi - 1 + 2 Y_A}{(\xi + 1) Y_A} - 2 Z_A Y_A Y_B^2 \frac{\partial \Delta g_{AB}}{\partial Y_B} \right]$$

(4.21)

$$RT \ln \gamma_B = \Delta G_{\text{XS}}^{X_B} = \frac{RT}{2} \left[ Z_B \ln \frac{\xi - 1 + 2 Y_B}{(\xi + 1) Y_B} + 2 Z_B Y_B Y_A^2 \frac{\partial \Delta g_{AB}}{\partial Y_A} \right].$$

(4.22)

As shown in section 3.1, the activity of the $i$-th component can be expressed as

$$RT \ln a_i = G_{i}^{\text{XS}} + RT \ln X_i.$$

(4.23)

Following equation 3.18 and the details of appendix B, the enthalpy of mixing can be expressed as

$$\Delta H' = (Z_A n_A + Z_B n_B) \frac{Y_A Y_B}{1 + \xi} \Delta g_{AB}.$$

(4.24)
5 Results for the KCl-MgCl\(_2\) system

The model presented in the preceding section is used to model the KCl-MgCl\(_2\) system. The free parameters are determined by curve-fitting to enthalpy of mixing (using experimental data from Kleppa and McCarty [17]) and to the activity coefficient of MgCl\(_2\) (using data from Ostvold [18] and Egan and Bracker [19]). The closed model is furthermore used to predict the activity of KCl (using data from Ostvold [18] and Egan and Bracker [19]). Reproduced data of the references is given in Pelton et al. [4].

5.1 Solution method

The provided data for enthalpy of mixing has a minimum close to \(X_{MgCl_2} = 0.4\). Transformed to coordination equivalent fractions, the distribution should have a minimum at \(Y_A = Y_B = 0\). Using equation 4.5, the ratio of coordination numbers is found to be

\[
\frac{Z_A}{Z_B} = \frac{2}{3}.
\] (5.1)

The coordination numbers \(Z_A\) and \(Z_B\) are chosen to be 4 and 6, respectively.

Experimental data for \(\Delta H\) and \(\ln \gamma_{MgCl_2}\) are fitted to high order polynomials (details provided in appendix C) in order to obtain more points to compare with the model. Given the approximated data set, the model equations for \(\Delta H\) and \(\ln \gamma_{MgCl_2}\) are optimized using the fzero routine in matlab (details provided in appendix D). The form of the closure relation (equation 4.18) is identified by direct experimentation, requiring that the number of free parameters was as low as possible. The model found yielding best results is identified as

\[
\Delta g_{AB} = g_0 + g_7 Y_B^7.
\] (5.2)

Given optimized parameters for \(\Delta H\) and \(\ln \gamma_{MgCl_2}\), a joint set of parameters, keeping the \(l_2\) error (defined below) as low as possible, was determined by graphical analysis\footnote{This approach was chosen as the original idea of simultaneous fitting did not yield satisfactory results}. The simultaneous set of parameters was used to predict \(a_{KCl}\).

The \(l_2\) error is defined as

\[
l_2 = \frac{1}{N} \sqrt{\frac{\sum (f_c - f_e)^2}{N}},
\] (5.3)

where \(f_c\) and \(f_e\) respectively represent computed and experimental values and \(N\) represents the number of points. The \(l_2\) error thus serves as an average error estimate.
5.2 Enthalpy of mixing

The optimized model for the entropy of mixing (computed with help of HmixFit.m given in appendix D) is given by

\[ \Delta g_{AB}^{\Delta H} = -17998 - 10789Y_B^7 \text{ (J/mol)}, \]  

yielding a \( \ell_2 \) error of 21.9 J/mol.

The model is compared to experimental data of Kleppa and McCarty [17] in figure 4.

![Figure 4: Optimized curve for enthalpy of mixing. The red solid line shows the model with optimal parameters while black circles show experimental points by Kleppa and McCarty [17].](image)
5.3 Activity coefficient of MgCl$_2$

The optimized model for the activity coefficient of MgCl$_2$ (computed with help of HmixFit.m given in appendix D) is given by

\[ \Delta g_{AB}^\gamma = -19450 - 14774Y_B^7 \text{ (J/mol)}, \]

yielding a $l_2$ error of 0.0123.

The model is compared to experimental data of Ostvold [18] and Egan and Bracker [19] in figure 5.

![Figure 5: Optimized curve for activity coefficient of MgCl$_2$. The red solid line shows the model with optimal parameters while symbols show experimental points by Ostvold [18] and Egan and Bracker [19].]
5.4 Complete model

The simultaneous optimization of the above parameters is performed by graphical analysis of the $l_2$ error in the space spanned by the coefficients of 5.2. A typical plot is given in figure 6.

![Figure 6: Typical plot of $l_2$ error for various values of $g_7$. Horizontal axis shows the values for $g_0$. $l_2$ error of $\gamma\text{MgCl}_2$ is scaled by factor 1000 to ease comparison.](image)

As seen from figure 6, the minima of the $l_2$ error curves do not coincide, possibly explaining the failure of the attempted simultaneous optimization of the two curves. The simultaneous parameters are thus chosen such that both $l_2$ errors are satisfactory small. The chosen parameters yield the expression

$$\Delta g_{AB} = -18470 - 10500Y_B^7 \text{ J/mol},$$

yielding $l_2$ errors

$$l_2^{\Delta H} = 42.8 \text{ J/mol}$$

and

$$l_2^\gamma = 0.0233.$$  

Comparison with experimental data with the simultaneous parameters is given in figures 7 and 8.
Figure 7: Enthalpy of mixing with simultaneous parameters. The red solid line shows the model while black circles show experimental points by Kleppa and McCarty [17].

Figure 8: Activity coefficient of MgCl$_2$ with simultaneous parameters. The red solid line shows the model while symbols show experimental points by Ostvold [18] and Egan and Bracker [19].
As seen from figures 7 and 8, the overall results are in agreement with the experimental data. The entropy of mixing is slightly under predicted while the activity coefficient is slightly over predicted. This is however expected from the dependence of $g_0$. A marginal improvement in the predicted activity coefficient is obtained by choosing $g_0$ closer to the optimal value, however this modification yields rather poor results for the predicted curve of enthalpy of mixing. This is as expected from the form of the $l_2$ error (figure 6), growing faster for the enthalpy than for the activity coefficient. For comparison, curves with simultaneous parameters and optimal parameters for the activity coefficient are given in figures 9 and 10.

**Figure 9:** Comparison of mixing with simultaneous parameters to activity optimal parameters. The red solid line shows the model while black circles show experimental points by Kleppa and McCarty [17].
Figure 10: Comparison of activity coefficients of MgCl$_2$ with simultaneous parameters to activity optimal parameters. Solid lines shows the model while symbols show experimental points by Ostvold [18] and Egan and Bracker [19].
5.5 Activity of KCl

Given the simultaneous model (equation 5.6), the activity of KCl is computed. A comparison between predicted values, Raoult’s law and experimental measurements by Ostvold [18] and Egan and Bracker [19] is given in figure 11.

![Figure 11: Predicted activity of KCl. The solid red line shows the predicted activity while symbols show experimental points by Ostvold [18] and Egan and Bracker [19]. The solid blue line shows the ideal Raultian behaviour.](image)

As seen from figure 11, the predicted values for the activity of KCl are very close to experimental points, with a $l_2$ error of $7.96 \cdot 10^{-4}$.
6 Closing remarks

The present report gives an overview of the thermodynamic background for the theory of solutions. Special attention is given to the Modified Quasichemical Model for binary solutions of Pelton et al. [4]. The Modified Quasichemical Model is used to model the KCl-MgCl$_2$ system, yielding satisfactory results when compared to experiments using only two free parameters. The benefit of the Modified Quasichemical formalism is that experimental data can be accurately reproduced using a relatively small set of consistent parameters. The computations needed to obtain these parameters are however somewhat more involved than what needed for more traditional approaches. Nevertheless, the power of the quasichemical formalism is clear from the promising results.

The quasichemical formalism is further generalized in a series of papers by Chartrand and Pelton [20], [21] and [22], yielding more flexibility and possible applications to ternary and higher order systems. The advanced form of the Quasichemical model is necessary to model complicated systems directly relevant for the Hall-Héroult process. This, though feasible (cf. Chartrand and Pelton [5], is well beyond the scope of the present work.
List of symbols

\( a_i \) : Activity of component i  
\( \Delta G' \) : Gibbs energy of mixing  
\( \Delta G \) : Molar Gibbs energy of mixing  
\( \Delta g_{AB} \) : Pair formation energy  
\( \gamma_i \) : Activity coefficient of component i  
\( \Delta H \) : Molar enthalpy of mixing  
\( n_i \) : Mole number of component i  
\( n_{ij} \) : Mole number of pairs ij  
\( R \) : Universal gas constant  
\( \Delta S \) : Molar entropy of mixing  
\( T \) : Temperature  
\( X_i \) : Mole fraction of component i  
\( Y_i \) : Coordination equivalent mole number  
\( Z_i \) : Coordination number of component i
References


A Equilibrium distribution

The equilibrium distribution in the binary solution is obtained by setting

$$\left. \frac{\partial \Delta G'}{\partial n_{AB}} \right|_{n_A, n_B} = 0.$$  \hfill (A.1)

The following substitutions are made in equation 4.14

$$n_{AA} = \frac{Z_A n_A - n_{AB}}{2}; \quad n_{BB} = \frac{Z_B n_B - n_{AB}}{2}$$ \hfill (A.2)

and

$$X_{AB} = \frac{2n_{AB}}{Z_A n_A + Z_B n_B}; \quad X_{AA} = \frac{Z_A n_A - n_{AB}}{Z_A n_A + Z_B n_B}; \quad X_{BB} = \frac{Z_B n_B - n_{AB}}{Z_A n_A + Z_B n_B},$$ \hfill (A.3)

thus expressing all pair fractions as functions of $n_{AB}$.

Differentiation yields

$$0 = \frac{1}{2} \Delta g_{AB} + RT \left[ \frac{1}{2} \frac{n_{AB} - Z_A n_A}{Z_A n_A - n_{AB}} + \frac{1}{2} \frac{n_{AB} - Z_B n_B}{Z_B n_B - n_{AB}} \right] +$$

$$+ RT \left[ \frac{n_{AB}}{Z_A n_A + Z_B n_B} \right] \left[ \frac{1}{2} \frac{1}{Z_A n_A + Z_B n_B} - \frac{1}{2} \frac{1}{Z_A n_A + Z_B n_B} \right]$$ \hfill (A.4)

As the first parenthesis computes to zero, and the denominators in the second cancel, one obtains

$$0 = \frac{1}{2} \Delta g_{AB} + \frac{RT}{2} \left[ 2 \ln n_{AB} - \ln (Z_A n_A - n_{AB}) - \ln (Z_B n_B - n_{AB}) \right]$$

$$= \frac{1}{2} \Delta g_{AB} + \frac{RT}{2} \left[ 2 \ln n_{AB} - \ln (4 n_{AA} n_{BB}) \right].$$ \hfill (A.5)

Rearrangement yields

$$\frac{n_{AB}^2}{n_{AA} n_{BB}} = 4 \exp \left( \frac{- \Delta g_{AB}}{RT} \right)$$

$$\Rightarrow \frac{X_{AB}^2}{X_{AA} X_{BB}} = 4 \exp \left( \frac{- \Delta g_{AB}}{RT} \right).$$ \hfill (A.6)
B Derivation of excess GFE and activity coefficient

Considering the equation for equilibrium

\[ \frac{X_{AB}^2}{X_{AA}X_{BB}} = 4 \exp \left( -\frac{\Delta g_{AB}}{RT} \right) = 4\Gamma, \]  
(B.1)

the denominator on the left hand side can be re-written in terms of the coordination equivalent fractions

\[ X_{AA}X_{BB} = \left( Y_A - \frac{1}{2}X_{AB} \right) \left( Y_B - \frac{1}{2}X_{AB} \right) \]
\[ = \frac{1}{4}X_{AB}^2 + Y_AY_B - \frac{1}{2}X_{AB} (Y_A + Y_B) \]
\[ = \frac{1}{4}X_{AB}^2 + Y_AY_B - \frac{1}{2}X_{AB}, \]  
(B.2)

where the last equality follows from \( Y_A + Y_B = 1 \). Inserting in equation (B.1) and solving the quadratic equation for the positive root of \( X_{AB} \) one obtains

\[ X_{AB} = \Gamma + \Gamma \frac{\sqrt{1 + 4Y_AY_B (\Gamma - 1)}}{1 - \Gamma}. \]  
(B.3)

Introducing

\[ \xi = \sqrt{1 + 4Y_AY_B (\Gamma - 1)}, \]  
(B.4)

one obtains

\[ X_{AB} = \frac{\Gamma (\xi - 1)}{1 - \Gamma} = \frac{4Y_AY_B (\xi - 1)}{\xi^2 - 1} \]
\[ = \frac{4Y_AY_B}{\xi + 1}. \]  
(B.5)

The excess Gibbs free energy is given by

\[ \Delta G^{XS} = \Delta G - \Delta G^{id}. \]  
(B.6)

Substituting equation (B.5) and the mass balance constraints, one obtains

\[ \Delta G^{\prime XS} = \frac{RT}{2} (Z_{AnA} + Z_{BnB}) \left[ \left( Y_A - \frac{2Y_AY_B}{\xi + 1} \right) \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} + \left( Y_B - \frac{2Y_AY_B}{\xi + 1} \right) \ln \frac{\xi - 1 + 2Y_B}{(\xi + 1)Y_B} \right] \]
\[ + \frac{RT}{2} (Z_{AnA} + Z_{BnB}) \left[ \frac{4Y_AY_B}{\xi + 1} \ln \frac{2}{\xi + 1} \right] + (Z_{AnA} + Z_{BnB}) Y_AY_B \Delta g_{AB} \]
\[ = \frac{RT}{2} (Z_{AnA} + Z_{BnB}) \left[ Y_A \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} + Y_B \ln \frac{\xi - 1 + 2Y_B}{(\xi + 1)Y_B} \right] \]
\[ - \frac{RT}{2} (Z_{AnA} + Z_{BnB}) \left[ Y_AY_B \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} + Y_B \ln \frac{\xi - 1 + 2Y_B}{(\xi + 1)Y_B} - \ln \frac{4}{(1+\xi)^2} \right] \]
\[ + (Z_{AnA} + Z_{BnB}) Y_AY_B \Delta g_{AB}. \]  
(B.7)

As the two last terms cancel, the excess GFE is identified as

\[ \Delta G^{\prime XS} = \frac{RT}{2} (Z_{AnA} + Z_{BnB}) \left[ Y_A \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} + Y_B \ln \frac{\xi - 1 + 2Y_B}{(\xi + 1)Y_B} \right] \]  
(B.8)
The partial excess GFE of component \( i \) can be found by differentiation

\[
\Delta G_{i}^{XS} = \left( \frac{\partial \Delta G_{i}^{XS}}{\partial n_i} \right)_{n_j \neq n_i}
\] (B.9)

Noting that \( \xi \) is a function of the coordination equivalent mole fractions \( Y_i \), which again is a fraction of mole numbers, the partial excess GFE of component \( A \) can be expressed as

\[
\Delta G_{A}^{XS} = \frac{RT}{2} \left[ Z_A \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} + Z_A n_A \frac{\partial}{\partial n_A} \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} + Z_B n_B \frac{\partial}{\partial n_B} \ln \frac{\xi - 1 + 2Y_B}{(\xi + 1)Y_B} \right] \] (B.10)

After some extensive algebra and repeated use of the mass balance relations, the final term can be greatly simplified, yielding the final expressions for the partial excess GFE

\[
\Delta G_{A}^{XS} = \frac{RT}{2} \left[ Z_A \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} + \frac{(Z_A n_A + Z_B n_B) Y_A Y_B \Delta \Delta g_{AB}}{\xi + 1} \right] \] (B.11)

and

\[
\Delta G_{B}^{XS} = \frac{RT}{2} \left[ Z_B \ln \frac{\xi - 1 + 2Y_B}{(\xi + 1)Y_B} + \frac{(Z_A n_A + Z_B n_B) Y_A Y_B \Delta \Delta g_{AB}}{\xi + 1} \right] \] (B.12)

So far, no other models have been applied other than the assumed form of the entropy. Using the model equation for \( \Delta g_{AB} \) (equation 4.18), the derivatives can be expressed as

\[
\frac{\partial \Delta g_{AB}}{\partial n_A} = -\frac{Z_A Y_B}{Z_A n_A + Z_B n_B} \frac{\partial \Delta g_{AB}}{\partial Y_B} \] (B.13)

\[
\frac{\partial \Delta g_{AB}}{\partial n_B} = \frac{Z_B Y_A}{Z_A n_A + Z_B n_B} \frac{\partial \Delta g_{AB}}{\partial Y_B} \] (B.14)

Using the above expressions, equations B.11 and B.12 reduce to

\[
\Delta G_{A}^{XS} = \frac{RT}{2} \left[ Z_A \ln \frac{\xi - 1 + 2Y_A}{(\xi + 1)Y_A} - \frac{Z_A Y_A Y_B^2 \partial \Delta g_{AB}}{\xi + 1} \right] \] (B.15)

and

\[
\Delta G_{B}^{XS} = \frac{RT}{2} \left[ Z_B \ln \frac{\xi - 1 + 2Y_B}{(\xi + 1)Y_B} + \frac{Z_B Y_B Y_A^2 \partial \Delta g_{AB}}{\xi + 1} \right]. \] (B.16)
C Polynomials to fit experimental data

The experimental enthalpy of mixing is found to be best represented by means of a 7th order polynomial

\[ \Delta H = \sum_{i=0}^{7} h_i X_i^B, \]  

(C.1)

with coefficients

**Table 2:** Coefficients for polynomial representing \( \Delta H \)

<table>
<thead>
<tr>
<th>( h_0 )</th>
<th>( h_1 )</th>
<th>( h_2 )</th>
<th>( h_3 )</th>
<th>( h_4 )</th>
<th>( h_5 )</th>
<th>( h_6 )</th>
<th>( h_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.503 ( \times 10^6 )</td>
<td>4.956 ( \times 10^6 )</td>
<td>-6.105 ( \times 10^6 )</td>
<td>3.377 ( \times 10^6 )</td>
<td>-6.901 ( \times 10^5 )</td>
<td>5.827 ( \times 10^4 )</td>
<td>-5.428 ( \times 10^4 )</td>
<td>-2.655 ( \times 10^4 )</td>
</tr>
</tbody>
</table>

The activity coefficient of \( \text{MgCl}_2 \) was found to be best represented by means of a 5th order polynomial

\[ \log \gamma_{\text{MgCl}_2} = \sum_{i=0}^{5} g_i X_i^B, \]  

(C.2)

with coefficients

**Table 3:** Coefficients for polynomial representing \( \log \gamma_{\text{MgCl}_2} \)

<table>
<thead>
<tr>
<th>( g_0 )</th>
<th>( g_1 )</th>
<th>( g_2 )</th>
<th>( g_3 )</th>
<th>( g_4 )</th>
<th>( g_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-8.272 ( \times 10^1 )</td>
<td>2.506 ( \times 10^2 )</td>
<td>-2.808 ( \times 10^2 )</td>
<td>1.333 ( \times 10^2 )</td>
<td>-1.524 ( \times 10^1 )</td>
<td>-5.135 ( \times 10^0 )</td>
</tr>
</tbody>
</table>
D Matlab scripts

HmixFit.m

The following script serves as the main interface for optimization

```matlab
function HmixFit()
% Script for optimization of thermodynamic data for binary solutions
% Written by Kristian Etienne Einarsrud 2008

%b = MgCl2
%a = KCl

% Set mole fractions for component B
xb = 0:0.01:1;
xa = 1 - xb;

% Set number of moles
n = 1;
na = n*xa;
nb = n*xb;

% Acquire enthalpy of mixing from polynomial
HExp = HmixPol(xb);
% Acquire activity coefficient from polynomial
lngbExp = lngbPol(xb);

% Set constants
R = 8.314472;
T = 1073.15; % Temperature
Za = 4; % Coordination numbers
Zb = 6;

% Set coordination equivalent fractions
Ya = Za.*na./(Za.*na+Zb.*nb);
Yb = Zb.*nb./(Za.*na+Zb.*nb);

% Set initial guess
P0 = [-10000,-10000];

% Set options for fsolve
options = optimset('MaxIter',50000,'MaxFunEvals'... ,75000,'TolFun',1.0e-16,'TolX',1.0e-16);

% Optimize
PH = fsolve(@HmixOpti,P0,options,R,T,Za,Zb,Ya,Yb,HExp,xa,xb);
Pg = fsolve(@lnbOpti,P,options,R,T,Zb,Ya,Yb,lngbExp);
```
%Compute optimal enthalpy and activity coefficient
Hmix = HmixOpti(PH,R,T,Za,Zb,Ya,Yb,0,xa,xb);
lngb = lnbOpti(Pg,R,T,Za,Zb,Ya,Yb,0,xa,xb);

%Compute L2-error
Herr = 1/length(Hmix)*sqrt(sum(abs((Hmix-HExp).^2)));
gerr = 1/length(lngb)*sqrt(sum(abs((lngb-lngbExp).^2)));

%Store L2-error for post processing
err=[Herr,gerr];

%Plot parameters
function Hd = HmixOpti(P0,R,T,Za,Zb,Ya,Yb,Hs,xa,xb)

%%% HmixOpti is an implementation of the enthalpy of mixing for binary systems using the Quasichemical model.
%%% Written by Kristian Etienne Einarsrud 2008

% Input:
% P0: Parameters for model equation
% R: Universal gas constant
% T: Temperature
% Za: Coordination number component A
% Zb: Coordination number component B
% Ya: Coordination equivalent mole number component A
% Yb: Coordination equivalent mole number component B
% Hs: Setvalue for enthalpy of mixing
% xa: Mole fraction component A
% xb: Mole fraction component B

% Output:
% Hd: Difference between model and setvalue

% Set model equation
dg = P0(1)+P0(2)*Yb.^7;

% Set ksi
ksi = sqrt(1 + 4*Ya.*Yb.*( exp(dg./(R*T)) - 1));

% Compute difference
Hd = (Za*xa+Zb*xb).*Ya.*Yb./(ksi+1).*dg - Hs;
lnbOpti.m

The following script contains the implementation of the activity coefficient.

function gd = lnbOpti(P0,R,T,Zb,Ya,Yb,gs)

% lnbOpti is an implementation of the activity coeffient of component B
% for binary systems using the Quasichemical model.
% Written by Kristian Etienne Einarsrud 2008

% Input:
% P0: Parameters for model equation
% R: Universal gas constant
% T: Temperature
% Zb: Coordination number component B
% Ya: Coordination equivalent mole number component A
% Yb: Coordination equivalent mole number component B
% gs: Setvalue for activity coefficient

% Output:
% gd: Difference between model and setvalue

% Set model equation
dg = P0(1)+P0(2)*Yb.^7;
% Set derivative of model equation
ddg = 7*P0(2)*Yb.^6;
% Set ksi
ksi = sqrt(1 + 4*Ya.*Yb.*( exp(dg./(R*T))-1));
% Compute difference
gd = 0.5*(Zb*log((ksi-1+2*Yb)./((ksi+1).*Yb)) + 1/(R*T)*(Zb*Yb.*Ya.^2)./(ksi+1).*ddg - gs;