



**NTNU – Trondheim**  
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# Measuring melting capacity with calorimetry

Low temperature testing with mixtures of  
sodium chloride and magnesium chloride  
solutions

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<p>Abstract:</p> <p>Salt application is an important part of winter maintenance activities. As the use of salt increases, there is a need for usage optimization due to environmental impacts. Several chemical alternatives and additive to salt exist, and a test method to accurately measure its ice-melting capacity is needed to compare different chemicals. The objective of this study was to acquire information on the behaviour of liquid deicers (salt solutions), particularly below <math>-10^{\circ}\text{C}</math> as salt begins to lose effectiveness at low temperatures. Further, the thesis focuses on a new test method that uses calorimetry, and a thermodynamic model (extended UNIQUAC), to measure deicers ice-melting capacity and look into the possibly to determine its freezing curve.</p> <p>The study consisted of a literature review, laboratory testing and calculations with the model. The experiment with the calorimeter was performed with mixtures of NaCl and <math>\text{MgCl}_2</math> solutions in different ratios, 50/50 and 80/20 respectively, at low temperatures (<math>-10</math>, <math>-15</math>, <math>-20</math> and <math>-23^{\circ}\text{C}</math>). To evaluate the test method's accuracy, results from an experiment with NaCl solution (done prior to the study) was presented.</p> <p>The main findings were that the NTNU calorimeter was able to produce results with high accuracy and good precision. Results from the NaCl and mixture experiments showed to averagely measure the melting capacity higher than theoretical values with 4.76% and 4.33% respectively. The calorimeter showed good potential in determining the freezing curve of an unknown salt, due to high accuracy of the measurements. The freezing point was predicted within the interval of <math>\pm 1.0^{\circ}\text{C}</math> for 81.1% of the cases from the NaCl experiment. The 50/50 mixture had a lower freezing point and higher melting capacities than the 80/20 mixture, though the difference was rather small. A larger difference from NaCl was obtained when the NaCl's freezing point were surpassed. This means that <math>\text{MgCl}_2</math> as an additive to NaCl had little effect on ice-melting capacity at temperatures higher than NaCl's eutectic point (<math>-21^{\circ}\text{C}</math>).</p> <p>The extended UNIQUAC model was able to predict the freezing points and melting capacities well. It correlated well with theoretical values and showed great potential in being used to indicate properties at low temperatures, given that information about the deicer was known. The model makes it possible to experiment and try out different chemicals and ratio, which can help discover new deicers that can be effective at very low temperatures.</p>
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Keywords:

1. Melting of ice
2. Ice-melting capacity
3. Calorimeter
4. Salt solution



# PREFACE

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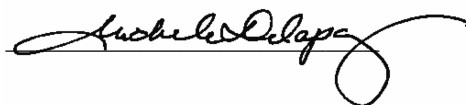
This thesis is submitted to the Norwegian University of Science and Technology (NTNU) as the concluding part of a two-year master's degree programme in Civil and Environmental Engineering. The work has been performed at the Department of Civil and Transport Engineering, Faculty of Engineering Science and Technology and has been completed during the spring of 2015.

My interest in the topic of road salting started with a lecture on the course Rehabilitation and Maintenance of Roads. Alex Klein-Paste held an inspiring lecture on winter maintenance and on the physical mechanisms related to the use of salt and chemicals on the road. The work with this thesis gave me a better understanding of that topic, as well as the process of laboratory testing. It made me aware of the amount of time and effort that lies behind each data point, together with the importance of precision and documentation. All in all, it has been a very educational experience.

I would like to express thanks to my main supervisor, postdoc. Johan Wåhlin, for excellent guidance and response that greatly helped me with the work. Thank you for always having time for discussions and for sharing your knowledge. I would also like to thank associate professor Alex Klein-Paste for inspiring me to choose the topic, and PhD Candidate Kine Nilssen for introducing me to the test method in use. Additionally, thanks to the Norwegian public Roads Administration for offering financial support.

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Trondheim, June 2015



Michele Ann Padiernos Delapaz



# SUMMARY

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Salt application is an important part of winter maintenance activities. As the use of salt increases, there is a need for usage optimization due to environmental impacts. For deicing purposes an important property is the chemical's melting ability; i.e. its ice-melting capacity. As several chemical alternatives and additive to salt exist, a test method to accurately measure this property is required to be able to compare different chemicals. The motivation of this thesis is the lack of information and test method that determine the chemicals melting ability.

The study objective was to acquire information on liquid deicers (salt solutions) behaviour, mainly below  $-10^{\circ}\text{C}$  as salt lose effectiveness at low temperatures. Further, the thesis focuses on a new test method that uses calorimetry, and a thermodynamic model (extended UNIQUAC), to measure deicer's melting capacity and possibly determine its freezing curve.

The study consisted of a literature review, laboratory testing and calculations with the model. Experiment with the calorimeter was performed with mixtures of NaCl and  $\text{MgCl}_2$  solutions in two ratios, 50/50 and 80/20 respectively, at low temperatures ( $-10$ ,  $-15$ ,  $-20$  and  $-23^{\circ}\text{C}$ ). The calorimeter measures the heat needed to melt an amount of ice. As ice-melting in a closed system causes temperature decrease, the calorimeter adds heat to counteract the temperature change which continues the melting process. The heat added to the system equals the required energy to melt a certain amount of ice, on the premise that the initial and final temperature is the same. The model calculated the solution's water activity, which was used to determine melting capacities and new freezing points. The experiment results were compared to the model, and to evaluate the test method's accuracy, results from an experiment with NaCl solution (done prior to the study) were presented.

The main findings were that the NTNU calorimeter was able to produce results with high accuracy and good precision. Results from the NaCl and mixture experiments showed to averagely measure the melting capacity higher than theoretical values with 4.76% and 4.33% respectively. Noting that with lower temperature, the measurement's accuracy reduced. The calorimeter showed good potential in determining the freezing curve of an unknown salt, due to high accuracy of the measurements. The freezing point was predicted within the interval of  $\pm 1.0^{\circ}\text{C}$  for 81.1% of the cases from the NaCl experiment. The 50/50 mixture showed to have a lower freezing point and higher melting capacities than the 80/20 mixture, though the difference was rather small. A significant difference from NaCl was obtained when the NaCl's freezing point were surpassed. This means that  $\text{MgCl}_2$ , as an additive to NaCl, had little effect on the melting capacity at temperatures higher than NaCl's eutectic point ( $-21^{\circ}\text{C}$ ).

The extended UNIQUAC model was able to predict the freezing points and melting capacities well. It correlated with theoretical values and showed great potential in being used to indicate properties at low temperatures, given that information about the deicer was known. The model makes it possible to experiment and tryout different chemicals and ratio, which can help discover new deicers that can be effective at very low temperatures.





# SAMMENDRAG

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Veisaltning er en viktig del av vintervedlikeholds aktiviteter. Etter hvert som bruken av salt øker, blir det behov for å optimalisere bruken pga. miljøforurensing. En viktig egenskap ved avisningsformål er saltets smelte evne (smeltekapasitet). Siden flere kjemiske alternativer og tilsetningsstoffer til salt eksisterer, kreves det en testmetode som nøyaktig måler denne egenskapen for å kunne sammenligne ulike kjemikalier/produkter. Motivasjonen for denne oppgaven er mangel på informasjon og testmetode som bestemmer kjemikaliers smelte evne.

Målet med denne studien var å skaffe informasjon om effekten til saltløsninger, spesielt under  $-10^{\circ}\text{C}$  da salt begynner å miste effektivitet ved lave temperaturer. Videre fokuserer oppgaven på en ny testmetode som bruker kalorimetri, og en termodynamisk modell (extended UNIQUAC), for å måle saltets smeltekapasitet og ser på muligheten til å bestemme frysekurve til saltløsningen.

Studien besto av en litteraturgjennomgang, laboratorietesting og beregninger med modellen. Eksperimentet med kalorimeteret ble utført med blandinger av NaCl og  $\text{MgCl}_2$ -løsninger i ulike forhold, henholdsvis 50/50 og 80/20, ved lave temperaturer ( $-10$ ,  $-15$ ,  $-20$  og  $-23^{\circ}\text{C}$ ). Kalorimeteret måler varmen som trengs for å smelte en viss mengde is. Siden smelteprosessen til is i et lukket system forårsaker temperaturreduksjon, tilsetter kalorimeteret varme for å motvirke temperaturendringen og for å videre fortsette smelteprosessen. Varmen som ble tilsatt til systemet er lik den nødvendige energi for å smelte en viss mengde is, med den forutsetning at start- og sluttemperatur er den samme. Modellen beregner saltløsningens vannaktivitet, som ble anvendt for å bestemme smeltekapasitet og nye frysepunkter. Resultatene fra forsøket ble sammenlignet med modellen, og for å evaluere testmetodens nøyaktighet, ble resultatene fra et eksperiment med NaCl-løsning (gjort før studiet) anvendt.

De viktigste funnene var at NTNU kalorimeteret var i stand til å produsere resultater med høy nøyaktighet og god presisjon. Resultater fra NaCl og blanding-eksperimentene målte i snitt høyere smeltekapasitet enn teoretiske verdier med henholdsvis 4,76% og 4,33%. Ved lavere temperaturer var målenøyaktigheten redusert. Kalorimeteret viste god potensial i å bestemme frysekurven for et ukjent salt, pga. høy nøyaktighet på målingene. Frysepunktet var forutsett innenfor temperaturintervall på  $\pm 1,0^{\circ}\text{C}$ , i 81,1% av tilfellene (NaCl eksperimentet). 50/50-blandingen hadde et lavere frysepunkt og høyere smeltekapasitet enn 80/20-blandingen, men forskjellen var nokså små. En vesentlig forskjell fra NaCl ble oppnådd ved temperaturer lavere enn NaCl's frysepunkt. Dette betyr at  $\text{MgCl}_2$  som en tilsetning til NaCl hadde liten effekt på smeltekapasiteten ved temperaturer høyere enn NaCl sin eutektiske punkt ( $-21^{\circ}\text{C}$ ).

Extended UNIQUAC modellen var i stand til å forutsi frysepunkt og smeltekapasiteter med god nøyaktighet. Det korrelerte med teoretiske verdier og viste god potensiale i å bli brukt til å avdekke egenskaper ved lave temperaturer, gitt at informasjon om saltløsningen er kjent. Modellen gjør det mulig å eksperimentere og teste ut forskjellige kjemikalier og forhold, som kan hjelpe å oppdage nye saltløsninger som kan være effektive ved svært lave temperaturer.



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# 1 INTRODUCTION

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## 1.1 BACKGROUND

Each winter large amounts of sodium chloride (salt) are used for maintaining the roads in Norway. This is to ensure good driving conditions, with high level of accessibility and safety, during the wintertime. However, the use of salt generates great debate regarding the impact of environmental pollution and corrosion. There are also several factors restricting the use of salt. At very low temperatures in particular (below  $-10^{\circ}\text{C}$ ), salt begin to lose effectiveness; it will still work but at a slower rate that generally requires additional applications (Koefod et al., 2015). To obtain optimal use of salt, and other chemicals, more information on their behavior at low temperatures is needed.

Several potential chemical alternatives to salt are gaining more attention, in addition to additives that either enhance the performance of the salt or mitigate its negative side effects (Holen, 2010). With increasing numbers of additives and products being introduced, a test method to evaluate their performance is needed in order to compare different products and to serve as a basis for improving their formulations. As field-testing is often costly and irreproducible considering uncontrolled weather and traffic conditions, laboratory testing can provide valuable information for evaluating the chemicals as it allows direct comparisons under controlled conditions, and is also useful for quality control.

The efficiency of a chemical/product can be characterized differently depending on the usage objective. The usage objective can be divided into three categories: Preventing a wet road from freezing (anti-icing), melting ice already formed in the pavement (deicing) and preventing falling snow to be compacted into hard crust on the road (anti-compaction) (Klein-Paste, 2014). For deicing purposes an important property is the chemical's ice-melting capacity, i.e. the quantity of ice melted per quantity of chemical. Standard test methods for measuring this property exist, but with great variation in accuracy and precision (section 2.5).

NTNU is working actively to develop a new measurement method for ice-melting capacity using calorimetry. Technical modifications have recently been completed and a new measurement procedure is now being developed. This master's thesis focuses on the use of this new measurement procedure.

### 1.3 OBJECTIVE, SCOPE, AND LIMITATIONS

The focus in this master's thesis has been on the development of a laboratory experiment, using the calorimeter as a device for measuring ice-melting capacity. The study consists of a literature review and laboratory experiments focusing on the properties of liquid deicers (salt solutions), specifically their behaviour under low temperature conditions. The aim of this study is to:

- Describe the ice-melting process that takes place in the calorimeter
- Determine the accuracy of the measurement system by comparing measured and theoretical melting capacity
- Consider the possibility of determining the freezing curve of an unknown salt with calorimetry
- Evaluate the use of a thermodynamic model (Extended UNIQUAC) to find liquid deicers freezing curve.

The scope of the study's work is on low temperatures (below  $-10^{\circ}\text{C}$ ), and consisted of testing two mixtures of sodium chloride (NaCl) and magnesium chloride ( $\text{MgCl}_2$ ) solutions.

### 1.4 REPORT OUTLINE

The report has the following outline:

- |  |   |
|--|---|
| <b>Chapter 2</b><br>Theory                 | Describes the theory behind the ice-melting process and the freezing point depression. A thermodynamic model and an overview on other ice-melting tests are presented.  |
| <b>Chapter 3</b><br>Methodology            | The procedure and materials for the laboratory test are described. The chapter also give details on the thermodynamic model.<br><br>The chapter is divided into four parts, and discusses: <ul style="list-style-type: none"><li>• The calorimeter's accuracy, with results from a previous test with NaCl solution.</li><li>• The findings from own experiment on NaCl/<math>\text{MgCl}_2</math> mixtures.</li><li>• The use of the thermodynamic model to predict melting capacity</li><li>• The overall experiment method, with a comparison to existing tests.</li></ul> |
| <b>Chapter 4</b><br>Results and discussion |   |
| <b>Chapter 5</b><br>Conclusions            | The thesis is finalized by highlighting the main conclusions.   |
| <b>Chapter 6</b><br>Future work            | A description of possible future work within the thesis's topic.  |

Lastly the references are presented, as well as the appendices.



# 2 THEORY

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## 2.1 STANDARD THERMODYNAMIC PROPERTIES

Thermodynamics is the science of energy that concerns with energy transformations and relations to matter. A short description on basic thermodynamics properties relevant to the test method and ice-melting process is presented.

### 2.1.1 Definitions

In thermodynamics, a part of the universe in study is termed as the system, while everything else is noted as the surroundings. Depending on the type of system, exchanges of heat or matter can take place between its boundaries. Heat is a type of energy associated with the movement of atoms and molecules in a substance. The faster the movement of the atoms, the higher the temperature of a material gets, and therefore the greater amount of energy is present as heat. In open systems both heat and matter can be transferred, while in a closed system only heat can be exchanged. When no exchange to the surroundings is happening, the system is isolated.

Heat transfer is the exchange of thermal energy from one medium to another, and can be transferred as radiation, conduction or convection. The study of the transfer in energy as heat during physical and chemical process is known as calorimetry, where a calorimeter is the device that measures this. The transfer of heat always occurs from the region with higher temperature to the lower temperature region. Thus by measuring the temperatures of the different regions, the direction of heat flow can be determined (Atkins and De Paula, 2014).

An important thermodynamic property is entropy, which is a measure of disorder in a system. This is a basic concept in physics, which enables the comparison of different states in an isolated system. The different phases of a substance would have different measure of entropy. For instance, gas would have more entropy than liquid and liquid more than solid. The solid state is therefore the most stable out of the three.

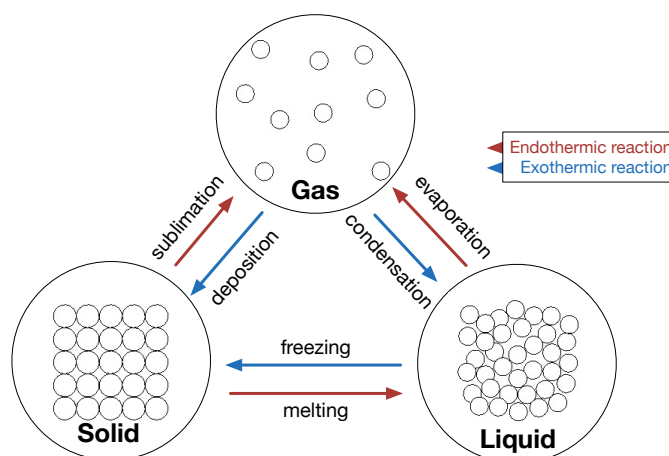


FIGURE 1: Phase transitions of water

Matter can exist in these three phases and it can also change from one phase into another; in other words, it can undergo a phase transition. Phase transitions occur at a characteristic temperature, and at this temperature the two phases are in equilibrium. Transitions can involve breaking intermolecular attractions, which would then require energy to break the forces between the particles. Examples of such transitions are melting, vaporization and sublimation. The inverse process would release energy and involves the forming of intermolecular attractions, e.g. freezing, condensation and deposition (Atkins and De Paula, 2014). The thermal energy that are released and absorbed in these processes are named latent heat, and refers to the amount of energy needed to change from one phase to another. A reaction is termed exothermic if it releases heat, while reaction that requires heat is endothermic (Figure 1).

### 2.1.2 Solution properties

The term solution is used for homogeneous mixtures of two or more substances. In such mixture a small amount of substance, known as solute, is dissolved in a solvent. Most solutions are aqueous solutions, meaning that their solvent is water, and when the mole fractions of the solute are small compared to the solvent, the solution is diluted.

In an ideal mixture, interactions in a microscopic level between the chemical species are the same. As a result, the mixture properties can be expressed in terms of simple concentrations of the substances present (e.g. Raoult's and Henry's law). This concept is fundamental to chemical thermodynamics, and for very dilute solutions, ideal properties are assumed. In contrast, the concept of non-ideal solutions is used for concentrated solutions. Since it is quite difficult to predict its properties when there are many forces that act on real mixtures. However, by identifying the strength and specifics of the intermolecular forces between molecules, the solution's properties can be identified (Martínez, 1992).

For those solutions whose property deviates considerably to the ideal, an activity coefficient is introduced. This is a factor used as a correction to account for deviations from ideal behavior because molecules in non-ideal solutions interact with each other, as they either attract or repel each other. Activity measures the effective concentration and determines the real chemical potential for a real solution. The chemical potential is defined as the ability of a medium to perform a change in system. Among other things, activity depends on temperature, concentration and composition of the mixture. Particularly, the activity of an ion is influenced by its surroundings. In this thesis, the activity for water will be used (see sections 2.4 and 3.3). Water activity describes the amount of water available for hydration of substances. Seeing as the water molecules interact with solutes and surfaces, it becomes unavailable for other hydration interactions, which is why the water activity is lowered when solutes are added. The water activity also usually increases with temperature and pressure increase (Chaplin, 2014d).

## 2.2 FREEZING POINT DEPRESSION

### 2.2.1 Basis and equation for freezing point depression

Water's freezing point is depressed when foreign molecules or ions are dissolved, which is known as a "colligative property". Colligative properties are physical properties of solutions that are dependent upon the amount of particles dissolved and not their structure (Atkins and De Paula, 2013).

The origin of this property is the change in the solvent's chemical potential. For instance, in an equilibrium mixture of pure water and ice at freezing point ( $0^{\circ}\text{C}$ ), the chemical potential of ice and pure water must be equal,  $\mu^{ice} = \mu^{liquid}$ . When solute is present the chemical potential of water is lowered. This is reduced by  $RT \ln x_w$ , which gives a new freezing point where  $\mu^{ice} = \mu^{solution}$ .

$$\mu^{solution} = \mu^{liquid} + RT \ln x_w \quad (1)$$

Where:  $x_w$  = The mole fraction of water  
 $R$  = The gas constant  
 $T$  = The new melting point of ice in contact with the solution

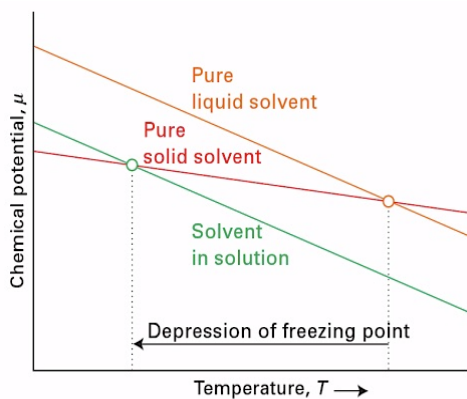


FIGURE 2: Chemical potential of pure solvent and solvent in a solution (Atkins and De Paula, 2013)

Figure 2 illustrates how the chemical potential decreases with higher temperature for pure solvent and solvent in solution. The intersection point where the chemical potential of the solid solvent (i.e. ice) rises above that of the liquid solvent (i.e. water) represents the freezing point of the pure solvent. Since the solid remains pure its chemical potential is unchanged, resulting in the intersection with the solvent in solution lying further to the left (Atkins and De Paula, 2013). In other words, the gap between the pure liquid solvent and the solvent in solution lines increases when more solute is added to the solution and thereby lowers the freezing point.

To calculate how far the freezing point can be depressed, an expression can be derived using equation (1) as the basis. A justification is included in Appendix B, which results in equation (2). This is a commonly used equation to express the lowering of freezing points when solutes are added, also known as Blagden's law. Blagden's law states that the depression of the freezing point of dilute solutions is proportional to the amount of the dissolved substance:

$$\Delta T = K_f \cdot m_s \cdot i \quad (2)$$

Where:  $\Delta T$  = The freezing point depression ( $^{\circ}\text{C}$  or  $\text{K}$ )  
 $m_s$  = The molality of the solution (moles solute/kg solvent)  
 $K_f$  = The cryoscopic constant (for water:  $1.8597 \text{ K/kg}\cdot\text{mol}$ )  
 $i$  = The Van't Hoff Factor

The Van't Hoff factor is a measure of particle dissociation in solution, and represents the number of particles that are liberated per molecule of solute dissolved. For instance, when NaCl is dissolved in water it dissociates into two ions, one each of Na<sup>+</sup> and Cl<sup>-</sup> for every NaCl formula unit. MgCl<sub>2</sub> dissociates into three ions, Mg<sup>2+</sup> and 2Cl<sup>-</sup>, giving it more particles dissolved for the same unit of substance. The Van't Hoff factors in this case are therefore 2 and 3 for NaCl and MgCl<sub>2</sub> respectively. Because of this, some solutes have a greater effect on freezing point depression than others.

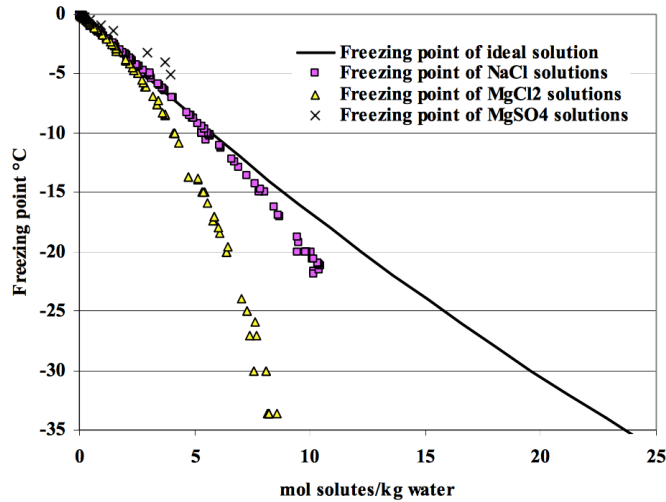


FIGURE 3: The theoretical freezing point depression of an ideal solution compared to the measured freezing point depressions of NaCl, MgCl<sub>2</sub>, and MgSO<sub>4</sub> solutions (Thomsen, 2009)

The figure also illustrates how the freezing points of the various solutions follow those of an ideal solution at higher temperatures, more so for sodium chloride solutions than for magnesium chloride. However, as the temperature passes below circa -5°C the freezing points start to deviate from the ideal line, increasingly so with higher molality (mol solutes/kg water). Equation (3) can therefore be used to indicate freezing point depressions at lower concentrations, as the deviations are relatively small, but when dealing with lower temperatures the importance of the solute's identity is increased.

Freezing curves are therefore often created using experimental data because of the deviation from the ideal solutions. Chaplin (2014a) states that the deviation is due to different types of interaction such as the bound water of hydration, ion pair formation, and also changes in the enthalpy of fusion with temperature. Thus at higher concentrations, i.e. non-ideal solutions, an expression with the water activity  $a_w$  can be used instead, to indicate freezing point depression (from appendix B, equation B.3):

$$\ln(a_w) = -\frac{\Delta H_{fus}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (3)$$

Equation (3) will be used later in section 3.3 when creating phase diagrams for mixtures.

However, the equations (1 and 2) and justification (Appendix B) are based on ideal solutions, since all solutes have identical colligative properties in ideal solutions. Since no solution is completely ideal, the freezing point depression will therefore depend on the identity and concentration of the solute. Figure 3 shows the freezing point for various salt solutions, and illustrates clearly that the freezing points are in fact dependent on the type of solute (Thomsen, 2009).

### 2.2.2 Phase diagram

The substance behaviour under different conditions can be summarized in a phase diagram. Such a diagram is illustrated in Figure 4 and consists of four areas separated by the freezing curve, the solubility curve, and the eutectic temperature.

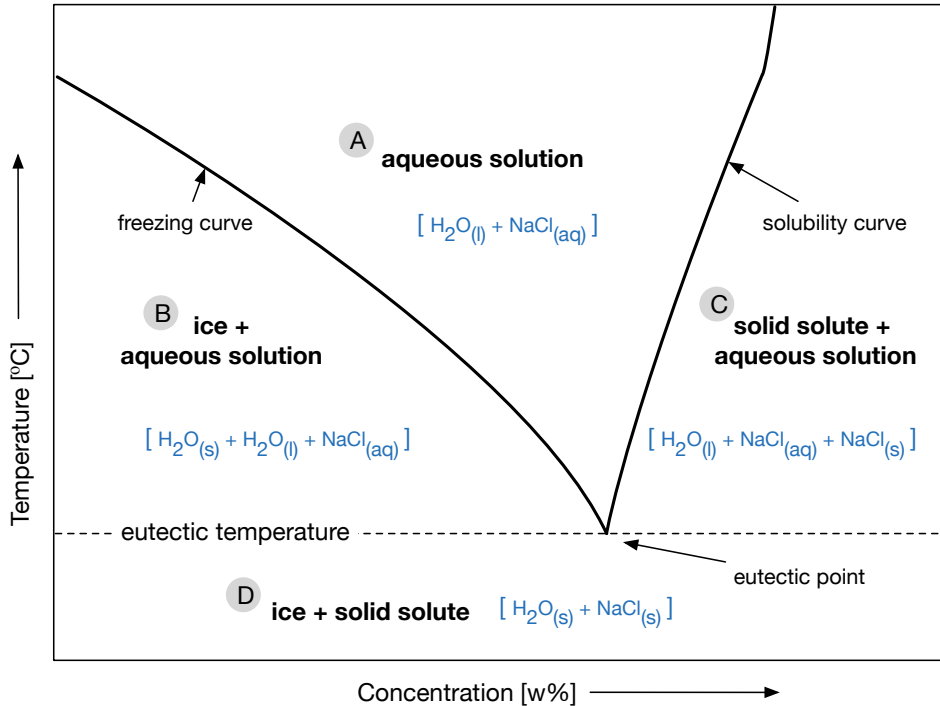


FIGURE 4: Description of different areas in a phase diagram

The freezing point temperature is the temperature at which ice crystals begin to form, and the freezing curve then illustrates the solution concentration (w%, weight percentage) needed to depress this. The freezing point can be lowered until it reaches the eutectic point, which is the lowest temperature at which the solution can exist at equilibrium. Beyond this is where the solubility curve starts, and this is the limit beyond which the solute cannot be further dissolved in water at a specific temperature. A change in phase occurs at a characteristic temperature for a given concentration. At these transition temperatures the two phases are in equilibrium, i.e. their chemical potentials are equal (Atkins and De Paula, 2014).

Figure 4 uses NaCl as an example of the different states a mixture of NaCl and H<sub>2</sub>O has for different composition and temperature, where (s), (aq), and (l) refers to solid, aqueous (dissolved), and liquid respectively. These areas are:

- A. Aqueous solution:** The solvent is in liquid form and the solute is dissolved.
- B. Ice + aqueous solution:** Some water is frozen, but some remains liquid since the temperature is not low enough. The amount of ice molecules will depend on the temperature and concentration – the closer to the eutectic temperature, the more ice exists, and the higher the concentration, the less ice exists.
- C. Solid solute + aqueous solution:** No ice exists, but the solute starts to crystallize.
- D. Ice + solid solute:** All water molecules and solutes are solidified.

### 2.2.3 Solution and ice-system in detail

Consider an ice cube being submersed in a solution at the same temperature. Depending on the concentration, ice will either melt or form, and thus energy must be either added or released. The transition from ice to water in particular is highly endothermic, as it would require 334 kJ to melt a kilo of ice. The molecules in the liquid state are much more energetic and move a lot more freely (they have a higher entropy) than in the solid state. So for ice molecules to go over to the liquid state, kinetic energy is needed, which they will initially take from their neighbouring molecules. This causes the ice temperature to decrease, but as the deicer has a lower freezing point, water molecules are prevented from freezing.

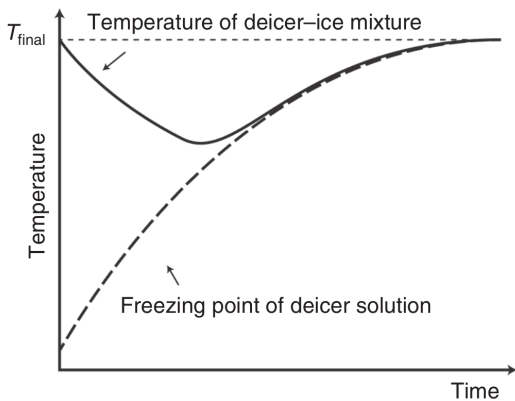


FIGURE 5: Temperature and freezing point development during the melting process with heat flow from the environment (Klein-Paste and Potapova, 2014)

However, as the melting process continues the deicer is diluted by the meltwater, which causes the freezing point to increase. Now, since the temperature of the ice and the solution have decreased they are getting colder than the environment (air, pavement, radiation). Because of this, heat from the surroundings is allowed to flow to the melting front and supports the melting process (Klein-Paste and Potapova, 2014). This development in temperature and freezing point is illustrated in Figure 5.

As the temperature decreases, heat from the environment can eventually warm up the system again. This allows further melting because a lower concentration of deicer is needed to keep the meltwater at its freezing point. The process stops when the temperature of the system has reached the freezing point of the deicer solution, as phase equilibrium is reached.

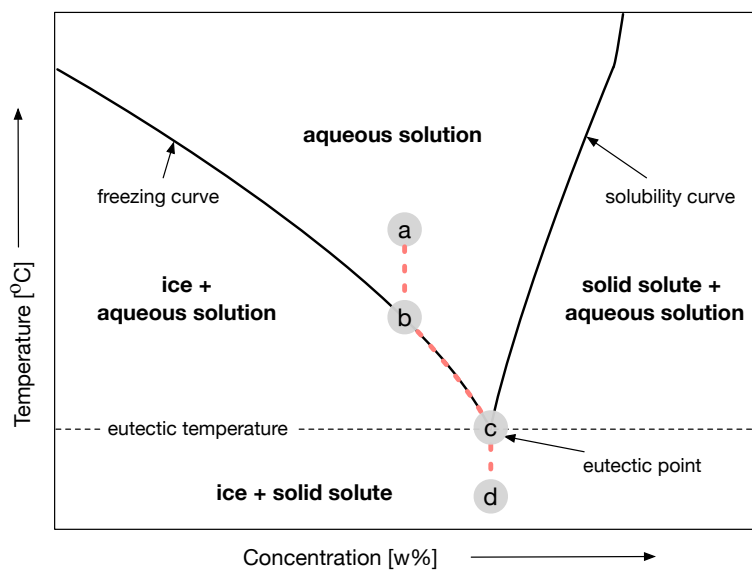


FIGURE 6: Freezing process in a phase diagram

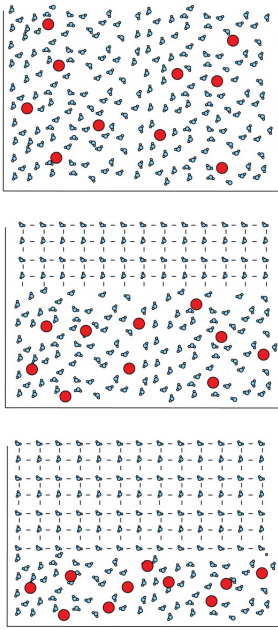


FIGURE 7: Freezing process of a solution on a molecular level (Klein-Paste, 2014)

The inverse transition, the freezing process, would lead to a higher solution concentration. To explicate the change in a phase diagram, one can think of a solution at point **a** in Figure 6; at this point the solution will not freeze. When the solution is cooled to a point where it meets the freezing curve (point **b**), some ice will start to form. The ice formation does not easily allow the solute in its crystal structure, and therefore only the water molecules solidify. This process is illustrated in Figure 7, where the red molecules represent the solute in the solution. The solute is excluded from the ice formation and the remaining liquid is therefore more concentrated. Note that the composition of the whole system is still the same, and would continue vertically in the diagram. But the solution's composition follows the dotted line in Figure 6, as a higher concentration leads to a lower freezing point. This continues until it reaches the eutectic point (point **c**, in Figure 6), where further cooling will only result in solidification of the remaining solution (point **d**).

### Freezing curves for NaCl and MgCl<sub>2</sub>

As explained earlier, different solutes will result in different freezing curves, solubility curves, and eutectic temperatures. The eutectic point for NaCl solution occurs at -21°C at 23 w% (5.17 mol/kg NaCl). The eutectic point for MgCl<sub>2</sub> solution occurs at -33°C at 22 w% (3 mol/kg MgCl<sub>2</sub>).

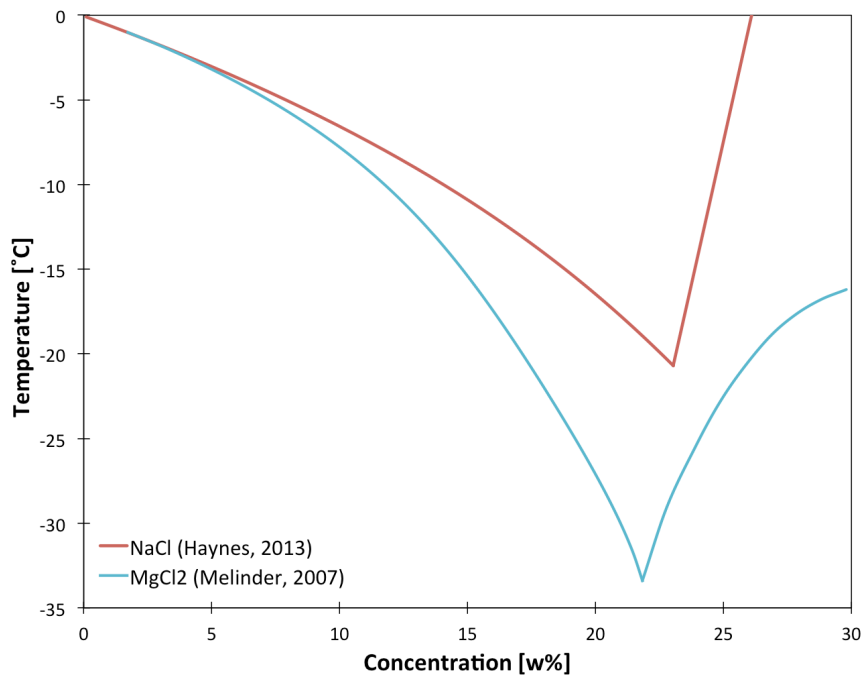


FIGURE 8: Freezing and solubility curves for magnesium chloride and sodium chloride

Freezing curves for NaCl and MgCl<sub>2</sub> are presented in Figure 8, created using data from Haynes (2013) and Melinder (2007), and shown with their respective solubility curves (Ketcham et al., 1996). Based on these data, equations for the freezing curves are found using regression:

$$NaCl_{C_{end}(T)} = -5.47e^{-6}T^3 - 0.00044457T^2 - 0.018024T - 0.00071303 \quad (4)$$

$$MgCl_{2_{C_{end}(T)}} = -2.666e^{-7}T^4 - 2.4026e^{-5}T^3 - 0.00085266T^2 - 0.018147T - 1.7985e^{-5} \quad (5)$$

### 2.3 ICE-MELTING CAPACITY

The phase diagram can also reveal information about a solute’s melting capabilities. How much ice in total can the solute melt – i.e. what is its ice-melting capacity? To explain this, consider a solution at point **a** in Figure 9. Here the temperature is -10°C and the concentration is 23 w%. When the solute melts ice, the solution is diluted by the meltwater which leads to a lower solution concentration. This process is shown as a horizontal dashed line, where as more ice melts, the solution moves closer to the freezing curve. This process stops when it meets the freezing curve. Here a MgCl<sub>2</sub> solution would be able to melt more ice than a NaCl solution because its freezing point lies further to the left. The blue dashed line here signifies the additional ice that MgCl<sub>2</sub> can melt at the same solution concentration.

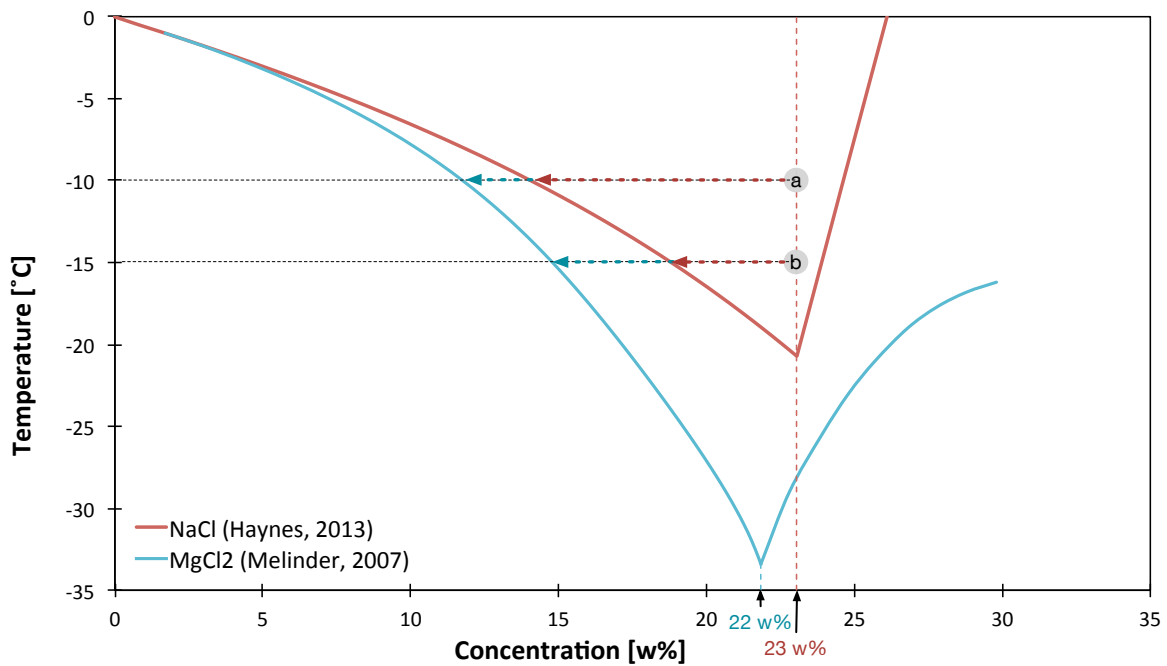


FIGURE 9: Phase diagram illustrating ice-melting capacity

From this figure, one can also see that the difference in melting capacity between the two solutes increases with lower temperature. At point **b**, for instance, at -15°C, MgCl<sub>2</sub> could melt almost twice as much ice as NaCl at the same concentration. Note that the total ice melt for MgCl<sub>2</sub> would be the sum of the red and blue horizontal lines.



### 2.3.1 Specific melting capacity

With the freezing curves defined, it is possible to calculate the theoretical ice-melting capacity. For a particular amount of the solution ( $m_{\text{solution}} = m_{\text{solute}} + m_{\text{water}}$ ), the melting capacity can be calculated with the following equation:

$$\text{Melting capacity} = \frac{m_{\text{solute}}}{C_{\text{end}(T)}} - m_{\text{solution}} \quad (6)$$

where  $C_{\text{end}(T)}$  is the concentration at which a solution will freeze at temperature T, found via equation (4 or 5), and  $m_{\text{solute}}$  is the amount of solute. Another way to express the melting capacity is the specific ice-melting capacity, which is measured by the mass of ice melted per gram of solute ( $m_{\text{ice}}/m_{\text{solute}}$ ). This can be found directly from the end concentration by using the definition of a solute concentration (weight percentage):

$$C = \frac{m_{\text{solute}}}{m_{\text{solute}} + m_{\text{water}}} \quad (7)$$

Here the  $m_{\text{water}}$  would be the same as the total amount of water molecules in  $C_{\text{end}(T)}$ . With this definition, the theoretical ice-melting capacity can be rewritten as the specific ice-melting capacity:

$$\begin{aligned} \text{Specific melting capacity} &= \frac{m_{\text{water}}}{m_{\text{solute}}} = \frac{\frac{m_{\text{solute}}}{C_{\text{end}(t)}} - m_{\text{solute}}}{m_{\text{solute}}} \\ \text{Specific melting capacity} &= \frac{1}{C_{\text{end}(T)}} - 1 \end{aligned} \quad (8)$$

Using equation (8) the ice-melting capacity per gram of solute can be found from the freezing point concentration obtained from equation (4) and (5).

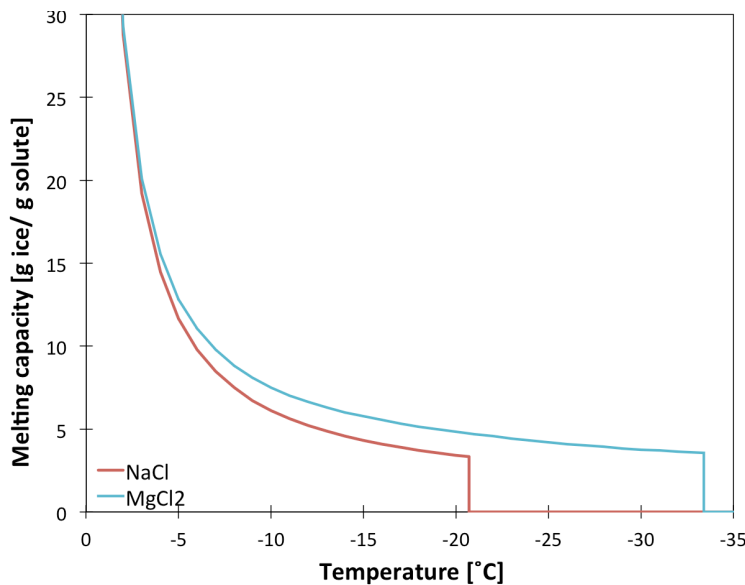


Figure 10 illustrates the specific melting capacity for a gram of NaCl or MgCl<sub>2</sub> at different temperatures. As seen from the figure, the melting capacity for MgCl<sub>2</sub> is slightly higher and is able to melt ice at lower temperatures than NaCl. This also shows that after the eutectic temperature is reached, the solute is not able to melt more ice, resulting in zero specific ice-melting capacity.

FIGURE 10: Specific ice-melting capacity at different temperatures, created using data from Haynes (2013), Melinder (2007)

### 2.3.2 Ice-melting rate and optimum solution concentration

Even though the ice-melting rate is not directly measured in this study, it is important to distinguish this from the ice-melting capacity. Ice-melting rate is the amount of time it takes for a solute to release all of the ice-melt it has available; in other words, it tells us how fast a deicer works. As discussed in the previous section, the ice-melting capacity is the fixed amount of ice-melt available for different solutes at a given temperature. The ice-melting rate on the other hand depends upon the mechanism of the melting process and can be affected by factors such as traffic action, temperature, deicer size, dry vs. pre-wetted deicer, etc. (Koefod et al., 2015).

The lowest experience-based operating temperatures for NaCl and MgCl<sub>2</sub> are found from a literature review (Holen, 2010) to be -10°C and -23°C respectively. Koefod et al. (2015) reveals that the reason they are considered ineffective below these temperatures is due to the ice-melting rate and not the melting capacity. In their study ice-melting capacity measurements were taken near the eutectic temperature for NaCl, at -20°C. The results show that NaCl has a substantial ice-melting capacity at this temperature, but the ice-melting rate is very slow. They also show that the melting rate was higher after pre-wetting the NaCl.

Another notable topic to clarify is the common misconception that the optimum solution concentration is at the eutectic point. As a solution with higher concentration than the eutectic point crystallizes at certain points, this limits its capacity to melt. However, this solid solute remains an effective deicer, as it will continue to melt ice when the temperature increases or the solution becomes sufficiently diluted by meltwater. So, as long as residual deicer remains on the road, it may continue to provide valuable ice-melting for periods of time that far extend the time of initial application. Therefore, from an ice-melting standpoint, there is no advantage to diluting the solute to its eutectic concentration, and it is most advantageous to use the highest concentration possible, as more solute will melt more ice (Koefod, 2008).

## 2.4 EXTENDED UNIQUAC MODEL

A thermodynamic model is used in this thesis to create phase diagrams for two liquid mixtures (see section 3.2.1). The extended UNIQUAC model is an extension of the original UNIQUAC model by Abrams and Prausnitz (1975), which is a liquid-phase activity coefficient model used to calculate fluid phase equilibria. The model in its current form is presented by Thomsen (1997). The model accounts for both the short-range and long-range interactions between all species (ions and solvent), and with the summation of these factors, an activity coefficient for ions or water can be calculated.

In this thesis, the model is used to calculate the water activity coefficient, which is used to find the mixture's phase equilibrium (freezing point); the method of use is further described in section 3.3. The main input and output parameters for the extended UNIQUAC model in use are illustrated in Figure 11.

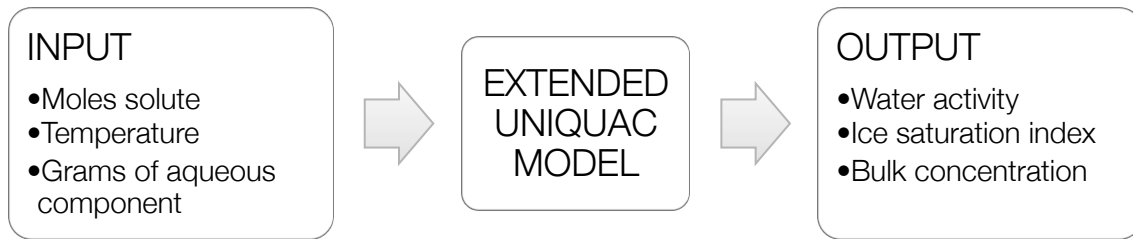


FIGURE 11: Input and output parameters for the extended UNIQUAC model in use

## 2.5 EXISTING TESTS

There are different test methods to characterize a deicer's performance. A literature review was conducted to identify existing ice-melting tests and to briefly describe issues regarding different tests. Additionally, a freezing point determination test (ASTM D1177) is described.

### 2.5.1 The SHRP ice-melting tests H-205.1 and H-205.2

The Strategic Highway Research Program (SHRP) sponsored the development of a handbook of test methods for evaluating chemical deicers. One of the standardized test methods for evaluating deicing performance is the ice-melting test for solid and liquid deicers (SHRP H-205.1 and H-205.2 respectively). The test measures the amount of ice melted by the deicer as a function of time and temperature.

The test uses a sheet of uniformly thick ice (3.175 mm) frozen in a flat circular Petri dish (22.86 cm diameter). After the desired temperature is reached, a weighed quantity of liquid deicer is distributed over the surface of the ice via a syringe. The amount of melted ice is measured at specified time intervals by decanting the water using a syringe. The water is then reintroduced to the sample so that the melting process can continue (Chappelow et al., 1992).

The SHRP test doesn't require heavy equipment, has a relatively simple procedure, and can test both liquid and solid deicers. On the other hand, this test method is prone to modifications which can complicate comparisons, and also suffers from a great deal of variation. Some sources of error are the difficulty of recovering all ice melt, and the lack of traffic simulation that slows the ice melting progress to an extent. For instance, Koefod et al. (2012) mentions that the ice-melting capacities of standard rock salt sodium chloride can vary by as much as 35% using SHRP H-205.1.

### 2.5.2 Modified SHRP ice-melting test

Since the SHRP ice-melting test suffers from a great amount of variability, several studies have performed modifications to the test. Table 1 shows some of the different modifications applied, which are based on specific applications and aim to make the test more reproducible.

TABLE 1: Modifications to the SHRP ice-melting test

Reference	Modification	Results/Conclusions
Nixon et al. (2005)	Water and deicer level was varied at four different temperatures to compare seven liquid deicers. The test uses less water and more deicer to attain more ice melting.	The test enables the comparison of deicer performance over a temperature range, and helps select the best deicer for a particular condition.
Shi et al. (2009)	The surface area is reduced (radius of 3.5 cm) to limit absorption rate.	Rate of dissolution of solid deicers may have affected reproducibility, as dissolution is dependent on the particle size and the amount of brine needed for precise measurements.
Akin and Shi (2012)	The test uses a smaller Petri dish requiring less ice and deicer, which also allowed more tests to be conducted simultaneously. It incorporates a reference substance using 23% NaCl to determine the acceptability of the procedure.	The study recommends fewer measurements (20 and 60 min after application). To discourage inappropriate comparisons, the average brine volumes and coefficient of variation (CoV) should be reported for the test deicer, unless it is less than 1.0 ml, in which case the standard deviation should be reported instead of CoV.
Koefod et al. (2012)	The test duration was extended to 5 and 7 hours (instead of 1 hour) and the deicer application rates were increased (4, 8, 12 and 16 g were tested).	The precision and accuracy of the test was improved significantly. Measurements for solid NaCl show that by increasing the application rate to 8 g or higher and increasing the measurement time to 5 hours or longer, the CoV decreased from about 19% and 23% to about 2% and 7%.

### 2.5.3 DSC thermogram test

The differential scanning calorimetry (DSC) thermogram test is an experimental method proposed by Shi et al. (2009) to investigate deicer performance. The DSC was used to quantify thermal properties by measuring the amount of thermal energy that flows into the deicer during the solid/liquid phase transition.

The DSC operates with a cell for an inert reference material and another cell for the test sample (the deicer). These are subjected to a warming/cooling cycle with a constant heating/cooling rate, where the DSC measures the energy needed to maintain a zero temperature difference between the two cells. For data analysis Akin and Shi (2012) found that the warming cycle is preferred since the cooling cycle data were sometimes compromised by the effects of supercooling.

Akin and Shi (2012) found the DSC to be reproducible for deicer tested at a given dilution ratio and cooling/heating rate. It was found that the results from the modified SHRP ice-melting test correlated with the DSC results, but since the DSC also provides the characteristic temperature, this test method is preferred. Overall this method can indicate the effective temperature and ice-melting capacity, and may be more reproducible than other

tests. However, the method is fairly new and still lacks standardization of parameters like temperature range, heating/cooling rate, and deicer concentration.

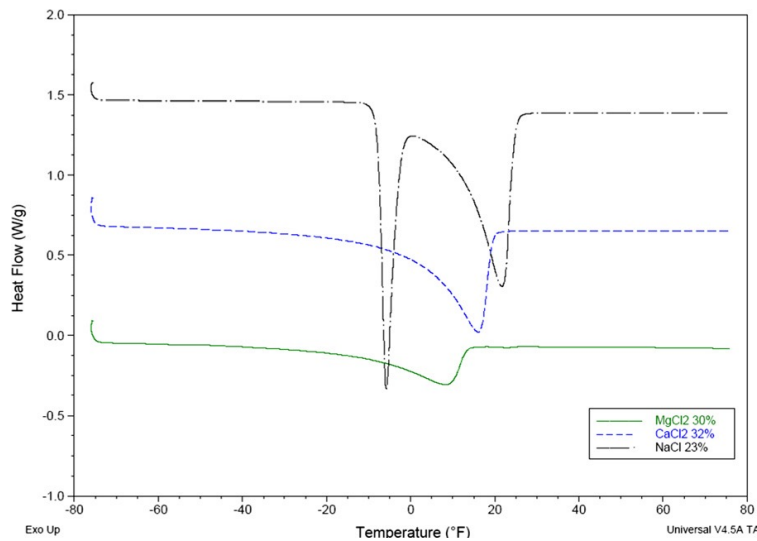


Figure 12 shows examples of DSC thermograms for three deicers: 23% NaCl, 32% CaCl<sub>2</sub>, and 30% MgCl<sub>2</sub> brines. The characteristic temperature can be found as the peak of the warmer temperature range. This is the point at which ice crystals begin to form, and corresponds well with the effective temperature of the deicer.

FIGURE 12: DSC thermograms of 23% NaCl, 32% CaCl<sub>2</sub> and 30% MgCl<sub>2</sub> brines (Akin and Shi, 2012)

#### 2.5.4 Mechanical rocker ice-melting test

Another experimental method for ice-melting capacity evaluation was developed using a martini shaker, and is able to simulate road conditions better than the standardized test. It was first developed by Gerbino-Bevins (2011) and later revised by Tuan and Albers (2014) with the objective of transforming it into a standardized procedure.

To conduct the test, 30 ml of the deicer chemical is chilled inside a thermos (shaker) and placed within a freezer at the desired temperature. A small number of ice cubes (33 ice cubes with 1.30 ml volume) are frozen in the same environment. Empty styrofoam cups are weighed with and without the ice cubes to determine the ice cube mass. Within the freezer the ice is added to the thermos with the deicer, and then taken out to be placed on a mechanical rocking platform. The platform is set to a particular tilt and rocked for a given period of time. The remaining ice is then sieved and weighed in another styrofoam cup. The ice melting capacity is determined by subtracting the final mass of ice from the initial mass and dividing the difference by the amount of liquid deicer used (Tuan and Albers, 2014).

#### 2.5.5 Ice cube titration

In an effort to measure ice-melting capacity more precisely, Koefod et al. (2012) developed an alternative approach. Since a key source of variation from the SHRP tests was recovering the meltwater from the ice, in this method the ice is instead removed from the deicer solution.

The method involves adding ice cubes to a beaker holding 400 g of the deicer solution with continuous stirring. The ice is then periodically removed and the weight of the beaker is measured, where the weight will increase as long as the ice is melting. System equilibrium is reached when the weight of the beaker stops changing and the deicer is not able to melt more

ice. The total amount of ice melted is calculated to be the difference between the initial and final weights of the solution.

An impracticality of this approach is that it can take a long time before system equilibrium is reached. A shortcut was therefore implemented by pre-diluting the deicer brine close to the limit of its ability to melt more ice. The ice cube titration is then carried out to determine the final amount of ice melted.

### 2.5.6 ASTM D1177

A standardized test method developed by the ASTM (American Society for Testing and Materials) for engine coolants has been adapted to provide freezing curves for deicers. The ASTM D1177 test is performed by slowly cooling down the brine by immersing it in a cooling bath. As the cooling process starts the brine is stirred, and the temperature is measured (ASTM, 2012).

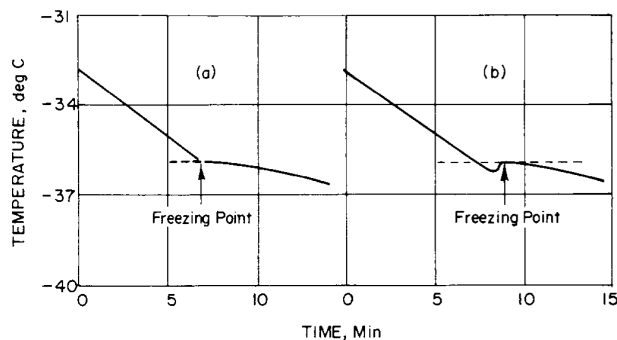


FIGURE 13: Time-temperature cooling curves for determining the freezing point (ASTM, 2012)

The freezing point is defined as the temperature at which crystallization begins and is determined as the intersection of the cooling curve and the freezing curve. As Figure 13 shows, there is a clear break in the curves plotted in this test. If the solution supercools, the freezing point is the maximum temperature reached after supercooling (Figure 13b).

Issues arise when testing deicers with organic additives (e.g. sugars, glycols, certain proteins). The additives behave as cryoprotectants, which slow down the freezing process without lowering the freezing point of water. Rather than a defined freezing point they have a “glass transition temperature” with a smoother curve, and they can thereby “fool” the freezing point test. This is discussed by Koefod (2008), where a cooling curve for pure liquid potassium carbonate was compared with a cooling curve for potassium carbonate liquid blended with 25% agricultural liquid. The transition from the cooling portion to the freezing portion is much less clear for the condition blended with 25% agricultural additive (Figure 14).

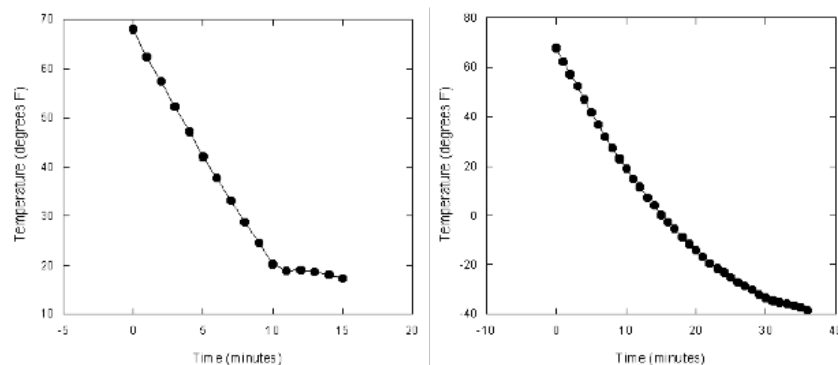


FIGURE 14: Cooling curve measured for pure potassium carbonate liquid (left) and potassium carbonate liquid blended with 25% agricultural liquid (right) using ASTM D1177 (Koefod, 2008)

# 3 METHODOLOGY

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## 3.1 NTNU CALORIMETER

In this section the materials required for conducting the laboratory experiments are presented. The calorimeter with hardware was developed by NTNU and was built prior to the tests.

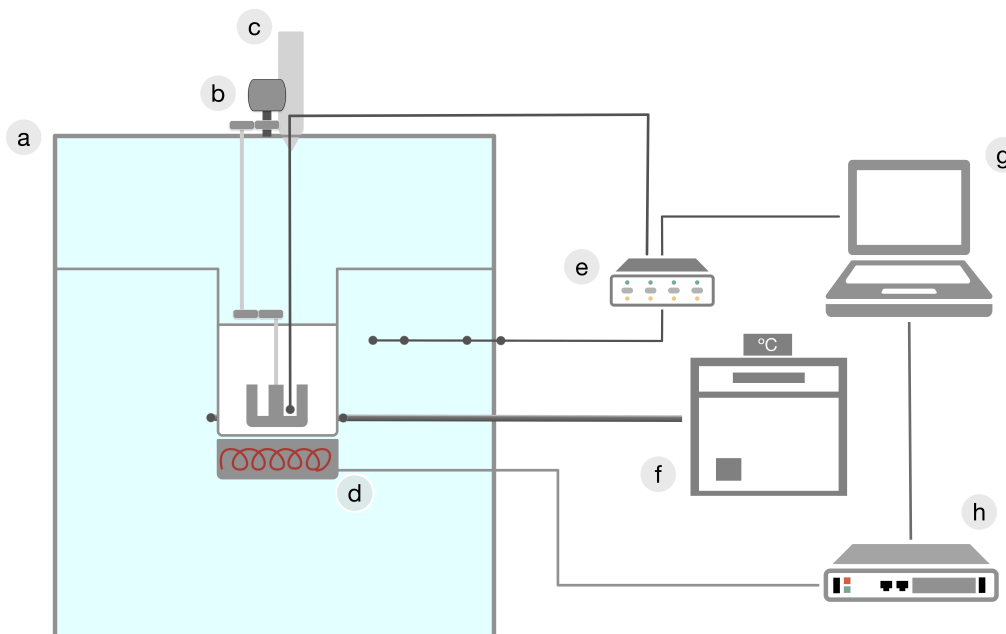


FIGURE 15: Components of the NTNU calorimeter

The calorimeter consists of the following components (Figure 15):

- a. **Insulated reactor** – The reactor is a cylindrical stainless steel container with a volume of 0.5 l. It has 12.5 cm thick polystyrene as insulation, a 10 cm thick lid, and an additional 5 cm overlapping the container.
- b. **Stirrer** – Placed on top of the lid, rotating at 15.5 rpm.
- c. **Hole for inserting ice** – This is covered with an insulation-filled syringe to minimize heat leakage. The syringe is temporarily removed when ice is inserted, and a funnel is used to assist the ice to pass through the opening.
- d. **Heater** – An electrical heater (500 W) is positioned below the reactor.
- e. **Data logger** – Actual output voltage and current are continuously measured and recorded by the data logger (National instrument type NI USB-6211). This registers the temperature of the solution, the air temperature outside the reactor, and the temperature through the insulation (2.5, 5 and 10 cm from the reactor).
- f. **Cryostat** – This cools the reactor and solution prior to the test. The tube with the cooling liquid surrounds the reactor once, minimizing the cooler's surface area.
- g. **Computer** – Regulates the heater as well as monitors the system's temperature with a programme named Labview.
- h. **Power supply** – A regulated 160 V DC power supply (max 4A) powering the heater.

The reactor was placed in the frost laboratory (Figure 16) and regulated to the same temperature for the specific tests. The solutions and ice were also stored in the same room giving consistent temperature settings.

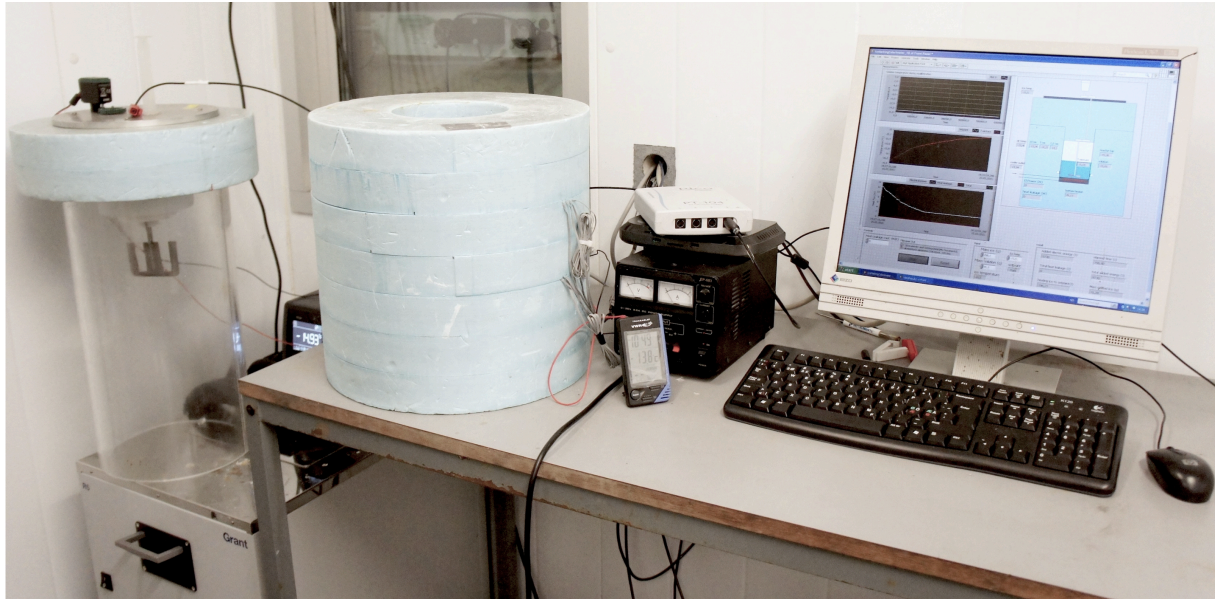


FIGURE 16: Equipment setup inside the frost lab

## 3.2 EXPERIMENT PROCEDURE

### 3.2.1 Test preparation

#### **Preparation of the solutions**

Two different mixtures of NaCl and MgCl<sub>2</sub> solutions were tested in this study. To prepare the solutions the required amount of the solute was dissolved in distilled water. The 23w% NaCl solution was prepared by weighing 230 g of solid NaCl and adding distilled water to the beaker so that the total weight was 1000 g (0.1 g accuracy). For the 22 w% MgCl<sub>2</sub> solution, 469.3 g of MgCl<sub>2</sub>-6H<sub>2</sub>O (hexahydrate) was weighed. Then distilled water was added until 1000 g total weight was achieved.

The prepared solutions were then mixed to obtain 50/50 and 80/20 mixtures of the NaCl and MgCl<sub>2</sub> solutions. Each mixture gives the following amount of salt:

TABLE 2: Solute mass and weight percentage of each mixed solution

Mixture (2000 g)	50/50 mixture	80/20 mixture
NaCl	230 g (11.5 w%)	368 g (18.4 w%)
MgCl <sub>2</sub>	220 g (11.0 w%)	88 g (4.4 w%)



## Ice preparation

The ice used in this experiment was prepared under low temperature conditions in the cold room. Ice cubes were crushed and sieved with an 8 mm sieve to remove small particles and to provide a more uniform sample. Originally snow was used in the tests, but this quickly proved to be unsuitable. The snow absorbed a lot of the solute, resulting in a lump of snow that formed and was mixed by the mixer. Therefore the temperature sensor was not able to measure the correct temperature as it remained in the air, altering the position. Compared to fine snow, crushed ice does not absorb water in the same way.

200 g of ice was added with the measurements taken at temperatures of -10 and -15°C, while 150 g ice was used at -20 and -23°C.



FIGURE 17: Ice and 8 mm sieve

## Cooling the solution

When the mixture was prepared, the amount used in the experiment was registered. The beaker with the mixture was weighed before and after the solution was poured into the reactor. The amount needed to be at least 90 g so that the solution could reach the temperature sensor located inside the reactor. The calorimeter with the mixture as well as the frost lab were cooled to the same temperature so that heat leakage was minimal. The computer monitored the temperature variation, and when the temperature through the insulation was approximately  $\pm 0.5^\circ\text{C}$ , a steady state was reached. The coolant was then turned off, since it was not possible to determine the energy the cooling liquid provide the system. To ensure minimal temperature variation, we waited approximately 5 minutes after the cooler was turned off. The test was then ready to begin, and the solution's start temperature (set temperature) was registered in Labview.

### 3.2.2 Ice-melting process in the calorimeter

The tests were conducted at four different temperatures (-10, -15, -20 and -23°C), where the objective was to study the mixture's ice-melting abilities in cold temperatures. Before starting the test, some input parameters had to be registered in Labview. These were the amount of solution added (in grams), the mass of ice (in grams), and the temperature of the ice.

As the ice was inserted in the reactor, the mixture started to melt the ice since there was enough solute to depress the water's freezing point below the set temperature. Given that the melting process is endothermic, the temperature dropped when ice was melted. To counteract this change in temperature, the heater added heat. The added heat depended on the temperature differences of the solution and the set temperature. The more the mixture was able to melt, the more heat had to be added so that the melting process could continue. The total heat added was what the calorimeter registered to calculate the total ice melted. As an example, Figure 18 shows the temperature development as well as the added heat for test\_149 (an experiment at -15°C).

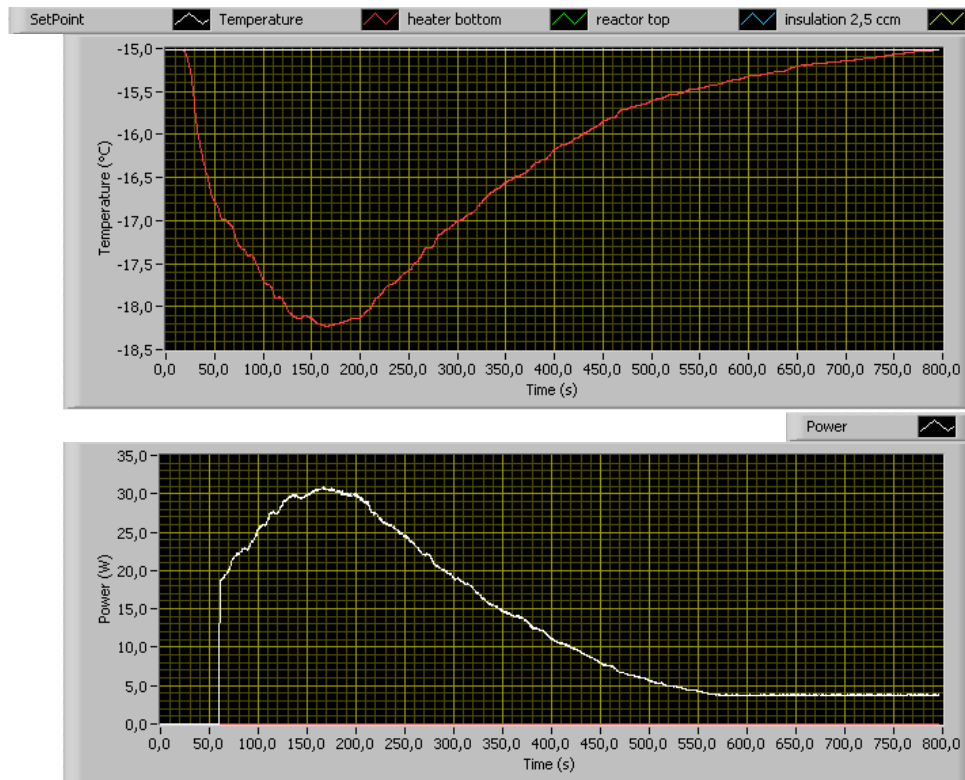


FIGURE 18: Temperature development inside the reactor at -15°C, test\_149

The figure shows the decline in temperature as the testing starts, and simultaneously, the added heat to counteract the change. In this way, the calorimeter accelerates the ice-melting by adding heat. This is comparable to the real-world situation, where ice would take energy from its surroundings (e.g. air, pavement, etc.). The melting process would continue due to the difference in temperature, since that enables the heat to flow to the melting front. The stirrer also induces simulation, similar to the stirring effect of traffic, and makes sure that all of the ice has contact with the mixture. Eventually, the heater will heat up the system,

illustrated as the increase in temperature (Figure 18). The increase in temperature would result in further melting due to lower solution concentration was needed to keep the melt water at its freezing point. This process continued until the set temperature was reached, as the mixture could not melt more ice and ultimately the programme ends the test. Note that as it approached the set temperature, less heat was added to accurately stop the test.

### 3.2.3 Amount of melted ice and the freezing point concentration

The Labview programme monitored the temperature change in the system, and regulated the heat added to the reactor. With the total heat added to the system registered, the programme also calculated the amount of melted ice, which can be expressed by:

$$m_{melted\ ice} = \frac{Q_{added} - C_p \cdot \Delta T \cdot m_{ice}}{L_{setpoint}} \quad (9)$$

where:

- $Q_{added}$  = Total heat added (J)
- $C_p$  = Specific heat capacity of ice (J/gK)
- $\Delta T$  = Difference between Setpoint and ice temperature (K)
- $m_{ice}$  = The amount of ice added (g)
- $L_{setpoint}$  = The latent heat at Setpoint (J/g)

The ice's temperature will likely differ from the set temperature, and the temperature difference from setpoint temperature was accounted for when calculating the total ice melted in the end of the experiment. The end concentration of the mixture can be calculated as:

$$C_{end} = \frac{m_{solute}}{m_{solution} + m_{melted\ ice}} \quad (10)$$

This was the solution concentration where equilibrium was obtained, as the solutes were not able to melt more ice at the particular temperature (set temperature). Equation (10) was used to create the solution's freezing curve. To convert the calculated freezing concentration to the specific ice-melting capacity curve equation (8) was used.

## 3.3 PHASE DIAGRAM FOR MIXED SOLUTIONS

The freezing curves for the mixed solutions were created using the calculated water activity coefficient  $a_w$  described in section 2.4. The input parameter needed to calculate this was the moles solute, temperature and grams of aqueous component (i.e. water). The model also calculated the ice saturation index and the mass % of the solutes (w%). Equation (3) is used and by solving the equation for T, the freezing point depression for the solution was obtained:

$$T = \left( \frac{1}{T_0} - \frac{R \ln a_w}{\Delta H_{fus}} \right)^{-1} \quad (11)$$

where:

- T = The new freezing point depression in K
- $T_0$  = The freezing point for water (273.15 K)
- R = The gas constant (8.3144621 J/mol·K)
- $a_w$  = The water activity coefficient
- $\Delta H_{fus}$  = The molar heat of fusion (6009.5 J/mol)

The 50/50 mixture was represented by 2.539/1.491 mol NaCl/MgCl<sub>2</sub> per kg water, while the 80/20 mixture was represented by 4.078/0.599 mol NaCl/MgCl<sub>2</sub> per kg water. The resulting water activity was inserted in equation (11), to calculate the new freezing point.

The amount of water in the input was increased to obtain different concentrations. Which resulted in different degree of water activity and enabled the freezing curves for the mixtures to be generated. The ice-melting capacity curves on the other hand, was created by using equation (8), which converted the freezing concentration to the specific ice-melting capacity.

# 4 RESULTS AND DISCUSSION

## 4.1 CALORIMETER ACCURACY

### 4.1.1 Results from the NaCl-experiment

One of the tasks for this master's thesis was to compare the measured ice-melting capacity of NaCl with the theoretical (calculated) melting capacity. To do this, measurements obtained by PhD candidate Kine Nilssen are presented. The experimental procedure was the same as described earlier; the only difference lies in the amount of ice added. The solid red line represents the theoretical ice-melting capacity (Figure 19) and freezing curve (Figure 20) for NaCl, while the data points represent the measurements obtained.

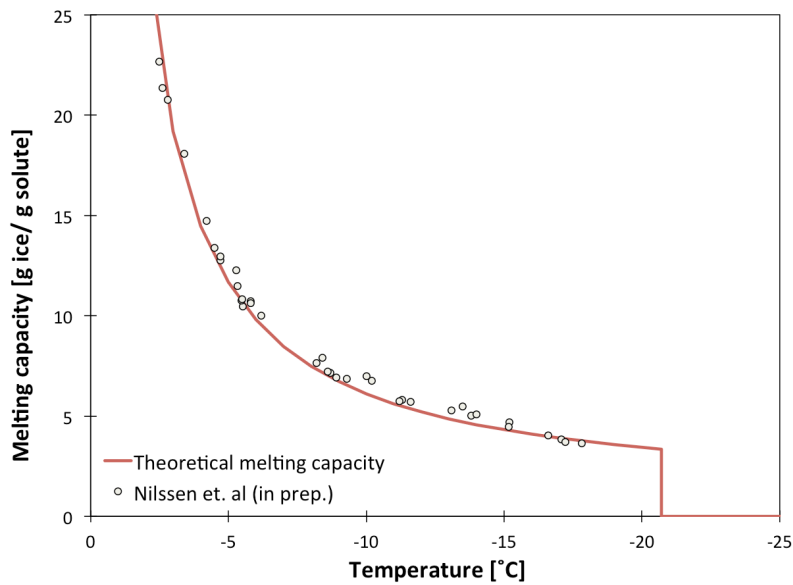


FIGURE 19: Ice-melting capacity results using 23 w% NaCl solution

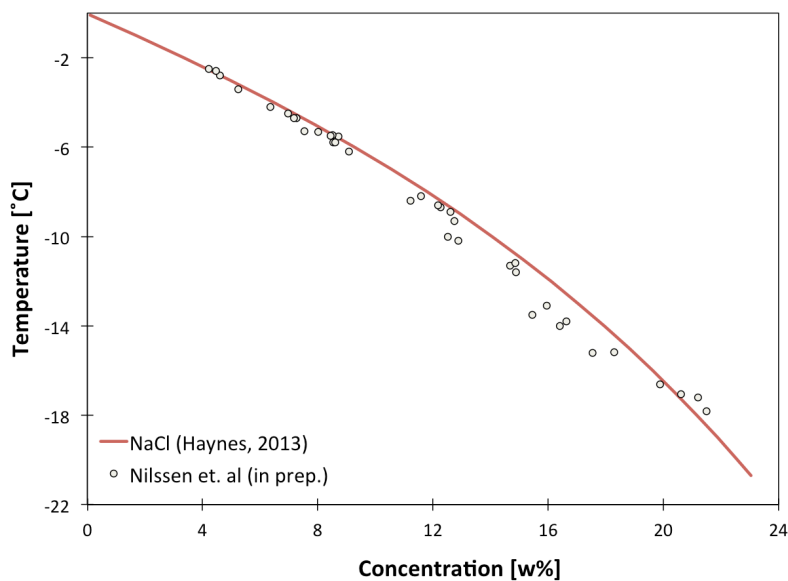


FIGURE 20: Freezing curve result from 23 w% NaCl tests

#### 4.1.2 Analysis and discussion

Since there was a good deal of literature investigating the melting ability of sodium chloride, the presented results (section 4.1.1) were compared to theoretical values, to illustrate the accuracy and precision of the test method.

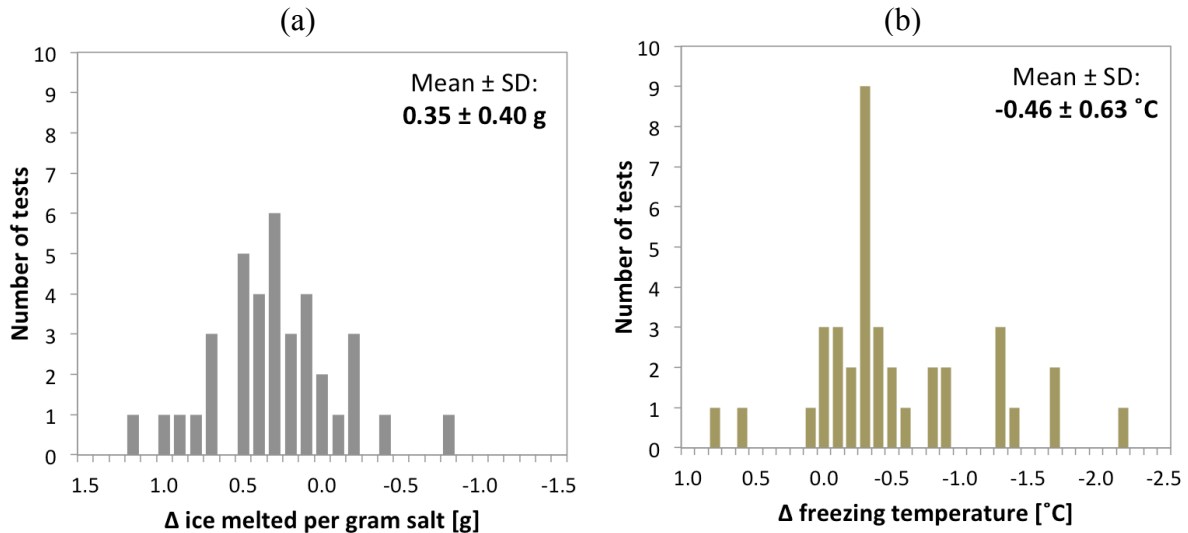


FIGURE 21: Difference in measured and theoretical values for NaCl experiments in: (a) grams ice melted, and (b) freezing temperature

The difference in the ice melted per gram solute shows a small amount of variation, with an average of 0.35 g more ice than the theoretical values and a standard deviation of 0.40 g (Figure 21a). Only 6 of the 37 tests measured a lower melting capacity than the theoretical values. This translated to averagely measuring the melting capacity 4.76% above the theoretical values.

A higher melting capacity leads to a deviation in freezing temperature on the lower side. An average of 0.46 $^{\circ}$ C below the theoretical freezing point was measured, with a standard deviation of 0.63 $^{\circ}$ C (Figure 21b). Note that the higher deviations ( $>1^{\circ}$ C) occurred at lower temperatures (around -10, -14 and -15 $^{\circ}$ C). These deviations could be due to a combination of several factors, described in the next section (4.1.3).

Overall, the results show that the calorimeter was able to measure the melting capacity accurately with fairly good precision. The calculated deviations from the theoretical freezing points depended on how accurate the measurements were, because these were calculated from the measured ice-melting. The freezing points were predicted accurately and precisely, as the error lies within the temperature interval of  $\pm 1.0^{\circ}$ C for 81.1% of the cases. This suggests good possibility to determine the freezing curve with calorimetry.

### 4.1.3 Sources of variance

There were potential sources of variation in measuring the ice-melting capacities, which could explain the discrepancy between results and deviation from the calculated values.

#### **Temperature measurement**

The heat added to the system was based on the temperature measured in the reactor, which may lead to deviation in the actual heat required if the temperature was measured incorrectly. The results show a consistent over-measuring of the melting capacity on all the tests of the mixtures (section 4.2) and NaCl, excluding 6 of the NaCl measurements. Upon examining the raw data, the temperature measurements occurred approximately every 0.6 seconds. This was considered accurate as the temperature in the reactor does not change a considerable amount. During the last seconds of a test, measured ice melted was at approximately 0.005 g per temperature measurement, since the heat added was quite small. If the test does not stop after reaching the set temperature an error would occur, as a higher ice-melting capacity would be measured. However, the additional melted ice measured would be quite small due to frequent temperature measurement. The uncertainty related to temperature measurement would lead to a systematic error since the measurement setup and process weren't altered in any of the tests.

Another temperature measurement uncertainty was related to the stirrer. During the experiment the stirrer continually stirred the mixture with the ice, to accelerate the melting process and so that the mixture was able to be in contact with all the ice in the reactor. However, as the rotation of the stirrer occurred around the vertical axis, and the heater was located below the reactor, a difference in temperature could occur. It would be possible that the mixture at the bottom was not fully mixed with the ice and mixture locating further up. This would lead the temperature at the bottom of the container (reactor) to be higher than the temperature registered, since the measurement device was located above the stirrer. This would cause a delay in a more accurate temperature measurements, and ultimately result in more heat added as the measured temperature was lower. To remove this error, a stirrer that rotates around the horizontal axis could be attempted to see if the measurements improved. This uncertainty in the temperature measured would again lead to a systematic error, as the measurements were not altered throughout the tests for the mixtures.

#### **Heat flow – temperature variation**

Before the test was started, the temperature variation in the reactor had to be obtained a rather steady state, with  $\pm 0.5^{\circ}\text{C}$  variation monitored. This was to ensure that the temperature throughout the reactor's insulation were fairly similar in order to minimize heat transfer. The results showed however, that as the temperature decreases, the percentage deviation from the calculated values was higher. This would be partly due to the total ice-melting capacities being quite small at low temperatures, where the same amount of melted ice would have had a greater impact percentagewise. Additionally, it might be possible that heat sources exist that might have had an impact on the measurements; the most likely of these were the stirrer, the cooler, and the cold room.

The stirrer continually stirred the mixture with the ice ensuring mixture to be in contact with all the ice in the reactor. The uncertainty due to heat from the stirrer would result in a systematic error, but this would be opposite from the error (deviation to theoretical values) measured in the experiments. Heat from the stirrer was thus considered to be insignificant. The stirrer should also have approx. same temperature as the solution due to constant contact.

Before the test began, the cooler was turned off, since it was not possible to determine the energy that the cooling liquid provided to the system. The cooler temperature was initially slightly lower than that of the solution, which was why we waited approx. 5 minutes before the test was started to minimize the temperature variation. There might be a therefore a slight change in the solution's temperature after measuring the set temperature. The set temperature would could actually be lower in reality and more heat was added than what was needed; thus more ice-melting would have been observed. The deviation due to this source of error would depend both on the temperature and its stability in the particular test.

The uncertainty due to the cold room was due to the difficulty in maintaining the specific temperature in the cold room. A change in the temperature in the cold room was observed when the door was opened, and also because of the researcher's presence in the room. This was most prominent at the lowest testing temperatures (-15 to -23°C). However, since the insulation around the reactor has a good thickness, this doesn't appear to have made significant amount of heat contribution.

#### **Weighing – preparing the mixtures**

Inaccuracy in the weighing of the solutes may lead to deviation in the results. The accuracy of the weighing was 0.1 g, and any deviation in the results would depend on whether the weighed solutes were higher or lower than the actual mass used in the calculation. An actual higher solution than calculated would lead to a higher ice-melting capacity, thus giving a lower freezing point concentration. This uncertainty in weighing would result in a systematic error since the same mixture was used in all of the tests.

#### **Amount of ice used**

The amount ice used in the tests had an impact on the results, since it has been observed that a smaller amount of ice leads to a lower melting capacity. The procedure in the NaCl and mixtures experiment was the same, with a difference only in the amount of ice added. For NaCl, amount of ice needed was calculated (theoretical value + 90 g), while 200 g and 150 g quantities were used in the mixtures. As no prior information about the melting abilities of the mixtures was given, a larger ice quantity was chosen to be certain that the melting capacity would be reached. Comparing the different mixture results with NaCl, it would seem that a proper amount of ice would result in less deviation from the theoretical curve. Then again, it should be possible to obtain precise measurements without prior information about the deicer. Any amount of ice used should be able to measure the melting capacity precisely. However, when researching the topic of comparing different deicers, it seems that the same amount of ice should be used for each deicer to correctly show the differences in their melting ability.



## 4.2 ICE-MELTING CAPACITY AND FREEZING CURVES FOR NaCl/MgCl<sub>2</sub> MIXTURES

### 4.2.1 Ice-melting capacity

In total 23 successful tests were performed: 12 tests for 50/50 mixture, 7 tests for 80/20 mixture, and 4 tests with 22 w% MgCl<sub>2</sub> solution to use as a reference. Further information about the tests is provided in Appendix C. Figure 22 shows the ice-melting results at different temperatures. The broken lines represent the calculated melting capacity from the extended UNIQUAC model, while the data points represent the measured results from the experiment. The melting capacity and freezing curves for NaCl and MgCl<sub>2</sub> were based on experimental data (see section 2.2.3).

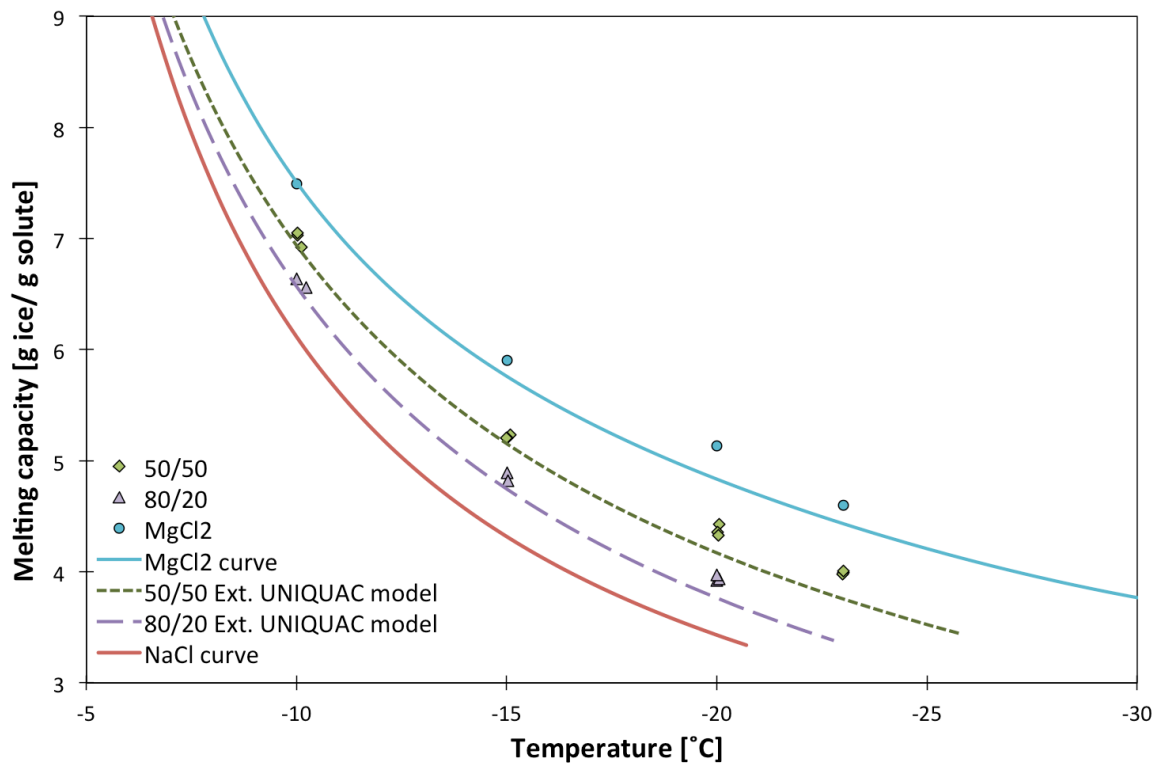


FIGURE 22: Ice-melting capacity results with NaCl and MgCl<sub>2</sub> curves created using data from Haynes (2013) and Melinder (2007)

The model calculated the lowest freezing points for the mixtures to be -25.9°C and -22.3°C for the 50/50 and 80/20 mixtures respectively. The 80/20 mixture was also tested at -23°C, but the solution started to form ice crystals under the cooling process. This indicated that the solution's freezing point had been exceeded, corresponding to the results from the model.

The measured specific ice-melting capacity was higher than calculated in the model, where the deviation becomes slightly greater with lower temperatures. Since the MgCl<sub>2</sub> solution tests measured higher melting, like the NaCl tests (last section), these indicate that it exists a consistent error that might have caused the over-measurement. Possible measurement faults were described in the previous section (4.1.3). However, it followed the curve calculated by the model and indicated good correlations.

#### 4.2.2 Freezing curve

The freezing points were obtained by using equation (10) to translate the amount of melted ice to the freezing points concentrations. The calculated freezing points for the tested mixtures are shown in Figure 23, together with results from the model.

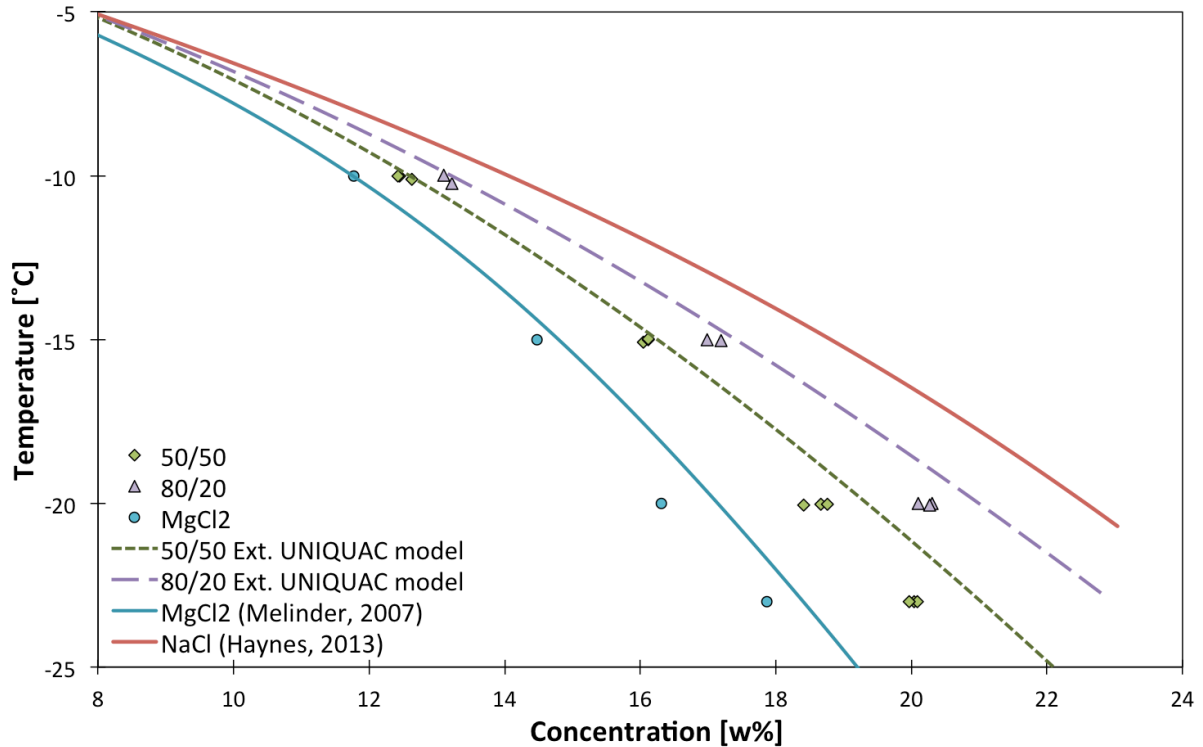


FIGURE 23: Freezing curve results

The results show that with more  $\text{MgCl}_2$  solution in the mixtures, the closer they get to the  $\text{MgCl}_2$  curve. The mixture with equal parts  $\text{NaCl}$  solution and  $\text{MgCl}_2$  solution appears to be at the centre of the curves, while the data points show it to be closer to the  $\text{MgCl}_2$  curve. On the other hand, this would be due to the measurement of ice-melting being greater than the calculated melting capacity. Since more ice-melting was measured, the freezing point would lie at a lower concentration. The freezing points were therefore reliant on the measured ice melted, and ultimately, the degree in accuracy to predict the mixture's freezing curve.

The deviations from the model and theoretical values, were further discussed in section 4.3, Generally, the deviations measured in the mixtures test and the  $\text{NaCl}$  test were similar. Both experiment measured a higher ice-melting and the deviations increased with lower temperatures. The deviations averagely were 4.33% and 4.76% for the tests with the mixtures and  $\text{NaCl}$  respectively, both of the experiments measured higher ice-melting than calculated/theoretical values. As mentioned earlier, it exist good possibility to use calorimetry to determine a deicer's freezing curve due to accurate measurements. Though the measurements should be done with small temperature intervals, with more data points than the measurements done for the mixtures, in order to define the freezing curve more accurately.

### 4.3 USE OF A THERMODYNAMIC MODEL TO PREDICT MELTING CAPACITY

The extended UNIQUAC model was used to illustrate the freezing point depression of the mixed solutions, and used for comparison as it doesn't exist literature with this information. By comparing theoretical curves with the curves generated from the model, a slight difference in freezing points was seen (Figure 24). The difference especially for MgCl<sub>2</sub> at the lowest temperatures was great, while NaCl generally had good correlation overall with experimental data (theoretical curve). Compared to the "ideal equation" curve, the generated curves from the model correlated much better with the theoretical values.

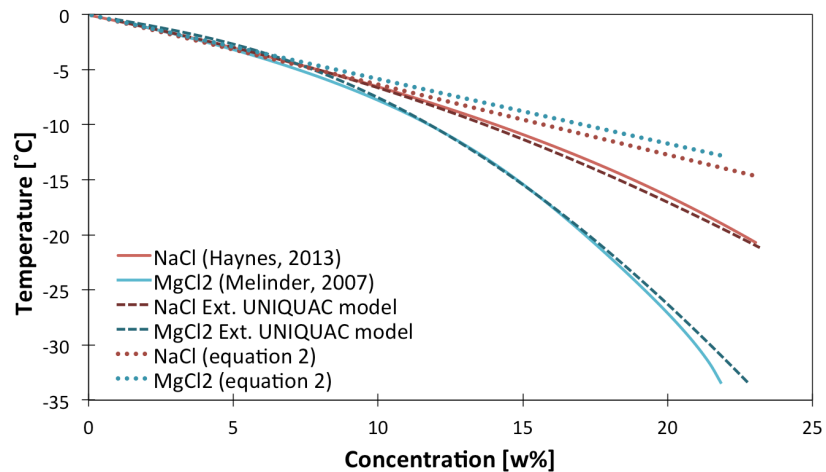


FIGURE 24: Comparison of the freezing curves created from the extended UNIQUAC model, experimental values and ideal solution (equation 2)

From the results, it appears that the measured melting capacity had a fairly consistent deviation from the calculated model. More ice melted was measured on all of the tests, with an average of 0.19 g more ice per gram solute and a standard deviation of 0.06 g (Figure 25).

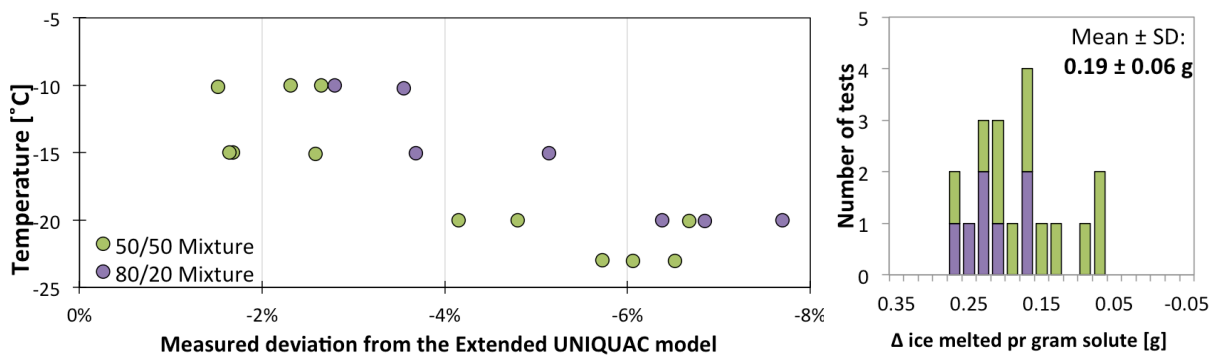


FIGURE 25: Measured melting capacity deviation from the Extended UNIQUAC model

The deviation between the calculated and measured results for ice melting capacity increased with lower temperature (Figure 25). This could be due to the total ice-melting capacities being less at lower temperatures and the same amount of ice melted measured would therefore have a greater impact percentagewise. At the same time, the importance in having consistent temperature was higher due to possible heat loss (see section 4.1.3).

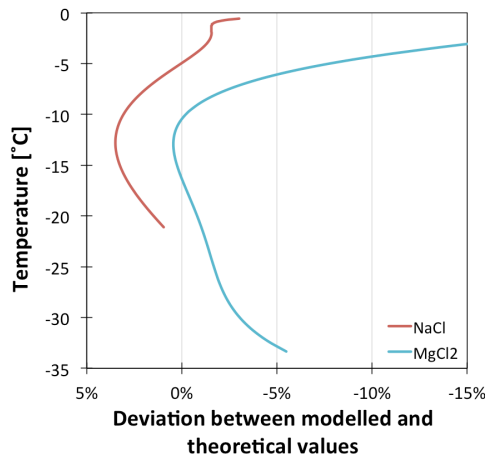


FIGURE 26: Melting capacity deviation between theoretical values (Melinder, 2007, Haynes, 2013) and values from the extended UNIQUAC model

Figure 26 illustrate the melting capacity deviations between modelled and theoretical values. Positive deviations signify higher calculated melting capacity from the model than from the theoretical values. The model showed greater deviation to the theoretical values for the  $MgCl_2$  curve, compared to the  $NaCl$  curve. The  $MgCl_2$  values calculated from Melinder (2007) however, was more uncertain than  $NaCl$  data due to the data quality and regression made (equation 5).

When the deviations observed in Figure 25 and Figure 26 was compared, it seems that the deviations between modelled and theoretical values had very small, or maybe not any, influence to the measured deviations observed in Figure 25. This could indicate that the measured melting capacity deviations from modelled values were mostly, or maybe entirely, due to the uncertainties related to the test method. However, as the extended UNIQUAC model have discrepancy to theoretical values, the calculated melting capacity deviations for the mixtures would still have different deviations to the actual ice-melting values.

To illustrate how an additive of  $MgCl_2$  affect the melting abilities of salt, the difference in melting capacity was plotted in Figure 27. Negative values signify that the  $NaCl$  solution had less ice-melting capacity than the mixtures, and positive values means it had more ice-melting. The figure showed that the  $NaCl$  solution produced higher melting capacities at higher temperatures, but below approximately  $-5^\circ C$  the two mixtures exceeded the  $NaCl$ 's melting capacity. The differences were even higher when  $NaCl$ 's eutectic temperature was exceeded, because it cannot melt ice at colder temperatures. Comparing the two mixtures, the differences between these were generally rather small. However, when the mixture with the lower  $MgCl_2$  content (80/20) reached its freezing point, the difference became greater.

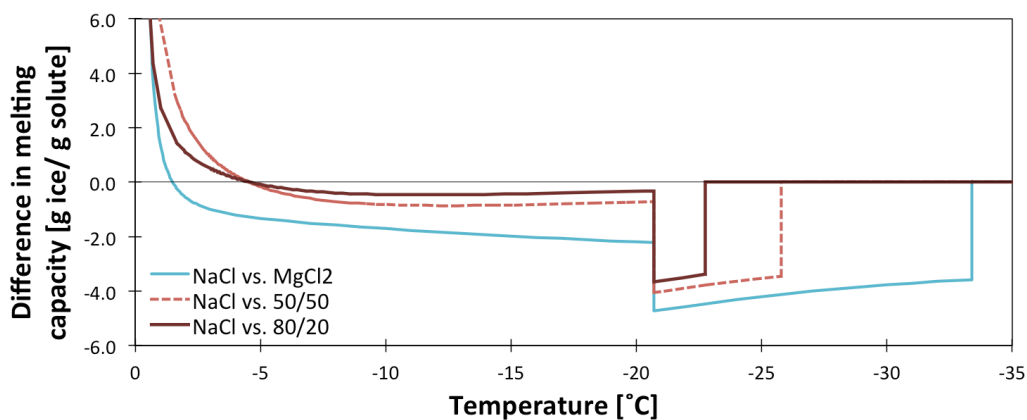


FIGURE 27: Comparison of the mixtures melting capacities (model) to  $NaCl$  solute (theoretical values)

The figure also compared NaCl to MgCl<sub>2</sub> and shows that the latter had higher melting capacities below -1.5°C. In this case, the melting capacity of MgCl<sub>2</sub> slowly increased with lower temperature, where the difference became greater after the mixture's freezing temperature.

Further, the figure indicated that the melting capacity of the 50/50 mixture lies in the center of both solutes, as the difference in melting capacity was half of that of MgCl<sub>2</sub>. As more solution of NaCl was added (80/20-ratio) the smaller the difference was from NaCl and further from MgCl<sub>2</sub>. This indicated that with the higher ratio of a solution, the more it resembles its pure substance. It also shows that by adding more MgCl<sub>2</sub>; the lower their freezing temperature becomes. In practice, this means that the effect of MgCl<sub>2</sub> additive would be quite low, since the additional melting capacity contribution was small. Though the effect would be greater at very low temperatures, especially below NaCl's eutectic temperature and should only be applicable then. At higher temperatures however (>-2°C), NaCl would still be the better choice.

With this, the model illustrated good correlations with both the experimental values and measurements done. It showed good potential in being used to indicate properties at low temperatures, given that information about the deicer is known. Compared to laboratory testing, as well as field-testing, using a model to predict melting capacity could be much more cost-effective. There would be no need for extra materials and equipment, and the sources of errors due to the test method would be non-existent. A comparison of different deicers would therefore be more precise, and results from the model could be achieved quicker. Since the time used in the laboratory testing were far greater than the time used for the model calculation. The model makes it possible to experiment and tryout different ratio and types of solute, which can help discovery new deicers that can be effective at very low temperatures.

## 4.4 EXPERIMENT EVALUATION

### 4.4.1 Ice-melting results from different studies

To indicate how well the different method measures the ice-melting capacity, results from different studies are shown in Figure 28. The results from standardized SHRP tests are shown as circular data points (Chappelow et al., 1992, Alger and Haase, 2006, Nixon et al., 2007, Shi et al., 2009, Gerbino-Bevins, 2011). Studies using modifications to the SHRP are shown with triangular data points (Nixon et al., 2005, Akin and Shi, 2012, Koefod et al., 2012). Additionally, studies using other ice-melting test methods are included: the Shaker test (Gerbino-Bevins, 2011), the MSU Mankato (Druschel, 2012), and ice cube titration (Koefod et al., 2012). This figure illustrates the resulting variations and deviations from the specific melting capacity of NaCl.

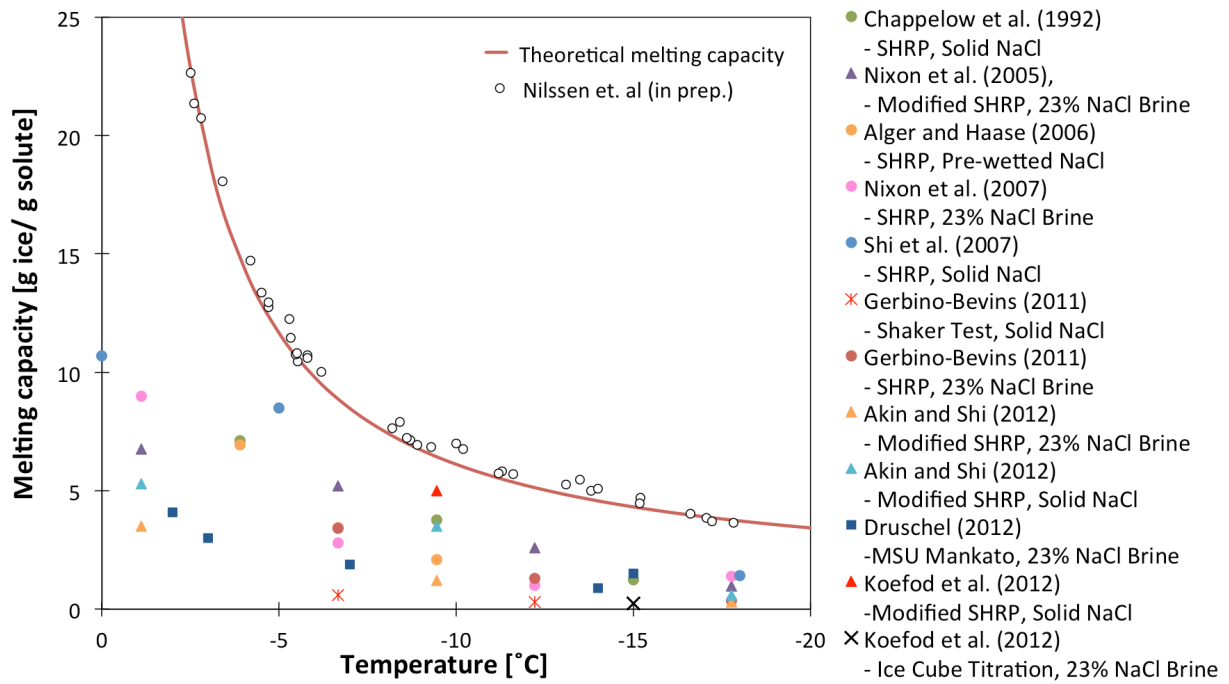


FIGURE 28: Ice-melting results from different studies

#### 4.4.2 Comparison to other tests

The ice-melting capacity tests reveal information about the performance of a deicer, which is quite useful in understanding how different chemicals compare in their ability to melt ice. The standardized SHRP melting tests are simple and have a relatively short testing time (often 1 hour). Since there is a demand for effectiveness in the field as quick as possible, information on how the chemicals work in a short period of time is quite valuable. On the other hand, the test lacks precision and varies in accuracy. This was shown in Figure 28, with the test from the NTNU calorimeter (section 4.1.1). From this, one could clearly see an underestimation of the measured melting capacity for the other tests, while the calorimeter shows better accuracy.

Reasons for the underestimation in relation to the other test were the difficulty of collecting all the ice melt, and also the short testing time, as this made it unlikely to reach the total melting capacity. At higher temperatures in particular ( $> -5^{\circ}\text{C}$ ), the other results deviations from the theoretical melting capacity were a lot higher (Figure 28). The SHRP tests were not able to come close to measuring the total melting capacities at higher temperatures due to the fact that it would require more time to melt more ice. In addition, many elements in the SHRP tests can be easily mishandled, which was also why many studies have modified this test method. Even with modifications however, results from studies shows that the tests were not able to fully measure the salt's melting capacity to the same degree as the calorimeter. Contrary to the other test methods, the calorimeter uses the solutions properties and heat transfer to fully measure its melting capacity. The calorimeter's constant addition of heat to the system, as well stimulation from the stirrer, accelerates the melting process. This made it possible for the total melting capacity to be fully measured at both higher and lower temperatures.

### **Experiment procedure**

Comparing the method, the DSC was the most similar test to the NTNU calorimeter. In this method however, there was no interaction between the ice and solution, which might not be ideal when studying the deicers performance. The calorimeter appears to be more comparable to field situations, both in the terms of interaction between ice and deicer, and the heat transfer that occurs. Such heat transfer in the calorimeter was comparable to a real-world situation, where the heat flow from the environment allows the melting process to continue. In this test method, the heat transfer was controlled and measured precisely, and with the combination of constant stirring and well isolated reactor, the melting capacity was able to be accurately measured.

In terms of the required equipment for testing, the calorimeter requires more than the existing tests. With the need of the different component such as the reactor, temperature monitoring and cold room, which were especially important at low temperature testing because of possible heat loss. Additionally, it would not be possible to do several tests simultaneously without an extra reactor.

### **Freezing point determination**

Regarding measuring the deicers freezing point, the calorimeter generally predicts the freezing point well, and appears to be a decent alternative to the ASTM test. The calorimeter might be appropriate when testing deicers with organic additives, where the break in cooling and freezing curves were shown to be challenging to differentiate in the ASTM test. In the calorimeter, the freezing point instead can be obtained from the total amount of heat added. As shown earlier (Figure 20 and 21), the freezing points were measured quite accurate. This means that the test method would also quite useful at anti-icing purposes, as it could reveal information about the deicers freezing point depression.

### **Ice-melting rate**

On the point of ice-melting rate, the test that measures melted ice as a function of time were able to show this well. The calorimeter does not measure this property directly, but by analysing temperature development in the different tests, the difference in melting rate can be revealed. A higher ice-melting rate would in this test method lead to a more rapid temperature decline in temperature development, thus a higher amount of heat would be added. Ultimately a deicer would have a higher melting rate when the testing time is shorter, given that the input parameters are the same. This is, as mentioned, an important property in real-world settings, as a slippery pavement due to slow ice melting, is a traffic hazard.

### **Concluding words**

Testing with the calorimeter provided fairly consistent results with small variation, and it was able to measure the melting capacity with better accuracy than other existing tests. It was a fairly lengthy test, but much of that time was spent waiting for the system to achieve a steady state. Operating at very low temperatures in particular resulted in a long period of cooling time (approximately 3 to 5 hours). Testing at higher temperatures would yield shorter cooling

times, but then the ice-melting time would be longer since the melting capacity would be higher. However, as illustrated in Figure 28, the calorimeter was able to measure the ice-melting capacity more accurately at both higher and lower temperatures.

Bearing these mentioned aspects in mind, the NTNU calorimeter shows great potential to become a cost-effective way to test deicer ability, seeing that it would be more efficient and less costly than field-testing. The calorimeter operated quite well at very low temperatures and could potentially be a good tool for comparing different deicers, as the measurements were quite precise. Compared to other existing tests, the calorimeter does not rely on measuring the melted ice manually but rather measures the added heat automatically with the computer, and was not subjected to as high sources of variations as the standardized ice-melting tests.



## 5 CONCLUSIONS

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An experiment with the calorimeter was performed to examine the deicers effect when two types of solutions (NaCl and MgCl<sub>2</sub>) were mixed in different ratios (50/50 and 80/20). The accuracy of the test method was analysed, and the use of a thermodynamic model (extended UNIQUAC) was discussed. The main findings from this thesis were as follows:

- The NTNU calorimeter was able to produce results with high accuracy and good precision. Results from the NaCl experiment (done prior to the study) showed to averagely measure the melting capacity 4.76% above the theoretical values, while 4.33% higher melting capacity than modeled values was measured with the mixtures experiment. A consistent over-measurement of the melting capacity was observed, and should be assessed to improve the accuracy of the method. The results from the NaCl and mixtures experiment showed that with lower temperature, the accuracy of the measurements was reduced.
- The mixture with the higher ratio of MgCl<sub>2</sub> solution added to NaCl solution (50/50) had a lower freezing point and higher melting capacities, though the difference was rather small. A significant difference from NaCl was obtained when the NaCl's eutectic point were surpassed (below -21°C).
- The calorimeter shows great potential in determining the freezing curve of an unknown salt, due to high accuracy of the measurements. The freezing point was predicted within the interval of ±1.0°C for 81.1% of the cases from the NaCl experiment.
- The extended UNIQUAC model was able to predict the freezing points and melting capacities well. It correlated well with theoretical (experimental) values and showed great potential in being used to indicate properties at low temperatures, and the deicers freezing curve, given that information about the deicer was known.



## 6 FUTURE WORK

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Although the results presented have demonstrated high accuracy in measurements, the calorimeter could be further developed. As mentioned in section 4.1.3, a different type of stirrer can be used to see if the measurements can be improved. The stirrer in this study had a rotation around the vertical axis, which could have lead to an uncertainty in temperature measurement, as the solution and ice might not be fully mixed. Temperature at the bottom of the reactor would be different from the measured temperature, since the heater was localized below and the sensor was located right above the stirrer. A stirrer that rotates around the horizontal axis can be attempted to see if the temperature can be measured more correctly.

Since this thesis limited its testing on mixtures of NaCl and MgCl<sub>2</sub>, it would be interesting to test other types of deicers. Particularly testing deicers with organic additives, to investigate if the calorimeter can be a good alternative to the ASTM test. A comparison of results from the calorimeter and ASTM test might be interesting to see whether the calorimeter would be able to measure the freezing points more accurately.



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# APPENDICES

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## APPENDIX A: TASK DESCRIPTION OF THE THESIS



## **MASTEROPPGAVE** (TBA4945 Transport, masteroppgave)

VÅREN 2015  
for  
**Michele Delapaz**

### Måling av smeltekapasitet med kalorimetri

#### Bakgrunn

I dag brukes store mengder salt for vinterdrift av vegene i Norge, noe som skaper stor debatt med hensyn til miljøforurensning og korrosjon på bilparken. Det finnes flere aktuelle kjemikalier som kan være et alternativ til salt (NaCl), i tillegg til tilsetningsstoffer som kan forbedre ytelse av salt. Det er viktig å få god forståelse på egenskapene til disse kjemikaliene og dermed er det nødvendig med gode testmetoder. En viktig egenskap er kjemikalets smeltekapasitet, altså hvor mange gram is man kan smelte per gram kjemikalie. På NTNU jobbes det aktivt å utvikle en ny målemetode for smeltekapasitet ved hjelp av kalorimetri. Flere tekniske modifikasjoner har blitt nylig gjennomført og en ny måleprosedyre blir nå utviklet.

#### Målet

Målet med oppgaven er å beskrive smelteprosessen som pågår i kalorimeteren og bestemme nøyaktigheten på målesystemet ved å sammenlikne målt og teoretiske smeltekapasitet for NaCl.

#### Oppgaven

Masteroppgaven omfatter en litteraturstudie og laboratorieforsøk, og gjennom dette arbeidet skal kandidaten utføre følgende oppgaver:

- Gi en beskrivelse av kalorimetri
- Beskrive smelteprosessen for is-salt-vann systemet i kalorimeteren
- Utføre et laboratorieeksperiment ved å smelte is med salt i kalorimeteren
- Sammenligne målte smeltekapasitet til NaCl med teoretiske beregnet smeltekapasitet
- Vurdere muligheten for å bestemme frysekurven av et ukjent salt med kalorimetri
- Evaluere bruken av en termodynamisk modell (Extended UNIQUAC) for å finne kjemikalets frysekurve.





## GENERELT

Opgaveteksten er ment som en ramme for kandidatens arbeid. Justeringer vil kunne skje underveis, når en ser hvordan arbeidet går. Eventuelle justeringer må skje i samråd med faglærer ved instituttet.

Ved bedømmelsen legges det vekt på grundighet i bearbeidningen og selvstendigheten i vurderinger og konklusjoner, samt at framstillingen er velredigert, klar, entydig og ryddig uten å være unødig voluminøs.

Besvarelsen skal inneholde

- standard rapportforside (automatisk fra DAIM, <http://daim.idi.ntnu.no/>)
- tittelside med ekstrakt og stikkord (mal finnes på siden <http://www.ntnu.no/bat/skjemabank>)
- sammendrag på norsk og engelsk (studenter som skriver sin masteroppgave på et ikke-skandinavisk språk og som ikke behersker et skandinavisk språk, trenger ikke å skrive sammendrag av masteroppgaven på norsk)
- hovedteksten
- oppgaveteksten (denne teksten signert av faglærer) legges ved som Vedlegg 1.

Besvarelsen kan evt. utformes som en vitenskapelig artikkel for internasjonal publisering. Besvarelsen inneholder da de samme punktene som beskrevet over, men der hovedteksten omfatter en vitenskapelig artikkel og en prosessrapport.

Instituttets råd og retningslinjer for rapportskrivning ved prosjektarbeid og masteroppgave befinner seg på <http://www.ntnu.no/bat/studier/oppgaver>.

### Hva skal innleveres?

Rutiner knyttet til innlevering av masteroppgaven er nærmere beskrevet på <http://daim.idi.ntnu.no/>. Trykking av masteroppgaven bestilles via DAIM direkte til Skipnes Trykkeri som leverer den trykte oppgaven til instituttkontoret 2-4 dager senere. Instituttet betaler for 3 eksemplarer, hvorav instituttet beholder 2 eksemplarer. Ekstra eksemplarer må bekostes av kandidaten/ ekstern samarbeidspartner.

Ved innlevering av oppgaven skal kandidaten levere en CD med besvarelsen i digital form i pdf- og word-versjon med underliggende materiale (for eksempel datainnsamling) i digital form (f. eks. excel). Videre skal kandidaten levere innleveringsskjemaet (fra DAIM) hvor både Ark-Bibl i SBI og Fellestjenester (Byggsikring) i SB II har signert på skjemaet. Innleveringsskjema med de aktuelle signaturene underskrives av instituttkontoret før skjemaet leveres Fakultetskontoret.

Dokumentasjon som med instituttets støtte er samlet inn under arbeidet med oppgaven skal leveres inn sammen med besvarelsen.

Besvarelsen er etter gjeldende reglement NTNUs eiendom. Eventuell benyttelse av materialet kan bare skje etter godkjenning fra NTNU (og ekstern samarbeidspartner der dette er aktuelt). Instituttet har rett til å bruke resultatene av arbeidet til undervisnings- og forskningsformål som om det var utført av en ansatt. Ved bruk ut over dette, som utgivelse og annen økonomisk utnyttelse, må det inngås særskilt avtale mellom NTNU og kandidaten.

**(Evt) Avtaler om ekstern veiledning, gjennomføring utenfor NTNU, økonomisk støtte m.v.**

Beskrives her når dette er aktuelt. Se <http://www.ntnu.no/bat/skjemabank> for avtaleskjema.

**Helse, miljø og sikkerhet (HMS):**

NTNU legger stor vekt på sikkerheten til den enkelte arbeidstaker og student. Den enkeltes sikkerhet skal komme i første rekke og ingen skal ta unødige sjanser for å få gjennomført arbeidet. Studenten skal derfor ved uttak av masteroppgaven få utdelt brosjyren "Helse, miljø og sikkerhet ved feltarbeid m.m. ved NTNU".

Dersom studenten i arbeidet med masteroppgaven skal delta i feltarbeid, tokt, befaring, feltkurs eller ekskursionsjoner, skal studenten sette seg inn i "Retningslinje ved feltarbeid m.m.". Dersom studenten i arbeidet med oppgaven skal delta i laboratorie- eller verkstedarbeid skal studenten sette seg inn i og følge reglene i "Laboratorie- og verkstedhåndbok". Disse dokumentene finnes på fakultetets HMS-sider på nettet, se <http://www.ntnu.no/ivt/adm/hms/>. Alle studenter som skal gjennomføre laboratoriearbeid i forbindelse med prosjekt- og masteroppgave skal gjennomføre et web-basert TRAINOR HMS-kurs. Påmelding på kurset skjer til [sonja.hammer@ntnu.no](mailto:sonja.hammer@ntnu.no)

Studenter har ikke full forsikringsdekning gjennom sitt forhold til NTNU. Dersom en student ønsker samme forsikringsdekning som tilsatte ved universitetet, anbefales det at han/hun tegner reiseforsikring og personskadeforsikring. Mer om forsikringsordninger for studenter finnes under samme lenke som ovenfor.

**Oppstart og innleveringsfrist:**

Oppstart og innleveringsfrist er i henhold til informasjon i DAIM.

**Faglærer ved instituttet:** Johan Wåhlin

**Bi-veileder:** Alex Klein-Paste

Institutt for bygg, anlegg og transport, NTNU

Dato: 27.01.2015 (revidert 28.05.2015)

Underskrift



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Faglærer

## APPENDIX B: DERIVATION OF THE FREEZING POINT DEPRESSION EQUATION

The following justification of the freezing point depression equation was obtained from Chaplin (2014a) and Atkins and De Paula (2013).

Using equation (1);  $\mu^{solution} = \mu^{liquid} + RT \ln x_w$  as the basis, the freezing point depression equation can be derived:

$$\ln x_w = \frac{\mu^{ice} - \mu^{liquid}}{RT} = \frac{-\Delta G_{fus}}{RT} \quad (B.1)$$

where  $\Delta G_{fus}$  is the Gibbs energy of fusion. To express the relation between the change in composition and the change in freezing temperature, both sides is differentiated with respect to temperature and by using the Gibbs-Helmholtz equation. This gives:

$$\frac{d \ln x_w}{dT} = \frac{1}{R} \frac{d\left(\frac{\Delta G_{fus}}{T}\right)}{dT} = -\frac{\Delta H_{fus}}{RT^2} \quad (B.2)$$

where  $\Delta H_{fus} = H^{liquid} - H^{solid}$ , the latent heat of fusion, which is the amount of thermal energy required converting solid form into liquid form. By integrating from conditions in pure water to those in solution and replacing  $\ln x_w$  with  $\ln(1 - x_s)$ , this leads to:

$$\ln(1 - x_s) = \frac{\Delta H_{fus}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (B.3)$$

where  $x_s$  is the mole fraction of the solute (moles solute/(moles water + moles solute)),  $T_0$  is the freezing point of pure water and  $T$  is the freezing point of the solution. Note that  $(1-x_s)$  may be replaced by water activity ( $a_w$ ) in this equation. If we assume a very diluted solution,  $x_s \ll 1$ , then  $\ln(1 - x_s) = -x_s$  and,

$$x_s = \frac{\Delta H_{fus}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) = \frac{\Delta H_{fus}}{R} \left( \frac{T_0 - T}{T x T_0} \right) \quad (B.4)$$

Another assumption is that  $T \approx T_0$ , an error that increases with lower temperature, but will result in the final simplified equation:

$$\Delta T = \frac{x_s R T_0^2}{\Delta H_{fus}} \quad (B.5)$$

Or as the commonly used expression

$$\Delta T = K_f \cdot m_s \cdot i \quad (B.6)$$

where  $\Delta T$  is the freezing point depression in °C and  $m_s$  is the molality of the solute (moles solute/kg solvent). While the cryoscopic constant,  $K_f$ , is a proportionality constant unique for different substances. For water, this is 1,86 (kg°C/m) calculated from  $K_f = M_w R T_0^2 / \Delta H_{fus}$ . Where  $M_w$  is the molar mass for water. The Van't Hoff factor  $i$  is a measure of particle

dissociation in solution, and represents the number of particles that are liberated per molecule of solute dissolved.

Equation (B.6) thus makes several assumptions. The assumption related to the constancy of  $\Delta H_{fus}$  introduces error. For instance, the specific heat of pure water increases on supercooling, while that of ice decreases. An error is introduced using molality  $m_s$  instead of the mole fraction  $x_s$ , which may be significant in higher solutions than a few molal. There is also the assumption of  $T \approx T_0$ , which increases with lower temperature (Chaplin, 2014a).

## APPENDIX C: DATA RESULTS FOR THE MIXED SOLUTIONS

Table C.1: Results for 50/50 mixture

Filename	Initial parameters				Total energy added [g]	Specific melting capacity [ $\text{g}_{\text{ice}}/\text{g}_{\text{solute}}$ ]			Difference in total ice melted [g]
	$T_{\text{setpoint}}$ [°C]	$m_{\text{solution}}$ [g]	$T_{\text{ice}}$ [°C]	$m_{\text{ice}}$ [g]		Measured	Calculated (model)	Difference [%]	
test_126	-10.01	92.9	-11.7	200.2	24 276	7.0	6.9	-2.3%	3.3
test_127	-10.02	91.0	-11.3	200.4	23 765	7.1	6.9	-2.6%	3.7
test_129	-10.12	91.1	-12.0	200.4	23 182	6.9	6.8	-1.5%	2.1
test_146	-15.08	91.3	-16.2	200.9	11 485	5.2	5.1	-2.6%	2.7
test_147	-15.01	91.9	-16.5	200.2	11 695	5.2	5.1	-1.7%	1.8
test_148	-14.99	90.8	-16.9	200.0	11 739	5.2	5.1	-1.6%	1.7
test_134	-20.06	90.2	-20.8	200.4	6 197	4.4	4.2	-6.7%	5.6
test_135	-20.02	90.5	-20.8	150.1	5 724	4.4	4.2	-4.8%	4.1
test_136	-20.03	90.6	-20.7	150.2	5 528	4.3	4.2	-4.2%	3.5
test_142	-23.01	91.3	-23.2	150.0	3 293	4.0	3.8	-6.1%	4.7
test_143	-22.99	91.3	-23.1	150.2	3 205	4.0	3.8	-5.7%	4.4
test_144	-23.01	91.6	-23.3	150.3	3 434	4.0	3.8	-6.5%	5.1

Table C.2: Results for 80/20 mixture

Filename	Initial parameters				Total energy added [g]	Specific melting capacity [ $\text{g}_{\text{ice}}/\text{g}_{\text{solute}}$ ]			Difference in total ice melted [g]
	$T_{\text{setpoint}}$ [°C]	$m_{\text{solution}}$ [g]	$T_{\text{ice}}$ [°C]	$m_{\text{ice}}$ [g]		Measured	Calculated (model)	Difference [%]	
test_132	-10.23	90.2	-11.5	200.1	21 050	6.6	6.3	-3.6%	4.6
test_131	-10.00	90.1	-12.5	200.0	22 027	6.6	6.5	-2.8%	3.7
test_137	-15.01	91.3	-15.5	200.1	9 728	4.9	4.6	-5.1%	5.0
test_138	-15.03	90.9	-16.9	200.1	9 800	4.8	4.6	-3.7%	3.5
test_151	-20.00	90.3	-20.6	150.4	3 449	3.9	3.7	-6.4%	4.8
test_140	-20.05	90.2	-20.6	150.2	3 494	3.9	3.7	-6.8%	5.2
test_149	-20.00	90.3	-21.0	200.0	3 971	4.0	3.7	-7.7%	5.8

Table C.3: Results for  $\text{MgCl}_2$  solution

Filename	Initial parameters				Total energy added [g]	Specific melting capacity [ $\text{g}_{\text{ice}}/\text{g}_{\text{solute}}$ ]			Difference in total ice melted [g]
	$T_{\text{setpoint}}$ [°C]	$m_{\text{solution}}$ [g]	$T_{\text{ice}}$ [°C]	$m_{\text{ice}}$ [g]		Measured	Calculated (model)	Difference [%]	
test_152	-10.01	90.6	-12.0	200.3	25 579	7.5	7.5	0.4%	-0.7
test_150	-15.00	90.7	-16.1	200.1	14 794	5.9	5.9	-0.8%	0.9
test_141	-20.01	90.5	-20.6	200.2	9 536	5.1	4.9	-4.2%	4.1
test_145	-23.01	91.4	-23.0	150.4	6 109	4.6	4.5	-1.6%	1.5

