Measuring melting capacity with calorimetry

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Abstract:

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Road salt is an important aspect in winter maintenance. To achieve better practices for winter maintenance it is necessary to obtain more knowledge about the different properties of salt and other chemicals used. An important property of a chemical is its ability to melt ice.
The purpose of this thesis is to develop and test a calorimeter. The calorimeter used in this thesis is build earlier, so the objective of this thesis is to determine the accuracy of the calorimeter for ice melting experiments. To test the accuracy of the calorimeter some initial parameters had to be determined. These parameters included heat capacity of the reactor, heat leakage and heat from stirrer. The most extensive testing to evaluate the accuracy was done with ice melting in pure water to predict the amount of ice melted. A few test was performed at cold temperatures with salt solution of NaCl.
The correlation between measured and theoretical values in room temperature was good, with an accuracy of 93,5 %. The remaining 6,5 % still seems to be an systematic error. The accuracy improved further when larger ice samples was used. The precision of the test performed at lower temperatures with salt solution turned out to be less accurate, with an accuracy of less than 70 %.
This means that the accuracy of the calorimeter is still not satisfactory, but it is potential to improve the measurements further. The biggest uncertainty lays in the heat leakage and it is therefore recommended to place the calorimeter in a cold room. The testing procedure should also be improved to obtain more consistent results, especially regarding cooling time and temperature of the ice samples

Keywords:

| 1. Calorimetry -Kalorimetri |
| 2. Melting of ice- Issmelting |
| 3. Melting capacity - Smeltekapasitet |
| 4. Accuracy - Nøyaktighet |

Linda Betten

PREFACE

This report is the final work of my five-year master degree at NTNU. The Report is written at the Department of Civil and Transport Engineering, Faculty of Engineering Science and technology. The subject, roadsalt, is chosen because it is an interesting subject, which I wanted to learn more about. It affects most road users and with better knowledge, it is possible to salt smarter and reduce effects on the environment.

Knowing little about chemistry and work in the laboratory this master has been a challenge in many ways. Both the understanding of the process and how time consuming work in the laboratory actually is. My experience with lab work has been restricted to well known experiment, with a step by step guide how to proceed. During these months I have learned the importance of precision and to document all the results. In particular for those experiment who failed, where we can learn the most. Unfortunately, much of the knowledge was comprehended while analyzing the results, which makes the list of suggestions on how to improve the experiment longer than wanted. Preferably I should have done many of these things myself, but it has been learning by doing, which is time consuming. Hopefully, this it is a lesson I will make use of in later work.

SUMMARY

Road salting is an important aspect of winter maintenance. There has been an increase in the usage of salt in later years to keep the road safe and accessible. It is a desire to reduce the amount of salt due to environmental aspects. To achieve better practices for winter maintenance it is necessary to obtain more knowledge about the different properties of salt. The motivation for this thesis is to develop a better method for determining the melting capacity for salt, which is an important property in deicing.

The calorimeter used in this thesis is build earlier, so the objective of this thesis is to determine the accuracy of the calorimeter for ice melting experiments. The calorimeter is able to measure the heat necessary to melt a given amount of ice, by using thermodynamic properties. Ice melting in a closed system will cause the temperature to decrease. This happens because the energy within the system is used to break the bonding between the ice molecules. To counteract this temperature fall, the calorimeter adds heat to the system. With the premise that the initial and final temperature is the same, the energy added to the system is equal the amount of energy necessary to melt a given amount of snow.

The calorimeter consists of an isolated reactor, a heater, a cooler and a computer that registers the temperatures and regulates the heat added to the reactor. To test the accuracy of the calorimeter some initial parameters had to be determined. These parameters include heat capacity of the reactor, heat leakage and heat from stirrer. The most extensive testing to evaluate the accuracy to predict the amount of ice melted, was done with ice melting in pure water. A few test was performed at cold temperatures with salt solution of NaCl.

In room temperature, with no heat leakage, the accuracy of the measurements was found to be 93,5%. The correlation between measured and theoretical values was good, and the measured value was consequently lower than the theoretical value. If only tests performed with an amount of ice of 45 g or higher was included the accuracy was almost 95%. The precision of the test performed at lower temperatures with salt solution turned out to be less accurate, with an accuracy of less than 70 %. This means that the accuracy of the calorimeter is still not satisfactory, but it is potential to improve the measurements further. The biggest uncertainty lays in the heat leakage and it is therefore recommended to place the calorimeter in a cold room. The testing procedure should also be improved to obtain more consistent results, especially regarding cooling time and temperature of the ice samples.

The calorimeter has the prospective to investigate the ice melting properties and determine the freezing curve of unknown substances. This is only possible if the accuracy and precision of the calorimeter is improved further.

SAMMENDRAG

Veisalting er en viktig del av vintervedlikeholdet. Det har vært en økning i bruken av salt i senere år for å holde veien trygt og fremkommelig. Det er et ønske om å redusere mengden av salt på grunn av miljømessige aspekter. For å oppnå bedre praksis for vintervedlikehold er det nødvendig å få mer kunnskap om de ulike egenskapene til salt. Motivasjonen for denne oppgaven er å utvikle en bedre metode for å bestemme smeltekapasitet til salt, som er en viktig egenskap i avising.

Kalorimeteret som brukes i denne oppgaven er ferdig bygget, så målet med oppgaven er å utvikle en testmetode som maksimerer nøyaktigheten på målingene. Kalorimeteret kan måle varmen som er nødvendig for å smelte et gitt mengde is, på grunnlag av is og vanns termodynamiske egenskaper. Når isen smelter i et lukket system synker temperaturen. Dette skjer fordi energien i systemet brukes til å bryte bindingene mellom ismolekylene. For å motvirke dette temperaturfallet, tilfører kalorimeteret varme til systemet. Energien tilført systemet er lik mengden energi som er nødvendig for å smelte en gitt mengde snø, med den forutsetning at start -og sluttemperatur er den samme.

Kalorimeteret består av en isolert reaktor, et varmeelement, en kjøler og en datamaskin som registrerer temperaturen og regulerer varmetilførselen til reaktoren. For å teste nøyaktigheten av kalorimeteret måtte noen innledende parametere måtte bestemmes. Disse parameterne omfatter varmekapasiteten i reaktoren, varmelekkasje og varme fra omrøreren. Den mest omfattende testingen for å evaluere nøyaktigheten, ble gjort med smelting av is i rent vann ved romtemperatur. Noen test ble utført ved lave temperaturer med saltløsning av NaCl.

I romtemperatur, uten noen varmelekkasje, ble nøyaktigheten av målingene funnet å være 93,5% av teoretisk verdi. Korrelasjonen mellom målte og teoretiske verdier var god, og den målte verdien var konsekvent lavere enn den teoretiske verdien. Dersom kun tester med en is mengde på 45 g eller mer er tatt med i beregningen var nøyaktigheten nesten 95%. Presisjonen for testen utført ved lavere temperaturer med saltoppløsning viste seg å være mindre nøyaktig, med en nøyaktighet på mindre enn 70%. Dette innebærer at nøyaktigheten av kalorimeteret er fortsatt ikke tilfredsstillende, men at det er et potensial for å forbedre målingene ytterligere. Den største usikkerheten ligger i varmelekkasjen, og det anbefales derfor å plassere kalorimeteret i et kaldt rom. Testprosedyren bør også bli forbedret for å oppnå bedre resultater, spesielt med hensyn til nedkjøling av saltløsning og temperaturmålingen av isprøver.

Kalorimeteret har potensial til å kunne bestemme smeltekapasitet og finne frysekurven til ukjente stoffer. Dette er mulig hvis nøyaktighet og presisjonen til kalorimeteret er ytterligere forbedret.

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1. INTRODUCTION

1.1 BACKGROUND

Each winter large efforts is put into keeping roads drivable in Norway. To keep the roads safe and trafficable during winter tasks like mechanical removal of snow and ice, chemical ice prevention and friction enchantments is applied (1). In 2010 it was used 201 000 ton salt, 417 000 ton sand and 55 000 km of road was cleared of snow, adding up to a total of 16 million km plowed(2). The amount of salt has in the later years increased, to improve safety and accessibility. At the same time, the focus on the negative impacts of road salt has amplified. It is desirable to reduce the amount of salt, both with a view to improve environmental impacts and reduce damages on vehicles in form of corrosion and wear.

In Norway there are three approaches to keep the friction on the road acceptable on winter roads. These are anti-icing, anti-compaction and deicing. Both anti-icing and anti-compaction are proactive measures to reduce the amount of snow and ice on the road. The goal is to avoid the formation of ice on the road. In anti-icing the salt solution prevents an already wet pavement to freeze when the temperature drops by depressing the freezing temperature of the water. In anti-compaction the salt solution is spread out before or during snowfall. This prevents the snow from compacting and attach itself to the asphalt, making the mechanical removal easier. Deicing is a reactive approach, removing ice that already has formed with a deicing chemical.

There is need for research on the different approaches of winter maintenance, to better understand the mechanisms on the road. This master will focus on the aspect of deicing in winter maintenance. There are different methods for measuring the performance of deicers. Some existing test to evaluate the melting performance of deicers are described in section 2.4.

1.2 OBJECTIVE, SCOPE AND LIMITATIONS

In this master the focus lies upon the development of the laboratory experiments. NTNU want to have a functioning calorimeter for research purposes. The calorimeter with hardware is build earlier, so the objective of this thesis is to determine the accuracy of the calorimeter for ice melting experiments.

The ultimate goal is to get a result where the melting capacity of NaCl is measured, in g melted snow per g salt at a given temperature. To get there the accuracy and the procedure has to be

optimized. As the experiments done are experimental, the method is changed continuously on the way. Therefore, the accuracy and reproducibility of the results vary, but these changes are necessary to improve the accuracy.

In this thesis there is no focus on other properties of salt nor the environmental effects of road salt, where these are already thoroughly investigated in other literature.

1.3 REPORT OUTLINE

The report will be structured first with theory that applies to the area of investigation. Then the method used is described, addressing each experiment by themselves. The tests are divided into two parts. The first part includes tests that is necessary to perform, before the testing of the accuracy can start. The results are described in chapter four, while the discussion is in chapter 5. After the analysis the conclusions of the experiment is highlighted. In the end there is a chapter describing further work. This is made quite concrete, explaining how I would proceed to make the test more accurate.

2. THEORY

Before starting the experiments, some knowledge of thermodynamics and calorimeter is prerequisite. Thermodynamics lays the foundation to the principles behind Calorimetry and explains the basic relationship between energy, heat and work. All reactions, releases or requires energy. Energy can be transferred as either work or heat and in Calorimetry it is the reactions transferring heat that is investigated.

2.1 THERMODYNAMICS

The first law of thermodynamic states that the energy of an isolated system is constant. This is often expressed by looking at the internal energy, U, of a system. Energy can be transferred in two ways, by either heat or work, and so the change in the internal energy can be expressed as below:

$$\Delta U = q + w$$

Where q is the heat energy added and w is the work done on it. This law is based on the law of conservation of energy, that states that "*energy can be converted from one form to another but can be neither created nor destroyed*", which means that the energy of the universe is constant(3).

The second law of thermodynamics states that in an isolated system, spontaneous processes occur in the direction of increasing entropy. This can also be stated as "*everything naturally tends to its most stable state* "(4) This means in every system seeks to find equilibrium, which is the most stable state.

A third law is also relevant to the calculations done later. This is **Hess's Law**. This law states that the change in enthalpy is independent of the pathway; the only thing that matters is the initial and final state of the substances. This means that the change in energy is the same whether the process goes through one step or four, as long as the initial reactants and final products are the same. Hess's law is valid when the pressure and temperature is constant. Hess's law is important to remember and it simplifies some of the calculations done later.

"*Hess's law allows the calculation of enthalpy changes for reactions which cannot be measured directly, either because they occur to slowly for the instrument to follow, or because they do not occur naturally*" (4)

State function is a property which is only dependent on which equilibrium state the system is in and not dependent on how the system got this way, i.e. not dependent on the path. Enthalpy, entropy and internal energy is state functions.

Enthalpy (H) is defined by the equation:

$$H = E + PV$$

Where E is the internal energy, P is pressure and V is the volume of the system. At constant pressure the change in in enthalpy is the same as heat added, q= ΔH. In a way, we can say that the enthalpy describes the "content of heat" in the system.

Entropy (S) is a quantitative measure of disorder in a system. The entropy in the universe will always increase. The entropy in a system is dependent on the degree of freedom. Solid materials has less entropy than liquids, which in turn has less energy than gases, see Figure 1.
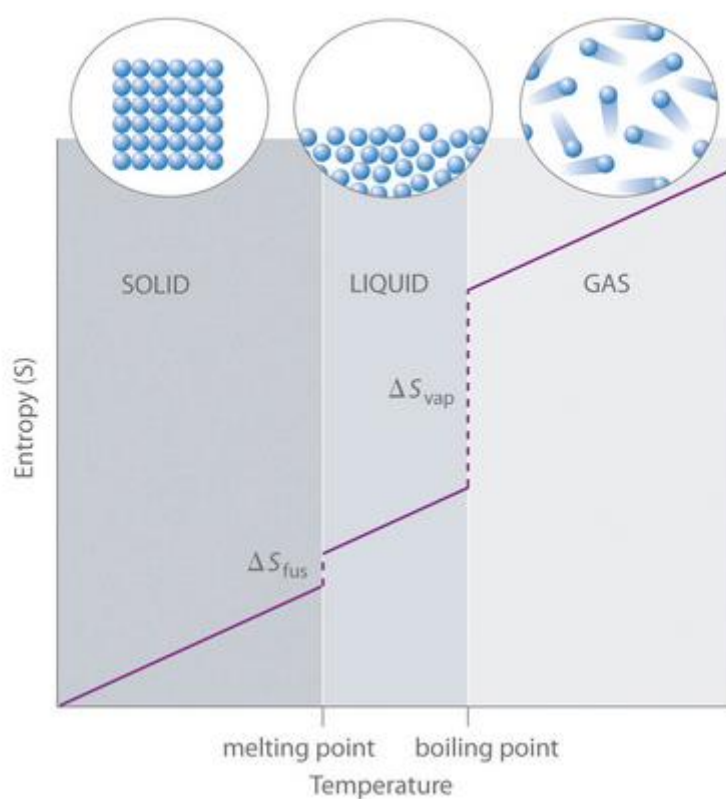

Figure 1 Generalized plot of Entropy versus Temperature (5)

Heat involves a transfer of energy. This is important to know the difference between heat and temperature. Where heat is the transfer of energy, temperature is a property that reflects the random motions of particles in a particular substance(3).When a substance releases heat, its

total energy will decrease and so will the temperature. If a reaction demands heat it is an *endotherm reaction*, but if the reaction releases heat it is an *exothermic reaction*.

A *system* is the enclosed area where the reaction occurs; this is the part of the universe where the focus is on. The surroundings includes everything else in the universe. There are different kind of systems, dependent on the transfer of mass and energy between the system and the surroundings.

- Isolated systems
    - No heat or matter is transferred between surroundings and system
- Closed systems
    - No matter is transferred between surroundings and system, but heat can be exchanged
- Open system
    - Both mass and heat can be transferred between surroundings and system
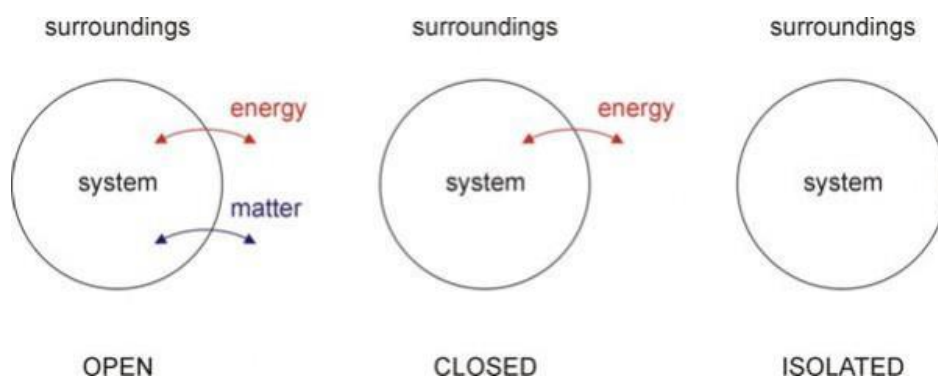
Figure 1 Different systems

Phase transition happens when a substance changes from solid to liquid or from liquid to gas. The phase transition is dependent on both pressure and temperature. To break the molecular bonds there is necessary to add more energy. In this transition, the temperature remains constant, as all the heat added goes to break molecular bonds. The enthalpy change that occurs at the melting point when a solid melts is called the ***heat of fusion***, or more accurately called ***enthalpy of fusion***.

Equilibrium is a position of a reaction in which the forward and reverse reactions rates are equal (3). In equilibrium the reaction is in its most stable state, with a given temperature and pressure.

Take the phase transition between water and ice as an example.

$$H_2O \ (s) \leftrightarrow H_2O \ (l)$$
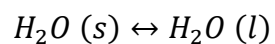
If the temperature is 20 °C, the process will go to the right, and all the ice will melt to water. At a temperature of -5 °C, the reaction will go to the left, and all the water will freeze, but if the temperature is 0°C, both water and ice will be present in the system.

Table 1 Overview of Symbols used in thesis

Quantity	Symbol	Unit
Entropy	S	J/K
Enthalpy	H	J
Energy	Q	J
Temperature	T	K or °C
Time	t	s
Power	P	J/s
Heat capacity (constant pressure)	C	J/K
Spesific heat capacity	C_p	J/gK
Ethalpy of fusion/ latent heat of fusion	L_{fus}	J/g

2.2 CALORIMETRY

Calorimetry has been used since 1780 to study reactive systems(4).The word calorimeter comes from the greek word *calor*, meaning heat, and *meter* which means measure. Measuring heats of reactions is the basic function of a calorimeter. When a reaction occur, the change can be obvious like a phase transition or subtle like fatigue of a material. Common is that in order for any reaction to happen, there needs to be a *transfer of energy*. As we know from the first law of thermodynamics is that energy can be transferred as heat and work. All processes that require a *transfer of heat* is a candidate to Calorimetry (3, 4).

Substances respond differently to being heated. A measure of the **heat capacity** is defined as (3):

$$C = \frac{Heat\ absorbed}{increase\ in\ temperature}\ [J/K]$$

Sometimes it is more useful to know the **specific heat capacity** [J/gK], which describes the amount of heat necessary to heat 1 g of substance with 1 °C. A calorimeter can be used to determine heat capacities and how substances react to thermal changes.

There is numerous kinds of calorimeters built for different purposes, using different techniques. How complex the calorimeter is and the accuracy of it depends on the objective of the test. A test developed to detect decomposition of a medical drug, needs to be very precise and detect small changes as the process is slow. Hemminger and Höhne (6) has tried to classify the variety of calorimeters based on three criteria, measuring principle, the mode of operation *or* the principle of construction.

Measuring principle refers to how heat is transferred between the surroundings and the system. There is three main measuring principles.
Heat conduction Calorimeter - The heat can be transferred to surroundings through conduction, keeping the temperature of the system nearly constant. Often is this obtained by using a heat sink and peltier units. The peltier units is located within the temperature gradient between the reactor and heat sink to measure the transmission of heat.
Heat accumulating calorimeter - The heat can be accumulated, allowing the temperature to rise or fall within the system. Exothermic reactions will lead to an increase in temperature, while endothermic reactions will lead to a decrease in temperature.
Heat exchange calorimeter - the heat is actively exchanged between sample and surroundings.

The rate of heat flow is determined by the thermal resistance between the sample and surroundings.

Mode of operation is determined by the temperature in the sample and surroundings during the experiment. *Isothermal* mode means that sample and surroundings are held at constant temperatures. *Isoperibol* mode means that surroundings stay at constant temperature, while sample temperature may alter. *Adiabatic* means that no heat exchange takes place between sample and surroundings. This can be achieved by keeping the temperature difference between sample and the controlled surrounding zero.

The construction refers to the measuring system used. Calorimeters can have one or two measurement systems. With two cells, the calorimeter can operate either in parallel or in scanning mode and is called a DSC (differential scanning calorimeter).

The calorimeter used in development of this test, may be defined as isothermal or isoperibol. The temperature of the sample varies through the execution of the testing, but the end temperature is the same as the start temperature, which makes the temperature difference zero. The heat to the system is controlled by a heating element during the test to increase temperature and is an active part in the test.

2.3 THE PROCESS OF ICE MELTING

For the ice to become water the ice has to go through a phase transition. For a pure water-ice solution the phase transition happens at zero degrees. This changes if other molecules is present in the solution. The freezing point of water will be depressed when molecules or ions are *dissolved* in the water. This is called a colligative property, as the depression of the freezing point only depends on the number of molecules dissolved, not the properties of the molecule itself. It is therefore possible to use all types of substances to depress the freezing point, as long as they are soluble in water. Figure 2 shows how much NaCl is necessary to depress the freezing point at different temperatures.
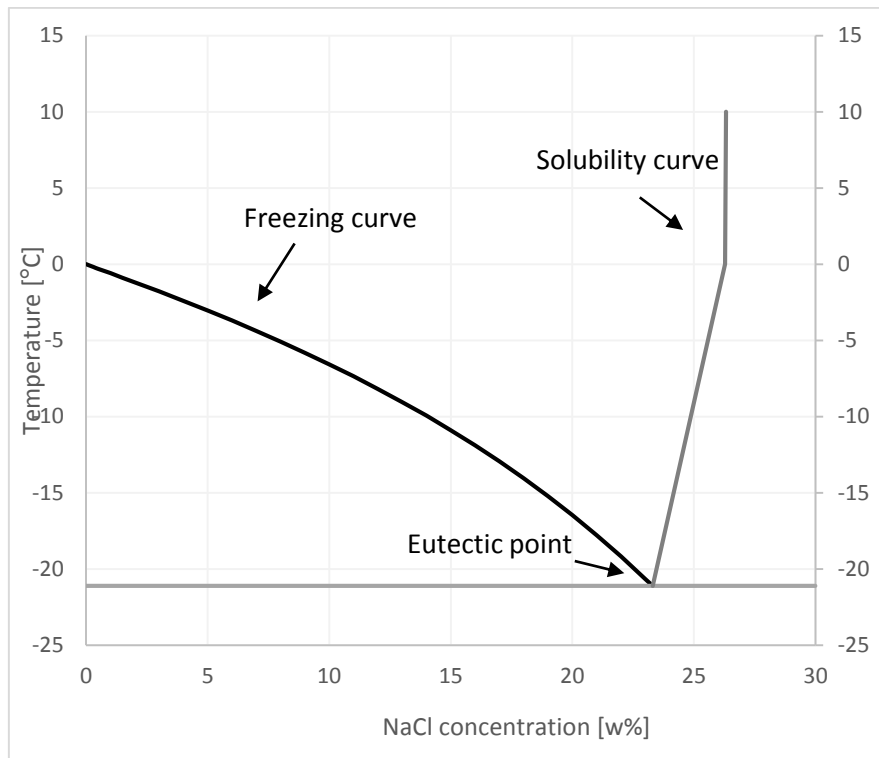
Figure 2 The freezing curve for NaCl- solution

In deicing, the ice is forced to melt with the use of a deicing chemical. The melting process starts when the temperature is above the melting point. Water molecules have more energy than ice and moves quite freely, while the ice molecules is more structured against the other and move less. For a ice molecule to break the bond from the other ice molecules and turn into liquid, it must obtain more kinetic energy. The molecule will take this energy from the surrounding molecules. This means that the molecules around have less energy and are moving more slowly. Since temperature is defined as how fast the molecules move, the temperature decrease during the transition from ice to water. In the case of pure water, the melting will stop at a temperature of 0 ° C, as the same amount of ice melts as the amount of water will turn to solid.

This point of equilibrium is changed with the presence of salt. Since the melting point is lowered, the melting process will be more attractive as long as it is above the 'new' melting point. The melting process will continue until the salt solution is so diluted that the melting point temperature is equal to the temperature of the system. When equilibrium is achieved, the amount of melting ice will be equal to the amount of water freezing (5).

In real life, out on the roads, the melting process will happen in an open system and the temperature of the surroundings will be constant. As the ice melts, the temperature of the

remaining ice goes down and in time there will be no more energy to collect from the remaining ice. To continue the melting process the ice will take energy from the surrounding air and pavement since this is warmer than the ice. This means the temperature of the system will reach equilibrium at same temperature as the surroundings. This is what the calorimeter tries to imitate, ice melting at a constant temperature. The development of the temperature as the ice melts in an open system is shown in Figure 3 Development of temperature in open surroundings.
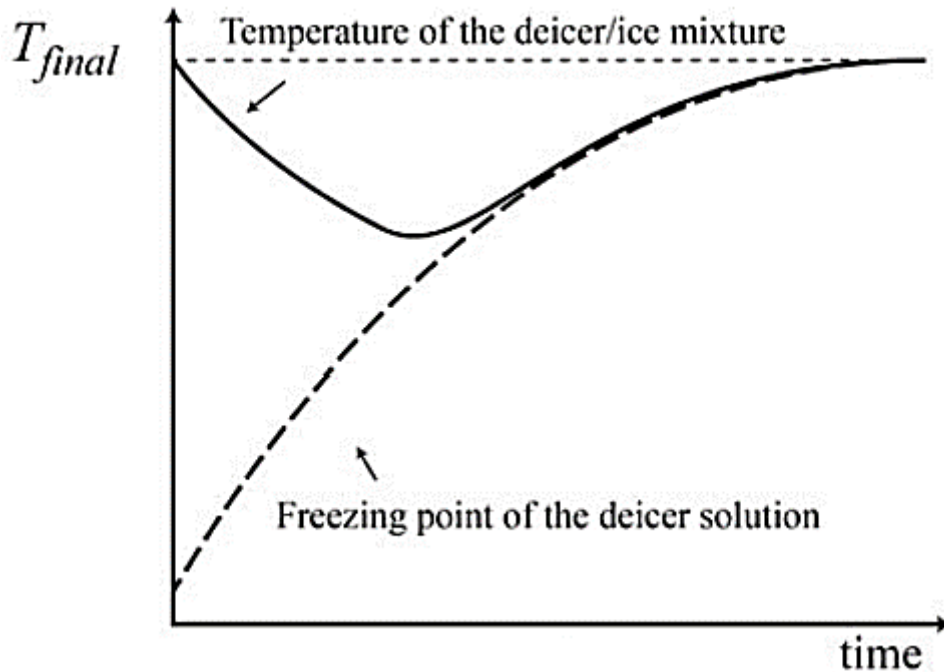

Figure 3 Development of temperature in open surroundings (7)

2.4 THEORETICAL MELTING CAPACITY FOR NACL

In this section, the method to calculate the theoretical melting capacity for NaCl is shown. In deicing there are a number of chemicals which can be used, but in Norway regular salt (NaCl) is used. As this is a chemical where the properties is thoroughly examined, this is a good chemical to use as a basis of comparison.

Theoretical melting values

In the CRC handbook the freezing curve is found empirically. (8)This is regarded as the theoretical foundation for the theoretical melting capacity. From the melting curve, it is possible to calculate theoretical melting capacity at given temperatures. As described in section 3.6.2, we can find the end concentrations at different temperatures. This means, with a given amount

of salt, it is possible to calculate the amount of water necessary to achieve this concentration. For an arbitrary value of temperature the equation is given in equation 1

$$C_{end}(T) = \frac{m_{salt}}{m_{salt} + m_{water}}$$ (1)

m_{water} refers to the ice melted. As solid salt has the possibility to melt ice, all the water in the equation is reagarded as melted ice. When equation X is changed with the respect to m_{water}, the equation looks like equation 2 below

$$m_{water} = \frac{m_{salt}(1 - C_{end}(T))}{m_{salt}}$$ (2)

From this we can find the theoretical melting capacity at any given temperature, defined by equation

$$Melting\ capacity = \frac{m_{water}}{m_{salt}}$$ (3)

Figure 4 shows the melting capacity at different temperatures graphically.
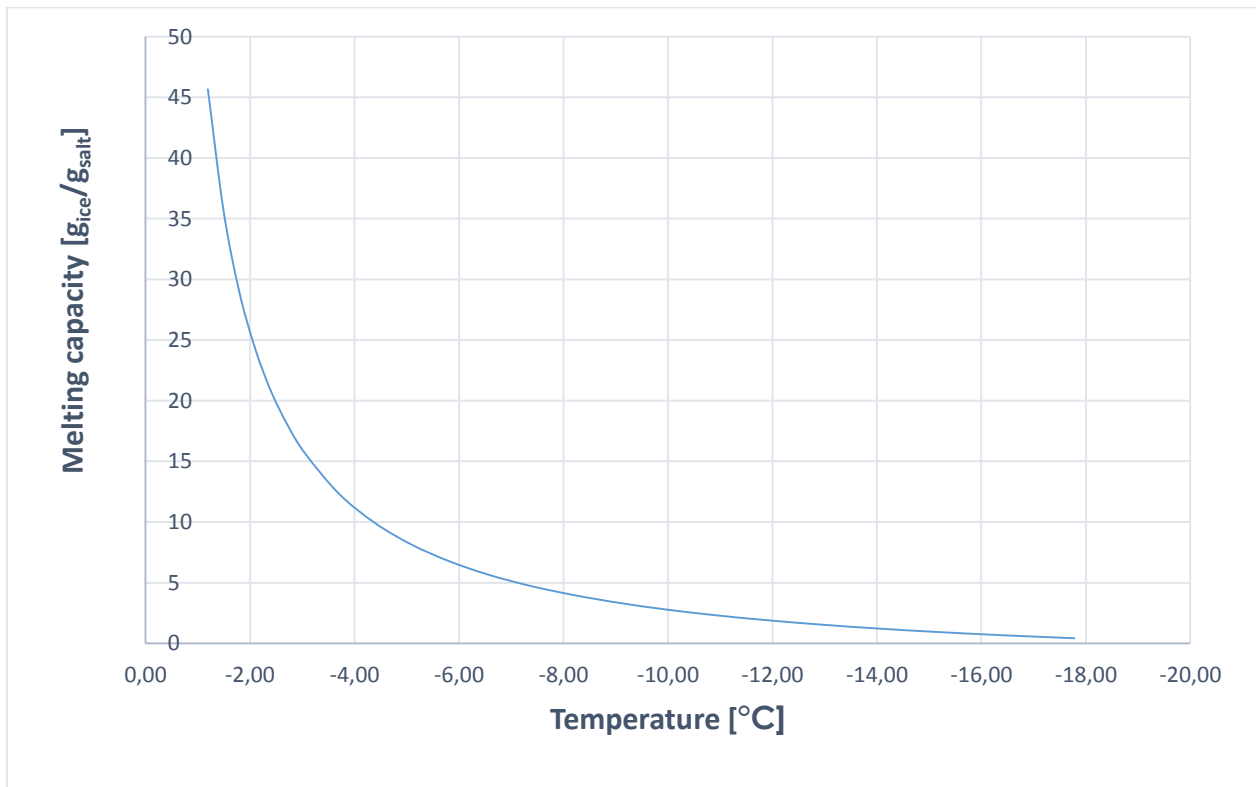

Figure 4 Calculated theoretical melting capasity in [g ice/g salt] at different temperatures

2.5 EXISTING TESTS

Melting capacity of a salt is often measured with respect to time and amount of melt produced for a given amount of salt. In deicing, it is a desire that the salt melts the ice as quickly as possible and the melting rate is an important characteristic. The time between the salt is added on the road, to the point where to the ice is melted away will be critical. In this intermediate phase, one has a situation with a frozen road surface with a thin water layer, which provides low friction and a traffic hazard.

2.5.1 Differential scanning Calorimetry

Differential scanning calorimetry (DSC) is a different type of calorimeter that is already been used on an experimental level to investigate the properties of deicers. The concept is to detect thermal changes by heating or cooling it alongside an inert reference. In scanning calorimeters, systematic errors will be eliminated as both sensors are subjected to the same thermal diversities. This enables the DSC to be highly sensitive and accurate (4).

The properties investigated with the DSC of deicers are the melting capacity and the effective temperature range in which the deicer can perform. Akin and Shi has proposed that the characteristic temperature found with DSC is a more reliable indicator of crystal growth than the eutectic temperature (9). The differential scanning calorimeter operates with two cells, one cell with inert material and the other with deicer. The samples are then subjected to a warming cycle with a constant temperature increase (2 °C/minute), where the DSC measures the energy that is required to keep a zero temperature difference between the materials. The principle of DSC is shown in Figure 5. To use a cooling cycle has proved to be more unreliable, due to the effect of super cooling. At temperatures near the phase change, it is need for more energy to melt the ice and there will be a characteristic peak in the heat flow, as shown in Figure 6. This peak will differ for different deicers, as will the surface area and temperature spread, Figure 7 DSC thermograms for MgCL (30%), CaCl (32%) and NaCl(23%) shows different thermograms for different deicers. The deicers with two peaks, the peak on the warmer side will be the characteristic temperature. (10)
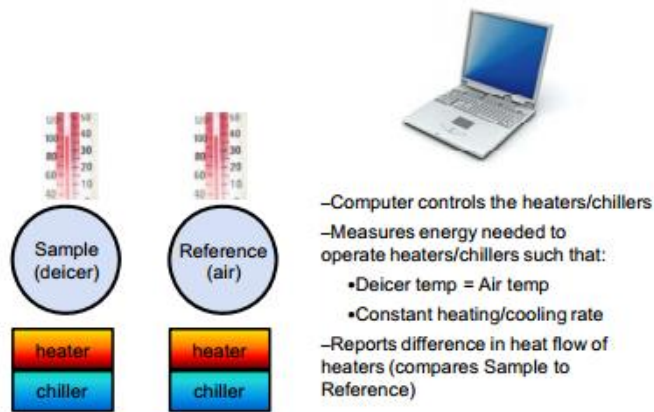
Figure 5 Consept of Differential scanning Calorimetry (10)

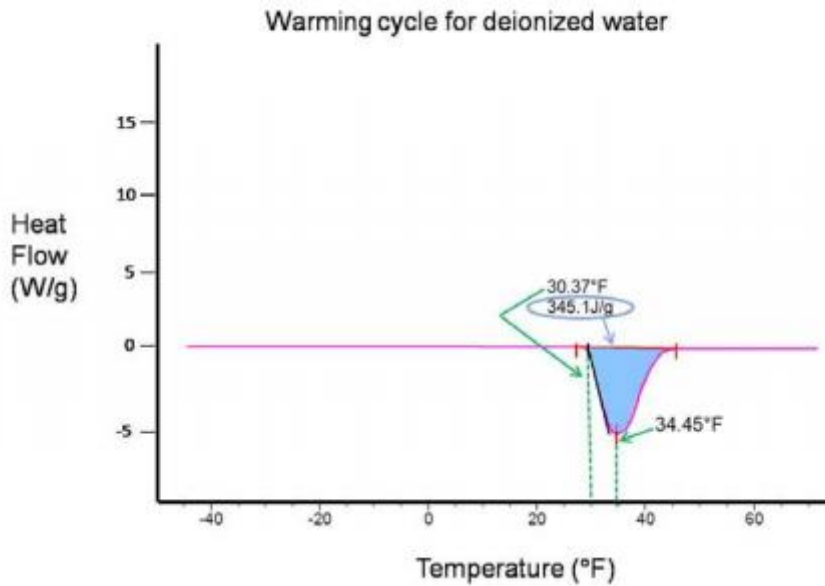*Figure 6 DSC thermogram of deionized water, warming cycle, 2 °C (10)*

The sample sized required in DSC is very little, around 10 µL, in each chamber. Melting capacity can be determined by using the amount of specific heat flow in the characteristic temperature peak, which will be the point at 34.45 F in Figure 6. For NaCl that had two peaks, the warmer peak indicates the efficient temperature, see Figure 7.
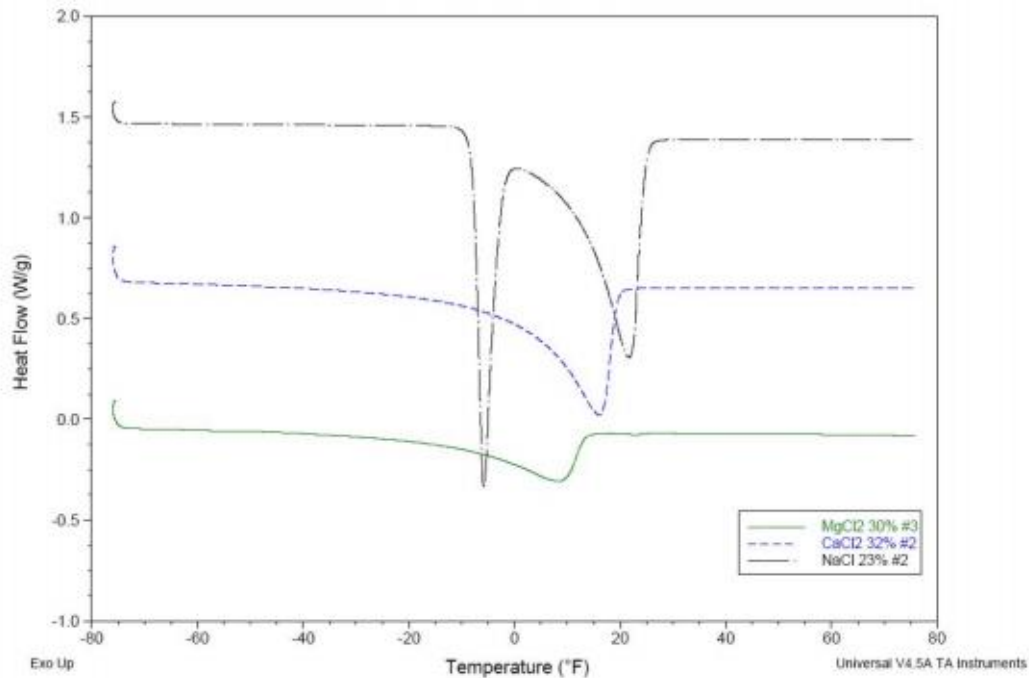
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Figure 7 DSC thermograms for MgCL (30%), CaCl (32%) and NaCl(23%) (10)

2.5.2 SHRP Melting capacity of ice

This test is a standardized test, which can be found in the Strategic Highway Research Program (SHRP), as test nr. 205.1 and 205.2, for solid deicer and solution respectively.

The aim in this test is to find the amount of ice metes regarding time and temperature. It is also possible to decide a temperature range in which the deicer is effective by performing the test at different temperatures.

The test is performed by freezing water to ice in a Petri dish, with a 3 mm thick ice layer. The Petridish has a diameter of 22,86 cm. The surface of the ice is smoothed to an even surface by partial melting and refreezing the surface. When the petri dish is placed in the temperature-regulated box, a thin layer of liquid deicer or solid particles is applied. When the test is performed with a solid material, it is important that the grain size is within a certain proportions. The amount of ice melted is measured at fixed times. This is done by decanting the Petri dish and use a syringe to measure the amount of water. The melted water is returned to the sample after each measurements. The duration of the test is normally an hour with at least four measurements.

The result can be presented as table with the total volume of a solution, at a given temperature and fixed weight of the deicer or as amount of ice melted per unit weight of the deicer.(11) Figure X shows the amount of ice melted over time.
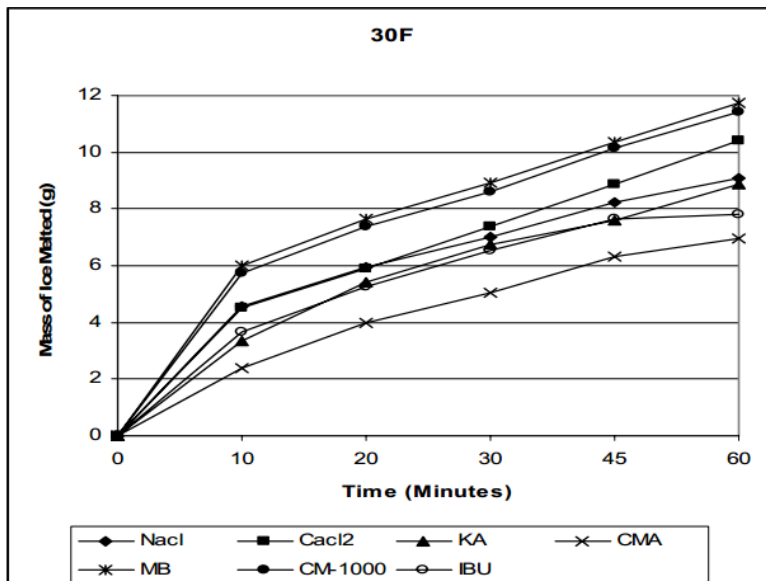

Figure 8 Ice melted at different times at 30 F (-1,1 C) (12)

2.5.3 Modified SHRP Ice Melting Capacity

Many different literature sources have modified the original SHRP test to make the test more reproducible (12, 13). One of the modified tests are developed by Akin and Shi (9) who made changes to increase the accuracy of the test. The changes made are:

- A smaller petri dish, requiring less ice and brine
- An increased number of number of tests conducted simultaneously
- A control dish with 23% NaCl to indicate success or failure
- Fewer samplings / measurements of liquid

Typical diagram melting capacity are prepared as shown in Figure 8 or in a table with the total amount of ice melted after one hour.

2.5.4 Shaker Test

This is an experimental method developed in a Master of Gerbino – Bevins (14) as a better method for determining the melting capacity with less uncertainty than SHRP test. It is designed to be easy and repeatable. The main problem with SHRP test is the need for a large freezer, to handle the sample in a cold room. In addition, the shaker test will simulate the conditions on the road better than the standardized test.

To perform the experiment must have an isolated cocktail shaker and freezer with thermostat. Both ice shaker and the salt is cooled to the desired temperature before the experiment is performed. The experiment is practiced by having accurately weighed ice and salt in the shaker and shake. For liquid solutions, the shaking is done in two cycles per minute, while for solid and prewetted salt there are three cycles per minute. The temperature is carefully measured throughout the experiment and the water is drained after toasting . To measure how much water is melted, the difference of the weight of ice before and after the experiment is measured.

The results of this experiment are presented as grams of ice melted per mL of liquid newspapers grams of ice melted per gram of solid salt or salt moisturized.

2.5.5 Ice Cube titration

This experimental test is a new test to improve the method to SHPR test and intends to measure melting capacity. The test is developed by Koefod et al. (15).

Instead of removing the melt water from the ice surface, as it is done in SHRP, the ice is removed from the deicer solution. To conduct the test, 400 g of salt solution is put in a beaker and ice cubes are added. The ice is periodically removed from the cup with salt solution the beaker. As the ice melts the beaker with solution be heavier. When the brine has reached equilibrium with the ice will stop the weight gain. A disadvantage of this approach is the long time it takes before equilibrium is achieved. The solution to this was to accelerate the point at which the solution was close to equilibrium before weighing the weight of the cup.

The result is the total amount of ice melted in grams. This is found by taking the difference between the initial weight of the cup and the final weight.

2.5.6 Summary

There are many tests developed to test the melting capacity. The standardized test is the SHRP Ice melting capacity test. Other tests are developed to improve the method, for better reproducibility and accuracy. Some of them have chosen to make smaller improvements to the standardized test, while others has made new tests. The one thing they all have in common is the removal of the water from the ice. On one hand this is an advantage, because it makes it possible to determine the speed of melting. But on the other hand this removal is hard to do without introducing heat into the system. The DSC is the exception, and the water and ice is not separate. In the DSC the solution goes through a warming cycle and the melting capacity is calculated based on the characteristic temperature peak. This is similar to the method developed

in this thesis, but this test is performed at constant temperature with both ice and solution present in the system.

3. MATERIALS AND METHOD

3.1 NTNU CALORIMETER

All the experiments are done in the Calorimeter and Figure 9 Picture of equipmentFigure 9show a picture of how the basic setup is.

Figure 9 Picture of equipment

The calorimeter is an isolated reactor with an electrical heater. The reactor is built with a cylindrical container with a volume of 0,5 L. The container is made of stainless steel, with a heater of 500W positioned under the bottom of it. The heater is powered by a regulated 160 V DC power supply (max 4 A). The actual output voltage and current is continuously measured and connected to the data logger, which makes it possible to control precisely how much heat is added to the system. The data logger is from national instrument type NI USB-6211.

The insulation is 12,5 centimeters thick and made of polystyrene. The lid of the reactor is made of 15 cm thick insulation and is overlapping with the inner circle with 5 cm (Figure 10). There is a hole in the lid that makes it possible to insert a syringe with ice during the experiments. The hole is always covered with a syringe

Figure 10 Cover with submerged insulation and stirrer

filled with insulation, to avoid heat leakage, and is only removed temporarily when the ice samples are inserted. A stirrer is attached to the lid. It has actual stirrer is a metal stick with a
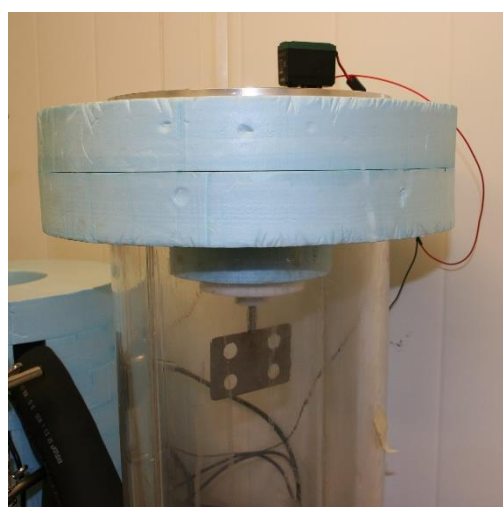
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metal sheet attached to it with holes in it to stir, see picture in Figure 9. The metal pin does not go directly through the lid, it is used gears to "break the path", to reduce heat loss. The stirrer is rotated with a speed of 15,5 RPM during all the experiments.

The system is equipped with a small cooler, to cool down both reactor and liquid prior to the experiments. The tube with the cooling liquid is placed only once around the reactor, to minimize the surface area of the cooler. The cooler is always turned off during experiments, since there is no possibilities to determine how much energy the cooling liquid supply to the system.

The computer controls the regulation system of the heater, based on the temperature difference between set temperature and measured temperature in the reactor. The heat added is expressed by equation 1 and 2.

$$Q_{added} = \int \dot{Q}_{electric} + \dot{Q}_{heat\ leakage} + \dot{Q}_{stirrer}\ dt$$
(1)

$$Q_{added} = \int U \times \dot{I} + C \times \Delta T + \dot{Q}_{stirrer}\ dt$$
(2)

From the heat measurements it is possible to calculate the amount of snow melted:

$$m_{melt} = \frac{Q_{added}}{L_{ice}}$$
(3)

This is if the initial temperature of the ice and salt solution is the same. If the temperature differs, the equation can be expressed as:

$$m_{melt} = \frac{Q_{added} - \Delta T \times m_{ice}}{L_{ice}}$$
(4)

3.2   SOLUTIONS

There are two different kind of solutions used in this tests. With the test done at room temperature, pure water was used. The water was measured in a beaker and it was used approximately 200 mL of water.

In the experiment with heat leakage, a solution of distilled water and NaCl was used. When the solution was prepared on beforehand, the salt and the water was weighted on a scale with the accuracy of 0,1 g. The solution was then properly stirred, until the salt had dissolved. The beaker was then weighted before and after the solution was poured inside the reactor. The amount of solution used was approximately 200 mL.

3.3   ICE

The ice used during experimenting is old snow, sieved so that the size of the snow crystals is between 1-2 mm. Old snow is more like small rounded ice balls. The sieving is done for two purposes, creating a big surface area, which makes the reaction to go quickly and obtaining a uniform size of the ice, which is important for consistency in the samples. A quick reaction is better for minimizing heat leakage and avoid a difference in temperature in water and ice. In contradiction to an ice cube, which will float on top on water, small crystals of ice will disperse in the water due to the stirrer and this will provide for an even temperature in the reactor. For extensive experimenting, the snow/ice has to be quite similar to obtained the required accuracy. The ice used in the experiment are shown in Figure 11. This is especially important for further experimenting, if the speed of the reaction is the main goal.

Figure 11 Ice samples (15)

Before experimenting the ice crystals are compressed into a syringe, as shown in Figure 11. Each syringe contains approximately 25 g of ice, making a density approximately 46 g/cm^3. During experimenting, it was noticed that it was important that the ice had sintered a bit to keep its shape when put into the reactor. This was done by putting the syringes in room temperature for a short period of time, less than a minute was adequate to obtain some melting of the ice crystals. After the snow was put inside the cold room, to let the temperature stabilize and to get a hard crust on top of the snow. The syringes was carried to the calorimeter in an isolated box. This was later upgraded to an insulation box with cooling elements to further prevent heat from warming the ice.

To keep the temperature measurements accurate proved to be hard, as the temperature sensors was taped outside the syringe. This solution should in further experimenting be improved. Preferably with smaller/ even sensors that is easier to place inside the syringe. Even though it is some drawbacks of the accuracy of the temperature measures, it will not amount to a big error. If the magnitude of error is one degree Celsius, it constitutes to 50 J per syringe added to the reactor.

3.4   METHOD

The experiments can be divided into two parts. The first part is the determination of the magnitude of other heat sources, other than from the electrical heater. This is mainly the heat leakage and heat from the stirrer. The heat leakage is used in both main experiments, but it will have a bigger impact on the results during the experiment at low temperatures. In addition a test determining the contribution of heat from the stirrer is performed.

3.5   PART 1

3.5.1 Heat capacity of reactor

Before the heat leakage can be calculated it is necessary to calculate the heat capacity of the reactor. The heat capacity describes how much energy goes to warm the reactor. The experiment to measure heat capacity was performed four times, and the mean value of the four results was used. The heat capacity of the reactor will only be used in the calculation of the heat leakage. Since the main experiment will have the same initial and resulting, $\Delta T = 0$, the contribution of the heat capacity of the reactor will be zero for these experiments, as indicated by the equation for heat capacity, given in section 2.2.

To do the experiment it is used:

- Thermos flask, with a temperature sensor
- Funnel with a rubbertube attached to the end
- Incubator/ Hot closet
- Warm water
- Reactor
- Picolog recorder

First the settings on the computer is prepared to log the temperature inside the container and the room temperature. The thermo flask is preheated by filling it with hot water, to keep the water from decreasing in temperature. The funnel is preheatet in a hot closet to approximately 60 °C. This is to avoid heat loss from the water as it is poured inside the container. 500 mL of hot water from the spring is poured inside the preheated thermo flask. The thermo flask with water is weighed at a scale with accuracy of 0,1 g. A thermometer, as shown in figure X is put inside the thermo flask to measure the temperature. The initial temperature of the water is registered after approximately 1 minute, allowing the temperature to be correctly measured. The temperature sensor is removed prior to testing. The funnel is removed from the hot closet and placed in the hole on top of the lid of the reactor, and the water is poured into the reactor. The water has a temperature of 56 °C and the reactor has a starting temperature at room temperature.

The principle of how the development of the temperature is within the reactor is shown in Figure 12. The time it takes for the temperature to stabilize inside the reactor is approximately 5 minutes. Since the time span is short, it is assumed that the heat leakage is zero and therefore the system is regarded as an isolated system.
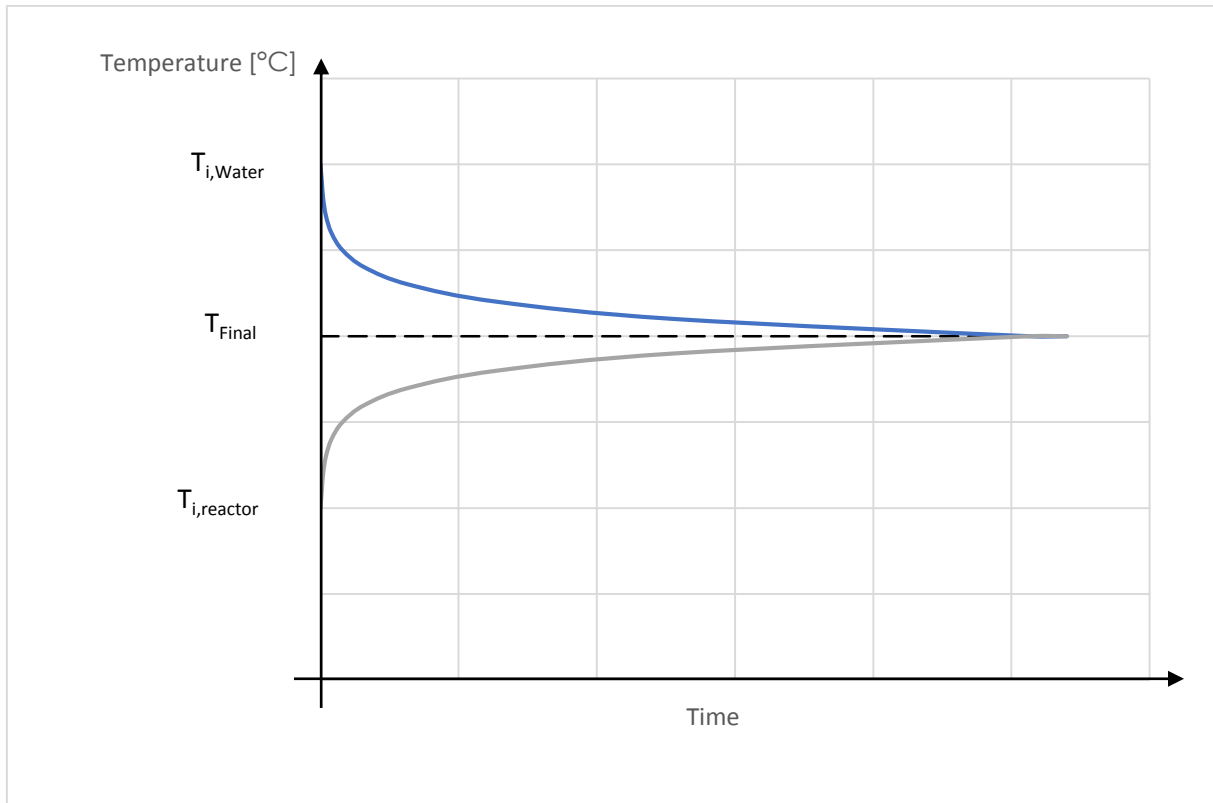
Figure 12 Development of temperature during heat capacity experiment

From the second law of thermodynamics we know that the total energy within an isolated system must remain the same. This means that the energy that goes to heat the reactor must come from the hot water. The heat capacity is calculated based on energy balance. The energy released by the water as it cools down equals the energy absorbed by the reactor. The deduction of the energy balance is shown below:

$$Q_{water} = Q_{reactor} \tag{5}$$

$$m_{water} \times C_{p,water} \times \left(T_2 - T_{final}\right) = C_{reactor} \times \left(T_{final} - T_1\right) \tag{6}$$

$$C_{reactor} = \frac{m_{water} \times C_{p,water} \times (T_2 - T_{final})}{(T_{final} - T_1)} \tag{7}$$

3.5.2 Heat leakage

Heat leakage is one part of the total energy added to the system. The heat leakage is he heat that conucts through the insulation and the stirrer rod. The gradient of the heat leakage will move in the direction of lower temperatures.

The principle behind this experiment is to see how much heat leaks into the reactor from the environment. This is done by letting cooled liquid heat up in the reactor until it reaches room temperature. The only sources of heat will be heat from the stirrer and the surroundings. Knowing the specific heat capacity for the liquid and the heat capacity of the reactor, it is possible to determine how much heat has leaked in over time.

The alcohol used in the experiment was technical alcohol containing 95% ethanol. The liquid was measured in a beaker and the beaker was weighted before and after the liquid was poured inside the reactor. The liquid and the reactor was cooled down to approximately -15 °C. When the calorimeter had reached wanted temperature, the cooler was turned off and the cooling liquid was drained from the tubes around the reactor. The temperature was registered every 30 seconds until the mixture had reached room temperature. During the experiment the stirrer was turned on, making sure the temperature of the liquid was uniform.

When the mixture inside the reactor is colder than room temperature the direction of the heat flux will be into the reactor. To know how much heat is required to warm the solution it is necessary to know the alcohols heat capacity. An equation for the heat capacity is found by regression of empirical data found in CRC handbook (16), the result is shown in Figure 13.

Figure: Spesific heat capacity for alcohol. $y = 0{,}0074x + 2{,}2637$. X-axis: Temperature [°C]. Y-axis: Spesific heat capacity [kJ/kg*K].
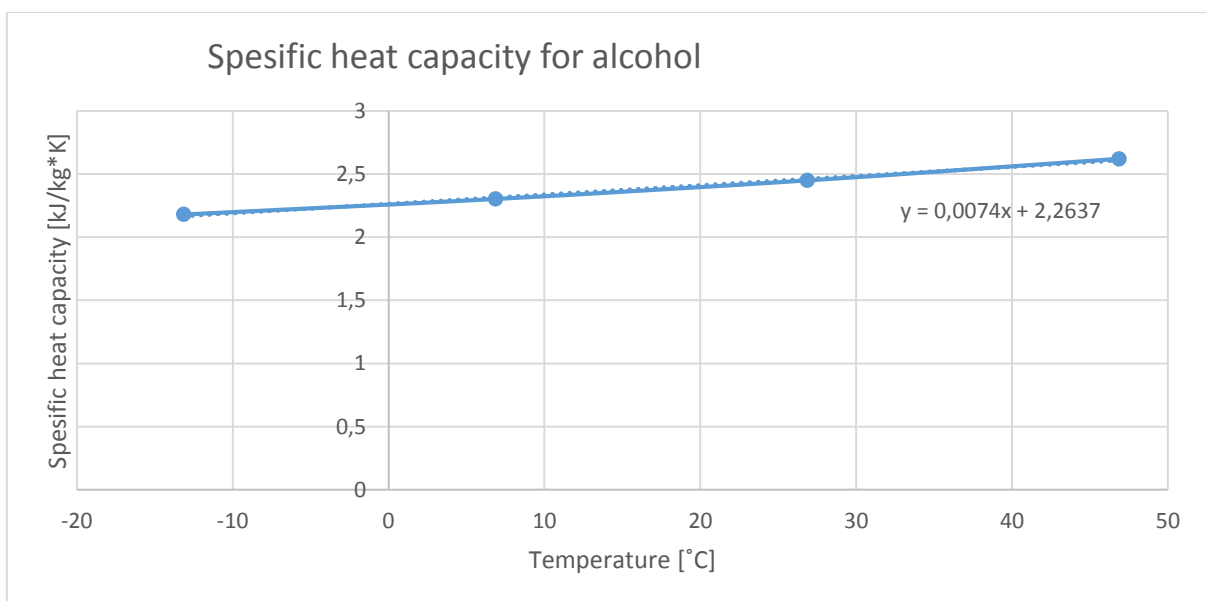
The calculations is done with one step per degree increase in temperature. Since the total temperature rise is 37 degrees, there is in total 37 steps. For each temperature step, the appurtenant heat capacity is calculated, by equation 8. From this, the energy necessary to increase the temperature by one degree is calculated and then the heat leakage equation 10 is used.

Doing this for every step, it is possible to plot the heat leakage and the temperature difference (between temperature in reactor and room temperature) as shown in Figure 20.

$$C_{p,i}(\overline{T_i}) = 0{,}0074 \times \overline{T_i} + 2{,}2637 \ [J/g \times K]$$

(8)

$$E_{Added,i} = C_{p,i} \times m_{alcohol} \times \Delta T_i + C_{container} \times \Delta T_i \ [J]$$ (9)

$$Q_{leakage,i} = \frac{E_{added}}{\Delta t_i} \ [J/s]$$ (10)

3.5.3 Heat added by stirrer

The objective of the experiment is to see how much heat the stirrer generates. This factor has to be accounted for in the energy equation.

The equipment used was the calorimeter and 477,5 g pure water. The reactor and water held room temperature. The amount of water was poured in the reactor and then the stirrer was started. A picoLog Recorder was used to register the temperature each second. If the temperature rises this is an indication that the stirrer add heat to the system. If the water and in reactor have the same temperature as the surroundings there will be no heat leakage.

The duration of the experiment was 50 minutes, assuming this was enough time to indicate a potential rise in temperature and since the duration of the experiments of accuracy is expected to be no longer than this.

3.5.4 Regulation systems

LabView regulates the heat added to the reactor based on the difference in the temperature of the solution and the set temperature. The set temperature is the temperature of the solution that

is registered in the moment the start button in the program is pushed. As the ice melts, the temperature will decrease and the heater adds heat to counteract this change in temperature.

The output of heat is defined as:

$$Output = k_c \times \varepsilon + \frac{1}{T} \int_{t=0}^{t} \varepsilon \; dt,$$

(11)

Where

$\varepsilon = T_{set\;temperature} - T_{measured\;temperature}$

$k_c - Proportional\;gain$

The output gives a value between 1 and max 10. This number is directly linked to the output of Voltage. The voltage varies between 0 and 160, so an output of 1 gives an voltage of 16 and a output of 10 gives an voltage of 160. This is the U described earlier in section 2.1.The integral at the end of equation 11 gives an input over time if the temperature difference is small.

In addition to give the output of the electrical heater, LabView also continuously adds the heat leakage to the total energy added. LabView measures the temperature 10 times each second and uses the mean temperature difference between T_{room} and $T_{reactor}$ each second to calculate the appurtenant heat leakage.

A few preliminary tests was done to decide the settings for the gain and integral factor. The tests was performed with cold salt solution and ice samples, prepared as described in section 3.3. The number of ice samples was not more than that the solution had the capacity to melt all the snow added.

It is important that the proportional gain is not too high, as this will lead to an excessive temperature rise. There is a lag between heat added and the melting of snow and the temperature rises too quickly, equilibrium is not obtained and the results are not valid, see Figure 14.
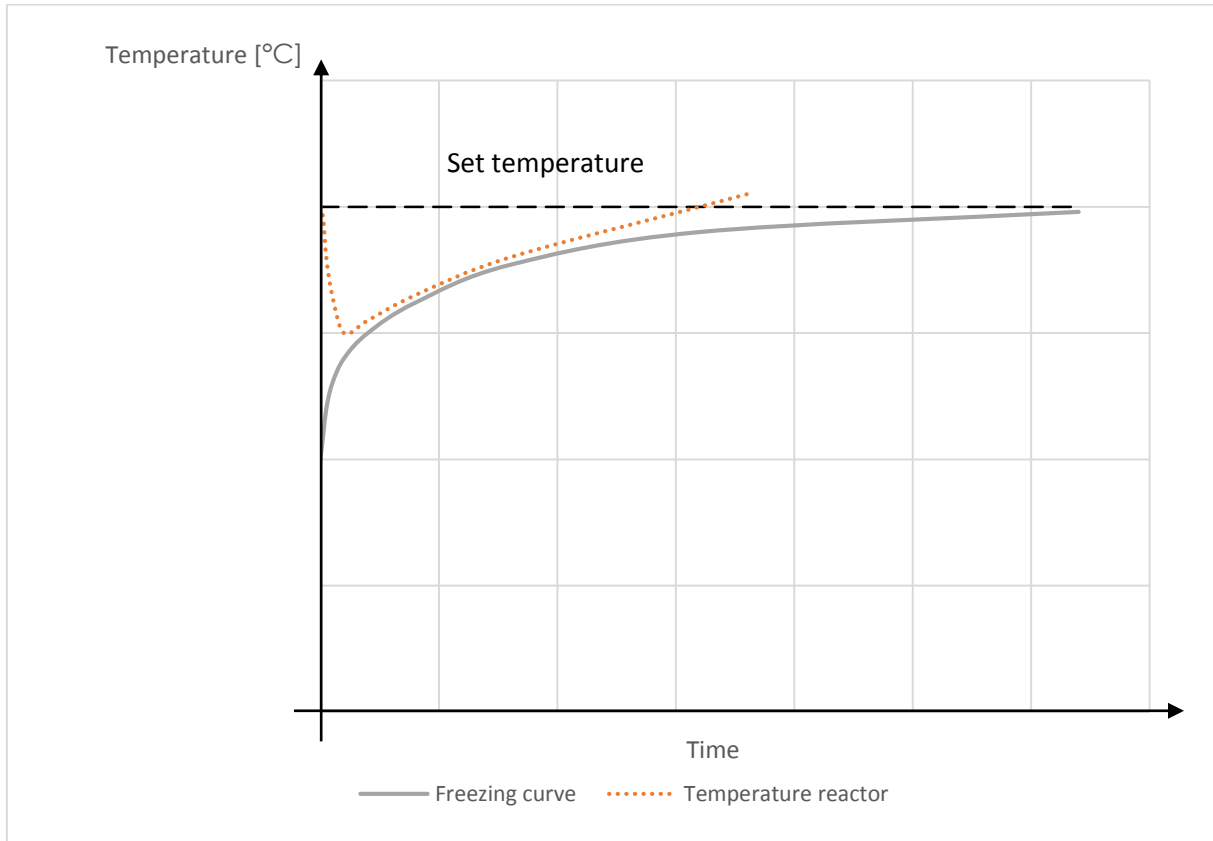
Figure 14 General principle with too much power

3.6   PART 2

3.6.1 *Ice melting in pure water at room temperature*

The experiment is performed to investigate the calorimeters accuracy to predict the amount of melted ice. The most comprehensive experimenting was performed at room temperature. In this environment, there heat leakage will be minimal, as the temperature difference inside and outside the reactor is little. The experiment was performed with pure water and ice samples. At room temperature all the added ice will melt, and it is possible to determine how well the computer program register heat added to the system and it is easy to calculate the theoretical energy necessary to do so.

The right settings in the calorimeter are preset to the settings found by tests done in part 1. The reactor is filled with approximately 200 mL of water at room temperature. The ice samples are prepared in advance, as described in 3.3. There was in total performed 22 tests, where 11 of these was performed with one syringe of snow, 4 tests with 2, 4 tests with 3, 3 tests with 4 syringes.

When the program in LabView and the ice is inserted four things happen from start to finish:

1. The ice is warmed up to melting temperature at 0 °C
2. The ice melts and the temperature drops
3. Heat is added
4. The melted ice is warmed up to set temperature

Since the temperature difference between start and end is zero, the water in the reactor is not a part of the reaction. The water in the reactor will cool down a bit as a result of the cold ice added and the melting, but in the end it will have the same temperature as the initial temperature. As Hess's law describes, the total energy use only depends on the start reactants and the end reactants. This means if the difference in temperature is zero, this reaction makes no impact on the total energy in the system, due to the simple fact that it takes the same amount of energy to heat up one kg of water that is released when the same amount of water cools down.

Of measurements it is important to know the exact amount of snow added, the temperature of the snow and the start temperature if the water in the reactor.

There are done some changes in connection with the interface, based on experiences from the first experiments. The user interface was improved. First many of the input parameters had to be inserted manually. This including heat leakage, gain intevall time, set temperature and ice temperature, as shown in Figure 24. As it led to too many processes at once, the layout and the programming was edited. After the changes, ice temperature and set temperature was recorded automaticly when pressing the start button in the program. The registration of continuous data in the computer was not done at first, but this was a feature that also was added before the testing of ice melting in room temperature. The measured amount of heat is compared to theoretical energy required to melt the ice. The theoretical energy is calculated by equation 12. Equation 13 is a deduction of equation 12.

$$Q_{theoretical} = Q_{warm\ ice} + Q_{melt\ ice} + Q_{warm\ melting\ water} \qquad (12)$$

$$Q_{theoretical} = C_{p,ice} \times m_{ice} \times (T_{melt} - T_{ice}) + L_{ice} \times m_{ice} + C_{p,water} \times m_{ice} \qquad (13)$$
$$\times (T_{set\ temp} - T_{melt})$$

The error is calculated as

$$Error = \left(1 - \frac{Q_{added}}{Q_{theoretical}}\right) \times 100\ [\%] \qquad (14)$$

3.6.2 Ice melting with saltsolution

The precision of the measurements was studied in the experiment of accuracy in room temperature. As this turned out to be rather consistent, there was an ambition to experiment the actual purpose of the calorimeter. The objective was to obtain results, which could be compared with existing data from other experiments. To achieve this it is necessary to perform experiment where the melting capacity of the solution is exceeded. This means there will be some snow that will not melt.

The settings was the same as in room temperature.

Before experimenting, it is necessary to decide a number of parameters to find an optimal start concentration. The parameters we need to set is:

- T_{set} - Set temperature
- $m_{water, start}$ - Amount of water at the start
- $m_{ice, melted}$ - Wanted amount of ice to melt

When the set temperature is given, it is possible to decide the end concentration based on the freezing curve Figure 2. The calculation is done with an equation found by using regression in excel, based on the empirical data from the handbook of chemistry and physics(16). The equation based on the regression and is given in equation 15.

$$C_{end}(T) = -0.000005 \, T^3 - 0.0004 \, T^2 - 0.0178 \, T - 0.0004 \tag{15}$$

Based on the definition on consentration, the amount of salt can be calculated from equation 16. With all the parameters set, it is possible to solve the equation with regard to the amount of salt, m_{salt}. As the only difference between the start and the end concentration is the ice melted, it is possible to calculate the start concentration.

$$C_{end} = \frac{m_{salt}}{m_{salt} + m_{water,start} + m_{ice,melted}} \tag{16}$$

Table 2 give the result of some of the calculations, given 200 g of water at the beginning and 69 g of melted snow. This corresponds to approximately three syringes with snow.

Set temperature	Start concentration	End concentration	Amount of salt [g]	Amount of melted ice[g]
-2	4,32 %	3,25 %	9,04	69
-5	10,47 %	8,00 %	23,39	69
-10	17,96 %	14,00 %	43,79	69
-15	23,98 %	19,00 %	63,10	69

The calorimeter was prepared by cooling down the liquid in the reactor. The cooler is turned off immediately before the experiment is started, without draining the cooling liquid out of the tubes. The computer record the experiment, the same way as it did on the previous experiment at room temperature.

When the snow is put inside the reactor, there are three possible outcomes:

1. The concentration of the salt brine has the ability to melt all the ice added
2. The concentration of the brine has no capacity to melt any of the ice added
3. The concentration of the brine has the ability to melt some of the ice added

Irrespective of the outcome the result of the calorimeter should, in theory, work in all three cases. Ice melting will lead to a decrease in temperature and when the temperature in the reactor differs from set temperature the calorimeter will add heat to the system to equalize the difference. Hence, in outcome number two, there will be no temperature drop and the experiment will end without any snow melting or any heat added. In outcome three, only some snow is melted. As the snow melts the salt solution will dilute and the melting temperature will increases, this will continue until equilibrium is reached. Equilibrium is obtained when the amount of melted snow has made the brines melting temperature equal the set temperature Figure 16. This assumes that it is a balance between energy added and the snow melting. If the heat added is too strong, the melting will happen faster than wanted and the temperature increase will to be too quick to obtain the wanted equilibrium. This situation will be as in Figure 14.There will be a small delay from heat added to the temperature rises in the reactor. If the heat added is too small, the experiment will take more time. Increased amount of time will result in a bigger heat leakage and more uncertainty.
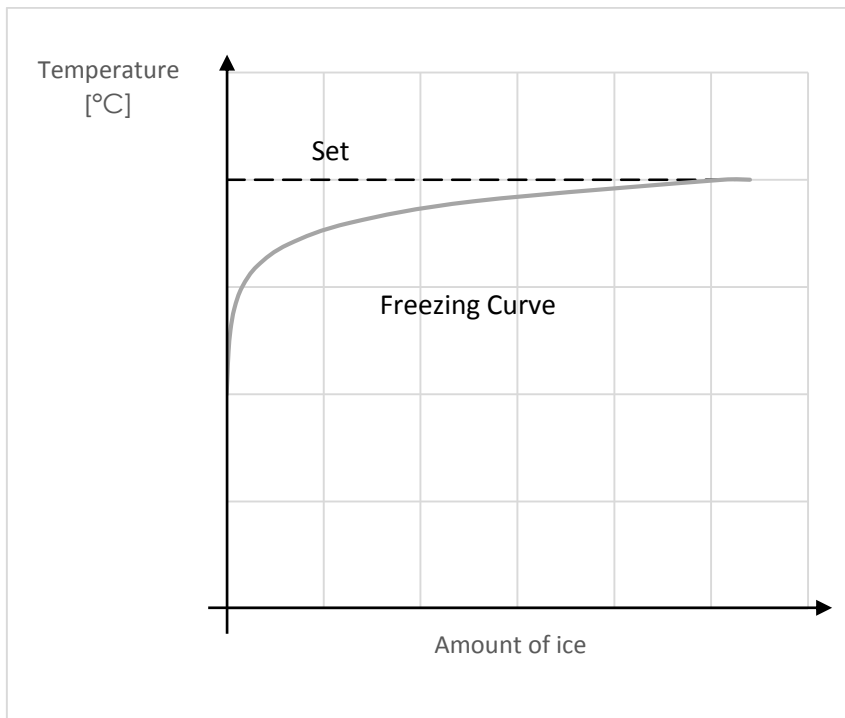
Figure 15 Process in the reactor as the ice melts
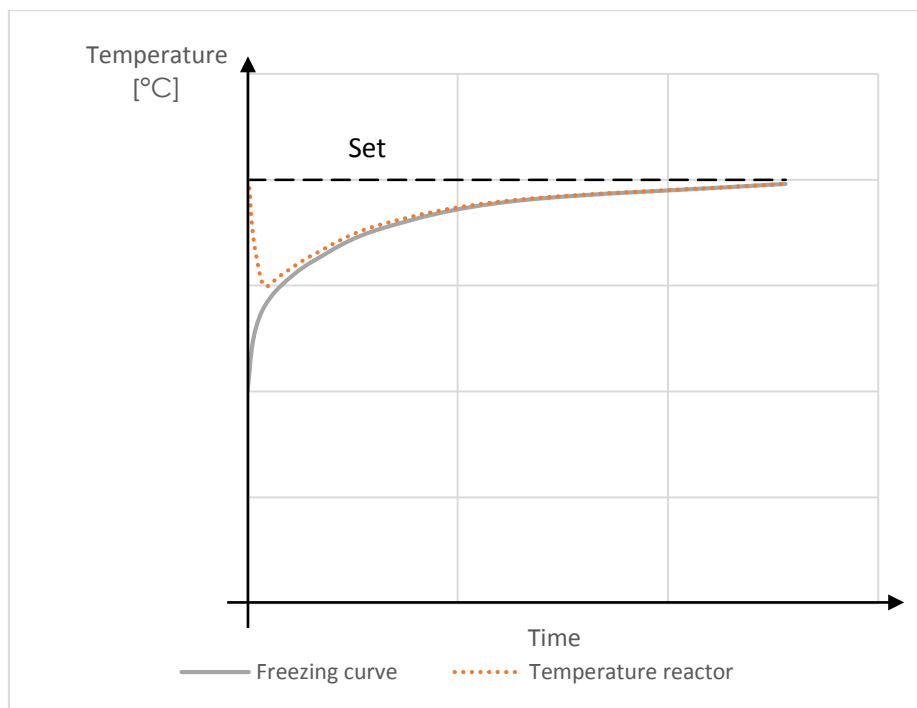
Figure 16 Ideal development of temperature in reactor

The theoretical energy of the processes is similar to equation 17, but in this case, not all of the ice melts, and there will be remaining ice left in the reactor.

$$Q_{theoretical} = Q_{warm/cool\ ice} + Q_{melt\ ice} \tag{17}$$

$$Q_{theoretical} = C_{p,ice} \times m_{ice} \times \left(T_{set\ temp} - T_{ice}\right) + L_{ice} \times m_{ice} \tag{18}$$

As the temperature in the calorimeter is lower than 0 degrees, there is a possibility that the ice is warmer or colder than the set temperature. This means it varies if the ice needs to cool down, or warm up. If the ice is warmer than the set point it will liberate heat in the process of cooling, adding a negative factor to the equation. The negative sign is because the theoretical energy is compared to the recorded heat, and the computer only register the heat added to the system through the heater and the heat leakage.

4. RESULTS

In this chapter the results from each of the tests performed.

4.1 PART 1

4.1.1 Heat capacity

The test to find the heat capacity was preformed 4 times. The results is represented in Table 3.

Table 3 Results from heat capacity experiment

	Unit	Symbol	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Date			06.02.2014	19.02.2014	24.02.2014	21.03.2014
Weight Thermos with water	[g]		1202,4	1182,8	1178	1198,8
Weight thermos without water	[g]		692	691,8	691,3	692,4
Weight water	[g]	mwater	510,4	491	486,7	506,4
Start reactor temperature	[°C]	T_1	21,3	22	22	20,3
Temperature water start	[°C]	T_2	64	64,6	64,6	64,5
Final temperature	[°C]	Tfinal	55,6	56,1	56	56
Specific heat capacity, water	[J/g*K]	Cp,water	4,1856285	4,1856285	4,1856285	4,1856285
Heat capacity, reactor	[J/K]	Creactor	523,19	512,28	515,28	504,67

A typical graph of the actual measured data is shown in Figure 17 .On the graph we see that the temperature inside the reactor rises quickly as the water is poured inside.
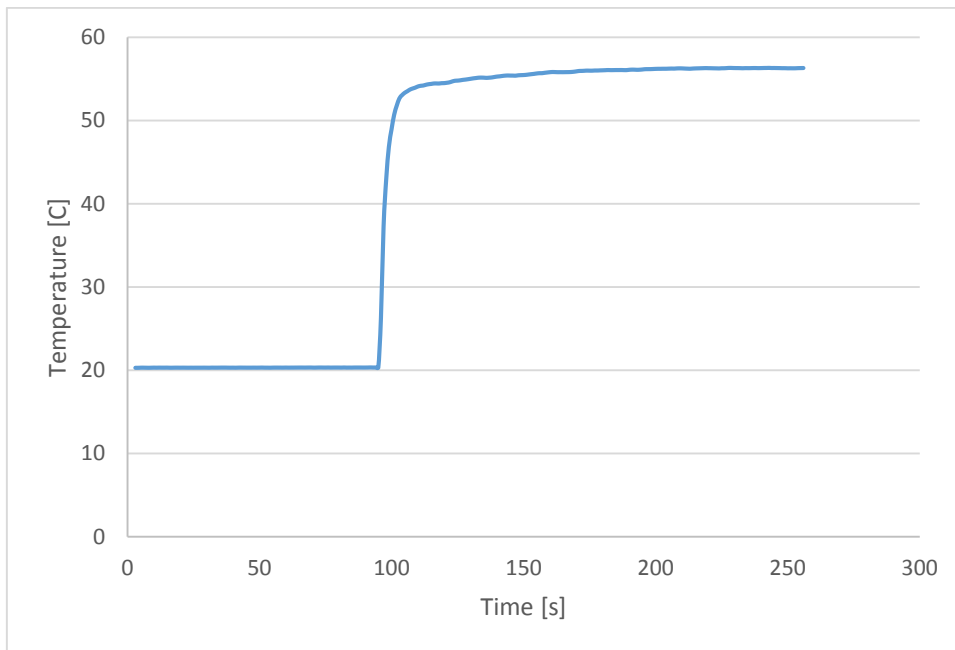
Figure 17 Typical temperature development in the test for heat capacity

The average heat capacity is calculated to be 514 J/K. This is the value that is used in the later experiments. Based on confidence limits the result will lay between 514 ± 24 J/K 95% of the time.

4.1.2 Heat leakage

The temperature inside the reactor varied with time as shown in Figure 18. The point where the temperature starts to rise was the point where the cooler was turned off, this happened after approximately 2 hours. The temperature in the reactor flattens around the time of 40 hours. The temperature in the container never exceed the room temperature, although the gradient of the temperature has a slight inclination, indicating there might be a crossing if the test had continued 24 hours more.
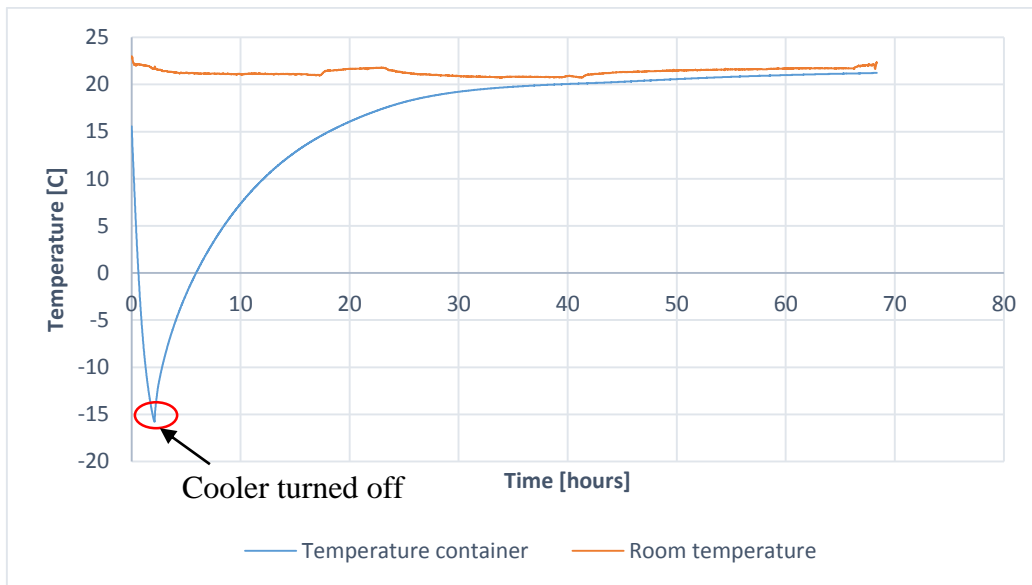
Figure 18 Temperature development during experiment for heat leakage
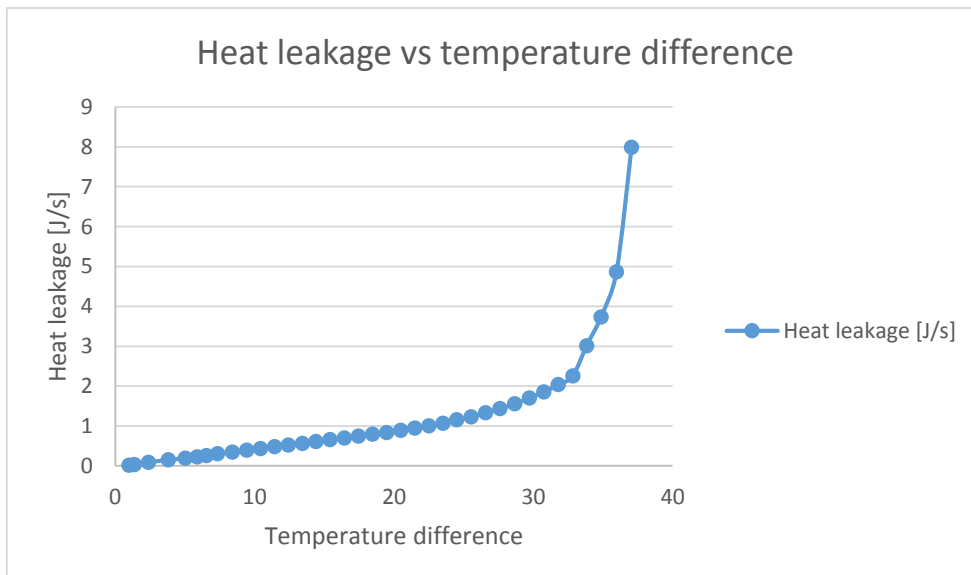
Figure 19 Heat leakage vs temperature difference

The heat leakage as a function of the temperature difference between the room temperature and the solution temperature is plotted in Figure 19. The development of the heat leakage is close to linear up to a temperature difference at 30 °C .The increases in heat leakage at temperature differences bigger than 30 is not linear and it is as high as 8 W at a temperature difference of 37. This is not accounted for in the final calculations, because was is assumed that it did not reflect the actual situation. The sudden rise in temperature could be explained by the drainage of the cold fluid. When this is drained, air with room temperature is introduced to the system.
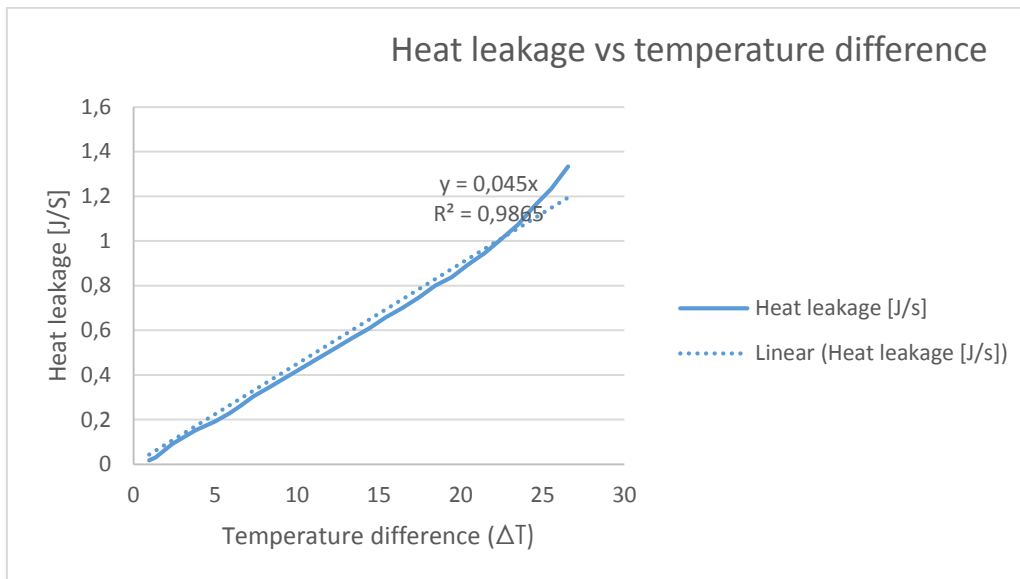
Figure 20 Heat leakage plottet versus temperature difference

Figure 20 shows the linear correlation at temperature differences less than 26 degrees. The inclination of the slope is by linear regression found to be 0,045 [W/K]. This makes it possible to include the heat leakage in the calculations directly on the computer.

4.1.3 Heat added by stirrer

The development of the temperature in the reactor is displayed in Figure 21. The temperature drop appears as the water is poured inside the reactor, indicating that the air temperature was slightly (0,05 °C) higher than the water.
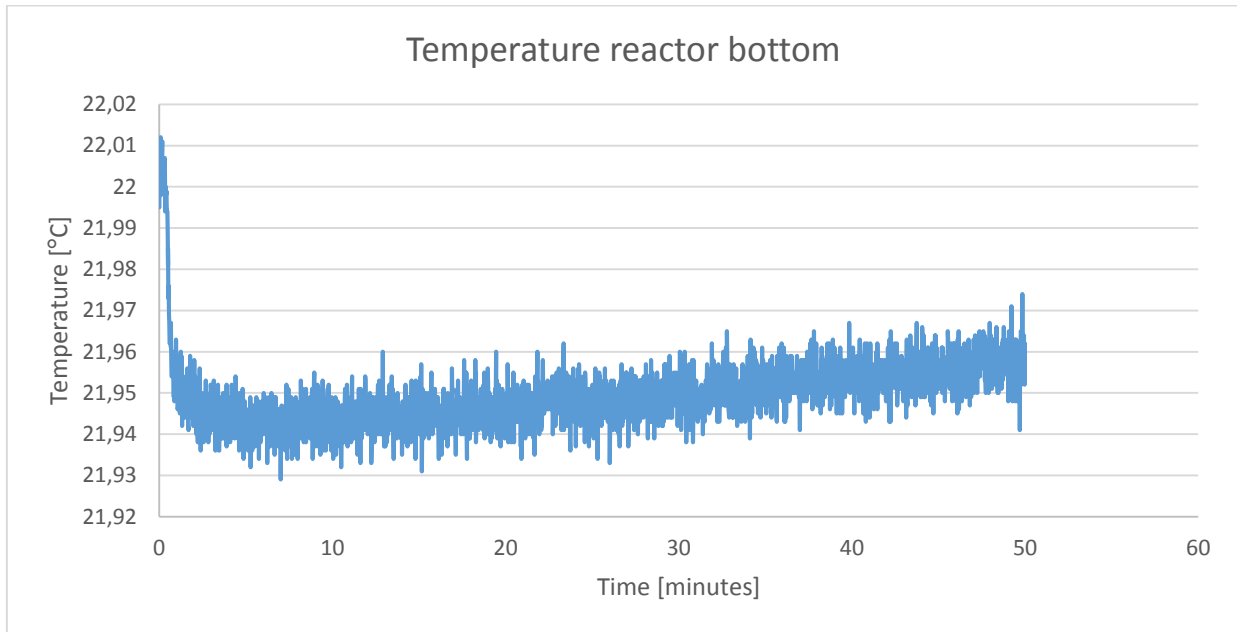
Figure 21 Temperature development during experiment with stirrer
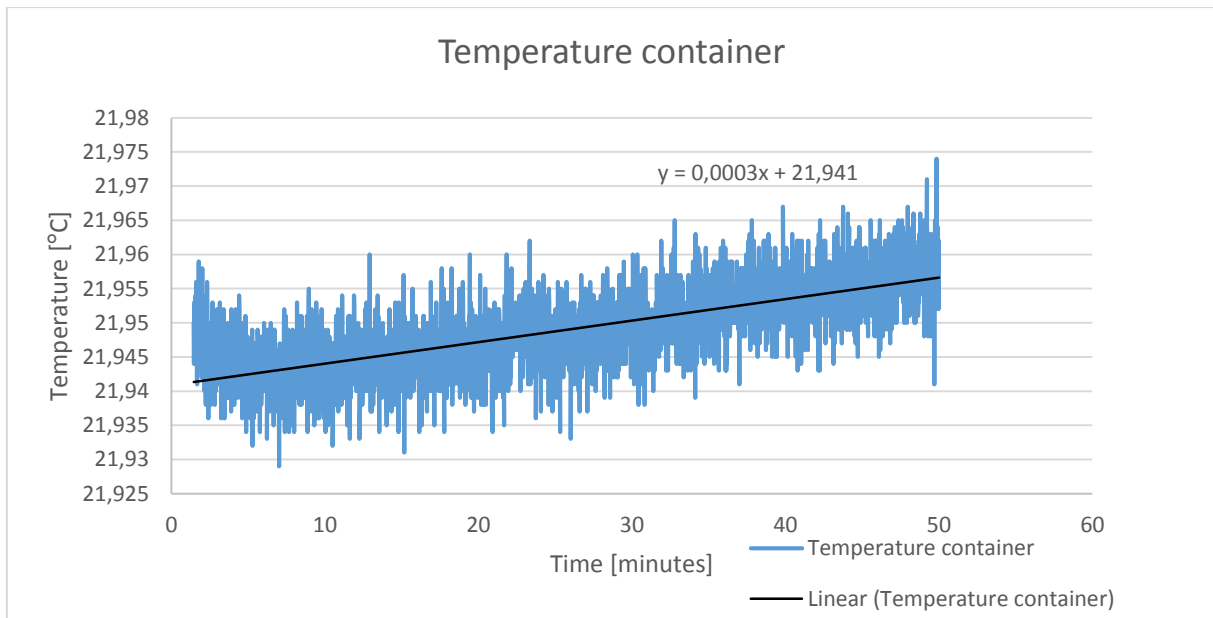
Figure 22 Basic data used in calculations

The rise in temperature is calculated between 1,5 minutes and 50 minutes, to exclude the temperature drop in the beginning and letting the temperature sensor stabilize. Figure 22 show the part of data that is included in the calculations. In this time interval the rise in temperature equal 0,015 °C, which equals an amount of energy of 29 J and 0,01 W. In addition, the room temperature is higher than the temperature of the water, contributing the heating by heat leakage.

Temperature difference	0,014565	°C
Time difference	2913	s
Amount of water	477,5	gram
Specific heat capacity	4,18	J/g*K
Energy added	29	J
Watt	0,01	J/s

If the heat leakage is set to be 0,045 W/K and the average temperature difference is 0,0075 over a time span of 2913 seconds, the contribution from the heat leakage is 0,98 J. This constitutes 3,3 % of the total energy and has little impact on the result.

Table 4 Summary of results, part one

What	Value	Unit
Heat Capacity	514	J/K
Heat leakage	0,045	W/K
Heat from stirrer	0,01	W

4.1.4 Regulation systems

During preliminary testing, to get to know the equipment there was two main things set:

- Input parameters
- The interface of the labview program

The input parameters was varied and tested in some initial testing. The results of the tests showed odd results when the integral time was set on something else than zero. The proportional

gain was also chosen to be 1, as bigger values resulted in an more sudden increase in temperature and the total energy added was more than the theoretical energy required.

Figure x shows the result of one test where the integral time was set to 0,01. There was displayed some strange variations in temperature, which also is too high. This only happened with tests where the integral time differed from zero. There was made no further testing to investigate the reasons for the odd measurements.
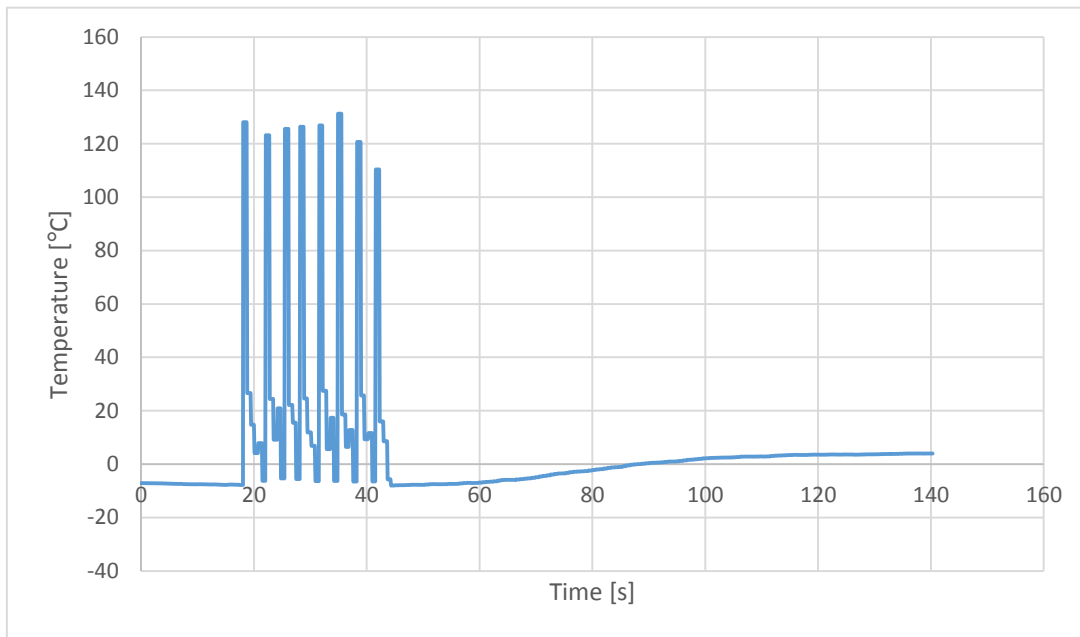
Figure 23 Test performed with a integral time of 0,01 s

The interface on the computer was changed from Figure 24 to Figure 25. First most of the settings had to be inserted when the program was opened. Heat leakage, Setpoint, proportional gain Integral time and the derivative. The latter was always zero. In addition the on/off swich to the left had to be turned on to start the registration of the temperature and power. This had to be swiched on in addition to the startbutton to the left, which started the registration of the total energy added.

After going through a few test rounds a few changes was made. The only input necessary was the heat leakage. There was only one start button and the set point is registered as the temperature of the liquid (reactor) in the moment the start button is pushed. It is also inserted a delay of 30 seconds in the program before it starts checking for differences in temperature. The delay makes it possible to insert the snow after starting the experiment. As the other input parameters were decided, these were added in the algorithm, but not displayed on the interface.

Figure 24 User interface start
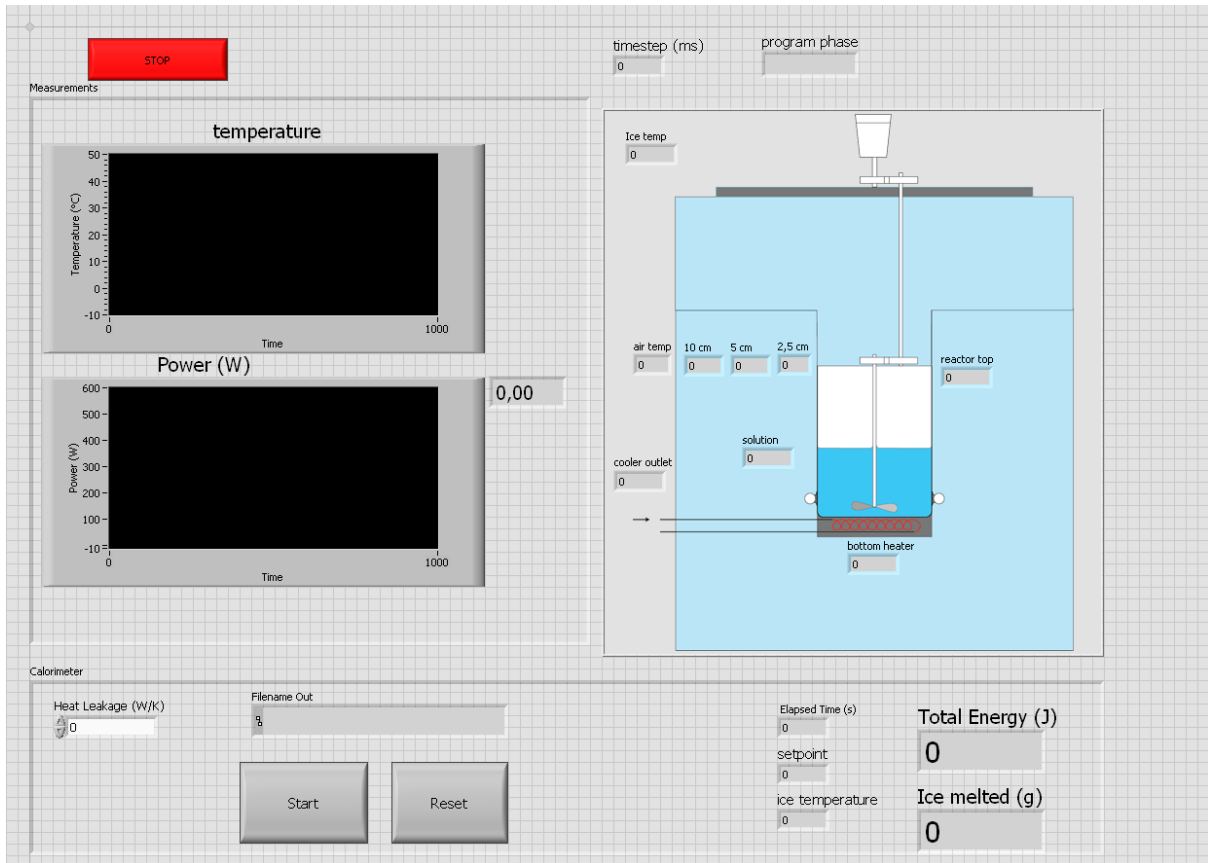
Figure 25 User interface after changes

4.2 PART 2

4.2.1 Ice melting in pure water at room temperature

In total there was performed 22 results, displayed in Table 5. 11 of those experiment was made with one syringe, the remaining experiments was performed with 2-4 syringes. All tests had the same setting, with a heat leakage of 0,045 W/K, a proportional gain on 1 and with an integral time of zero.

The measure the accuracy the calorimeters measured value was compared to the theoretical value.

At room temperature, there were 22 experiment with consistent results.

Table 5 Results from tests done in pure water at room temperature

Test nr	m ice [g]	T ice [°C]	T set [°C]	Qadded [J]	Error [%]	Temperature drop [°C]	Time [s]
27	23,1	-3,66	30,66	10 329	5,09	3,88	1246
28	25,6	-5,78	30,40	11 964	1,27	3,62	1178
34	23,1	-6,44	17,64	8 632	12,76	2,97	869
35	23,9	-5,69	18,18	9 058	11,35	3,14	926
36	23,9	-4,08	20,15	9 214	10,71	3,44	865
38	46,2	-17,87	19,75	19 775	6,14	10,63	778
40	23,9	-6,39	21,37	9 603	8,72	3,88	931
41	23,7	-6,68	21,42	9 646	7,53	3,71	867
42	72,1	-5,70	21,44	30 001	4,71	7,73	1108
43	47,6	-5,41	20,45	19 707	4,08	7,18	740
44	72	-5,21	20,54	29 648	4,64	7,93	931
47	93,6	-5,34	21,86	38 838	5,24	11,14	910
48	23,7	-5,34	21,89	9 467	9,33	3,64	903
49	99,5	-6,40	21,89	41 215	5,98	9,08	1254
51	70,6	-9,58	22,67	30 442	4,13	11,20	590
53	25,8	-5,68	22,52	10 477	8,39	4,59	694
55	46,43	-7,55	14,02	17 661	7,41	6,20	585

56	22,48	-4,94	14,61	8 205	11,10	4,30	562
57	100,15	-5,62	16,12	39153	5,70	8,64	962
58	25,47	-4,35	21,02	11 131	-1,37	7,88	127
59	50,55	-5,09	20,30	20 865	4,08	9,97	291
60	48,58	-3,70	20,45	19 742	5,14	8,10	600

A typical result of the process is displayed in Figure 27 and Figure 26. Figure 27 shows that the temperature drops quickly as the ice is incerted.The time it takes to finish a test varies a lot, as shown inTable 5 and in Figure 28
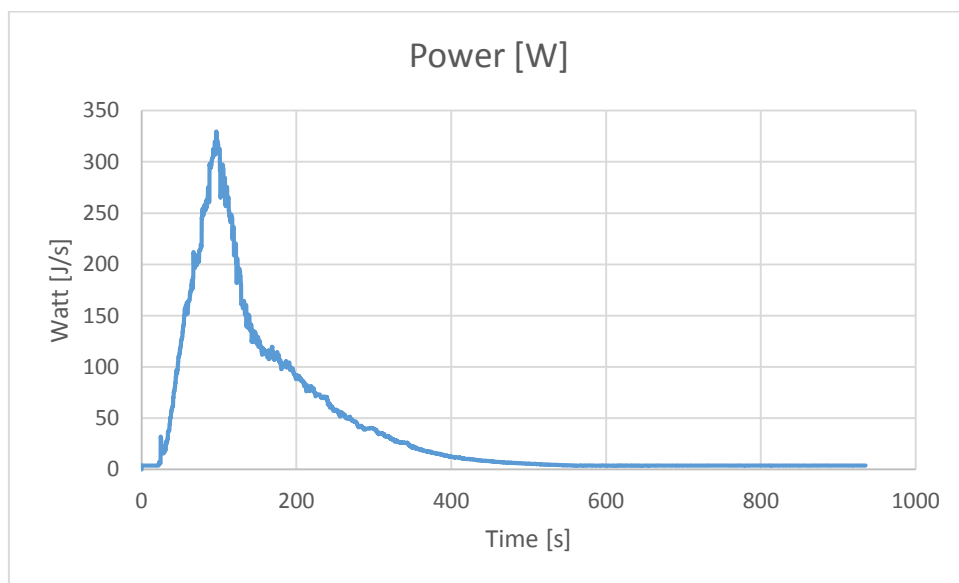
Figure 26 Power over time
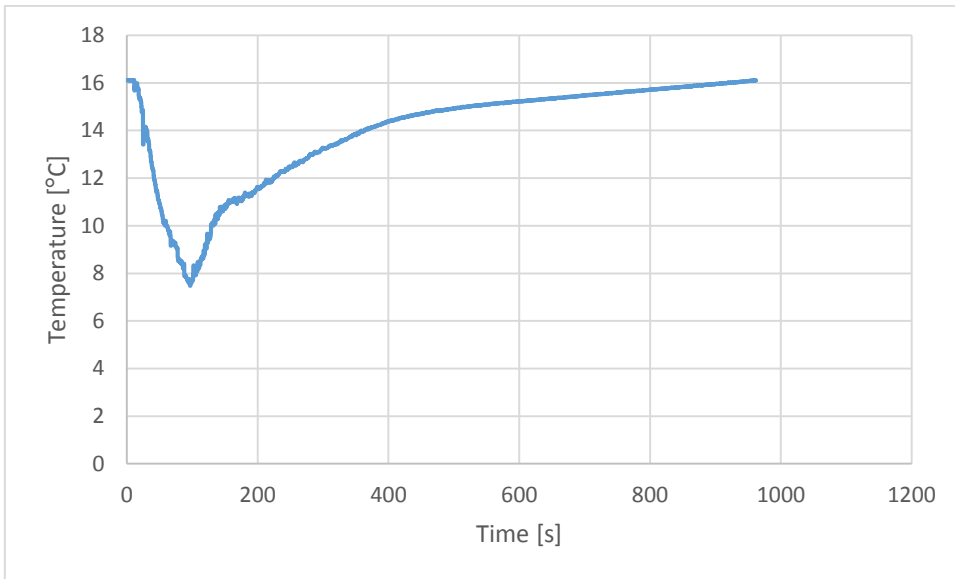
Figure 27 Temperature development
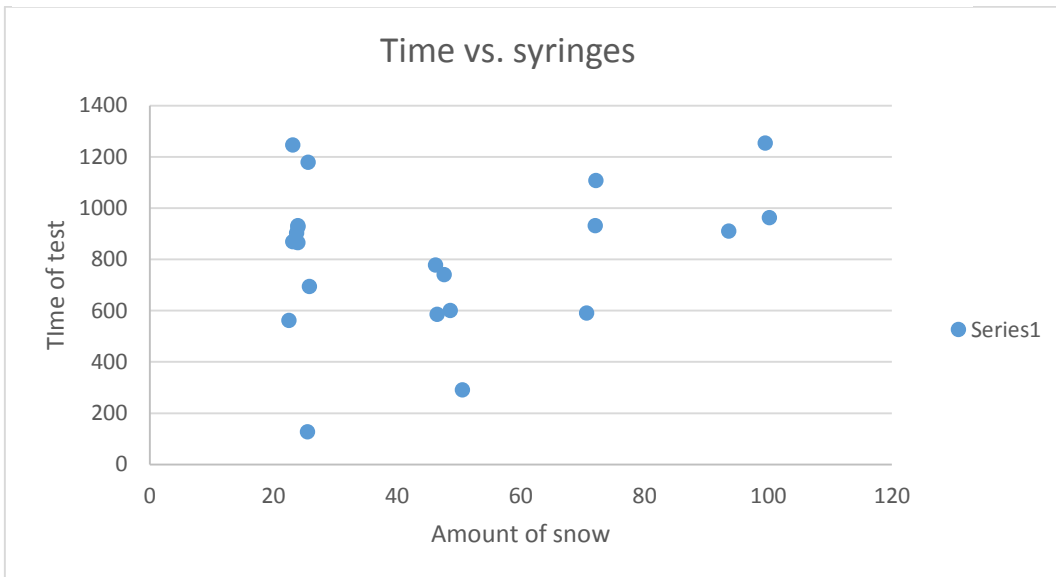
Figure 28 Duration of tests versus amount of snow
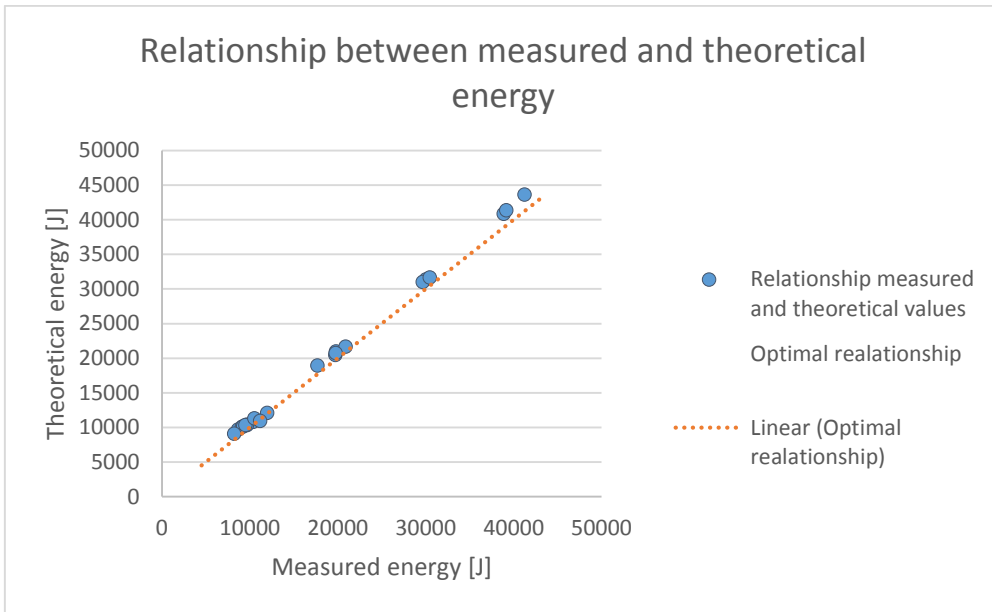
Figure 29 Relationship between measured and theoretical energy
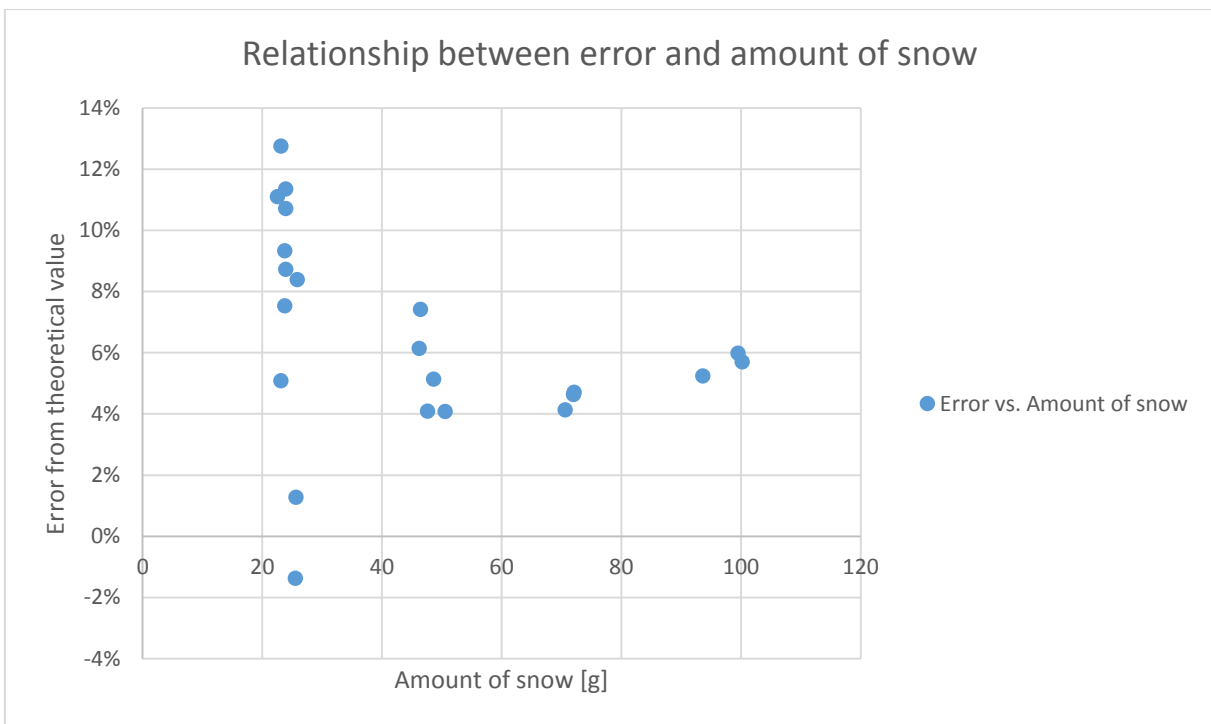
Figure 30 Relationship between measured and theoretical energy

Figure 30 shows the plot with error against the amount of snow. What we see from the figure is two things:

- The error goes down with increasing amount of ice
- The scattering decreases with increasing amount of ice

An important aspect is the fact there is fewer experiment with more ice. It is therefore chosen to compare the result with one syringe (23-25 g snow), with results from two syringes more (46-100 g snow), which have 11 experiment each. Table 6 show the standard deviation and the mean of the tests with only one syringe and two or more, and a total error based on all the test. In Figure 31 it is easy to see there is a much smaller standard deviation for two or more syringes, than for only one syringe, indicating better accuracy on the measurements done with more ice

Table 6 Statistical data for tests done at room temperature

Number of syringes	One	Two or more	Total of all tests
Mean error	7,72 %	5,20 %	6,46 %
Standard deviation	4,41 %	1,04 %	3,38 %
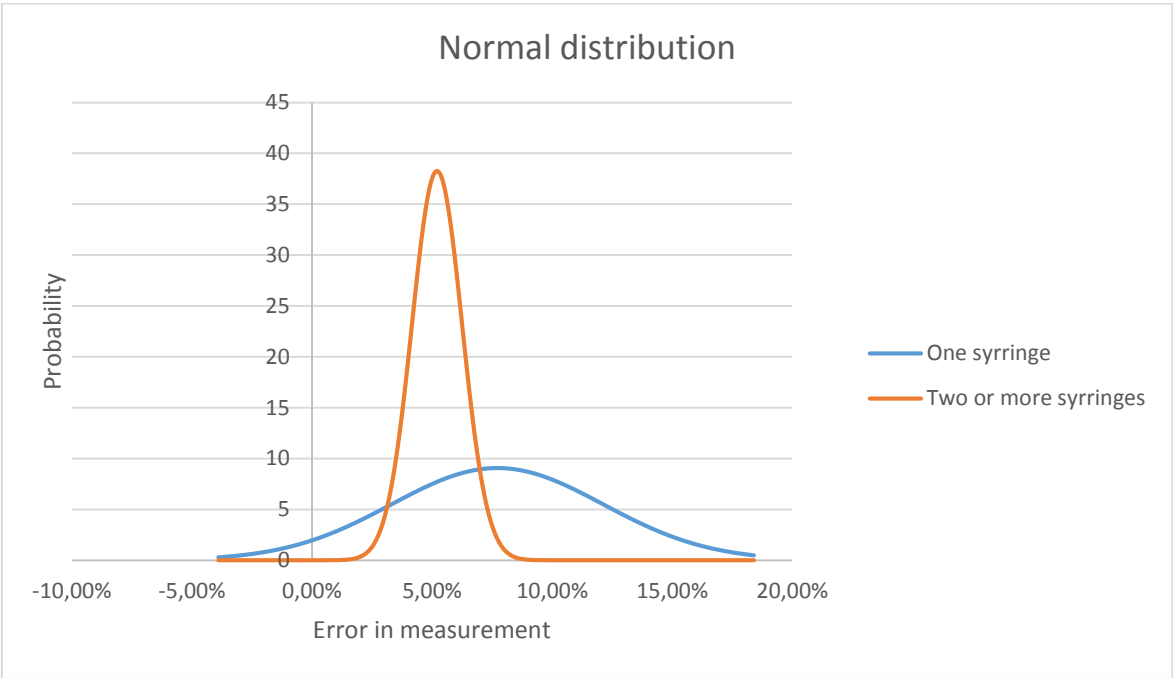
Figure 31 Distribution of error in experimenting at room temperature

4.2.2 Ice melting with saltsolution

In total there were performed 7 experiments, where 5 failed before the experiment was completed. The result of the 3 experiment that carried through, the results of these experiment is summarized in Table 7. An overview over all successful experiments is shown in Table 8. The number in parenthesis indicates the number of the test, which indicated the number of the test in the raw data.

Table 7 Summary of all experiments performed with salt solution

Experiment nr	m_{salt}	m_{ice}	Set temperature	Status
1	7,2	~46	-1,8	Fail
2	34,3	~69	-9,3	Fail
3 (69)	34,9	96,8	-8,2	Success
4 (71)	35,2	99,1	-7,9	Success
5	34,7	~92	-8,5	Fail
6	35,4	~92	-9,1	Fail
7 (75)	36,3	48	-9,4	Success

Table 8 Results from completed experiments

	Experiment 3	Experiment 4	Experiment 7
Concentration salt solution			
Set temperature [°C]	-8,18	-7,91	-9,44
Amount of ice inserted[g]	96,84	99,11	48,19
Amount of snow melted [g]	49,98	63,05	25,03
Calorimeters energy [J]	12 089,8	15 255,3	3 740,75
Total theoretical energy added [J]	17 447,90	21 465,24	8 094,08
Ratio	0,69	0,71	0,46
Duration of test [s]	4 132	2 408	721

5. ANALYSIS AND DISCUSSION

The analysis is divided in three parts. The first part treat the first experiments performed, where the initial conditions was set. The second part addresses the experiments performed to test the accuracy of the calorimeter. The progress of the test with salt solution is explained more in detail, as there was more inconcistency in the measurement procedure than or the other tests. The third part discusses how the calorimeter is evaluated compared to the other tests for melting capacities. In addition other applications of the calorimeter is discussed in this section.

5.1 PART 1

5.1.1 Heat capacity

The heat capacity was estimated to be 514 J/K. The time it took for the temperature inside the reactor to stabilize was short, approx. 5 min, and it is assumed that the heat leakage is zero. If the actual heat leakage was 1 W, this add up to 300 J and will make a little less than a 2% difference in the result. The consequences of not taking heat leakage into account:

- The calculated heat capacity is too big
- The calculated heat leakage based on this value will be a bit lower than the actual heat leakage.

As the experiment is executed at much higher temperatures than the main experimenting, this can be a source of error. Since the reactor is made of solid material, it is assumed that the heat capacity will be approximately the same in different ranges of temperature, but this will not affect the results significantly.

The variance of 24 J/K constitutes 4,7 % of the result. The variance is probably mostly from the temperature measurement of the water. A 0,4 degrees deviation in the measurement of the start temperature of the water will change the outcome with 4,7%. The temperature measurement is probably too high, because heat is lost when pouring the water in the container. The amount of heat leakage will depend on the temperature of the water, the time it took from the lid was taken off the thermos and how hot the funnel was when it came in contact with the water. This is all uncertainties and will affect the result. The amount of water can also be a source of error, as some water droplets may stick to the funnel. The error in the water measurement is not likely to be more than 2 gram, which only explains 0,3% of the error and

contributes solitary in one way, as it is most probable there is less water in the container than measured.

To minimize the error both water and the funnel should be the same temperature during each test. To obtain this, both the water and the funnel could be placed in the heating cabin, for a given amount of time, where the temperature in the heating cabin is the same for all the tests. Although this will minimize some variance, there is still an uncertainty from the water is out of the cabin and poured into the reactor.

The measurement is performed four times, which reduces some of the uncertainty. The result are consistent, especially considering the sensitivity of the water temperature. There is probably some systematic errors in the measurements, but as the heat capacity is only used to calculate heat leakage the possible error of margin will have little impact on the final results of the accuracy of the samples.

5.1.2 Heat leakage

The heat leakage was calculated to be 0,045 W/K. With a temperature difference between the surroundings and the reactor of 30°C, the heat leakage is 1,35 W. This is a lower than the measured value of 1,88 W, and the difference increase for higher temperature differences.

The test for the heat leakage is only preformed once. This is an uncertainty by itself as it is nothing to compare the result with, especially since the start values are left out in the final calculations. Still there is possible to point out errors that can influence the accuracy on the result.

The gradient through the insulation is not linear, as shown in Figure 32. The reason for this is that there was not sufficient time with cooling. This is not ideal, because this means there is still heat within the reactor insulation that goes into the system. Instead of the reactor absorbing heat it is releasing heat, which means not all of the heat comes from the surroundings. Another source of unwanted heat is introduced to the system is when the cold liquid in the cooling system was drained. This led air with room temperature in to the reactor and affectet the result. These two sources of error combined is probably the biggest reasons for the sudden rise in temperature in the beginning of the test.

In the later test with ice melting in salt solution, there was a problem with a lack of temperature drop. This indicates there might be wrong to exclude the sudden rise in temperature at the beginning. One possible reason for the sudden temperature rise could be the measurement itself.

When the cooler is on, the temperature sensor is very close to the tube with the cold liquid. It may be that the temperature the sensor measures is the cold liquid, and that the actual temperature in the reaction is lower. Another possible error is the assumption of a linear heat leakage; this may as well be exponential.

The stirrer adds heat to the system. This was later calculated to be 0,006 W, if this is accounted for in the calculations it will contribute with a reduction of heat leakage of 0,0005 W/K. This is not a significant value, but is part of the uncertainty of the result.
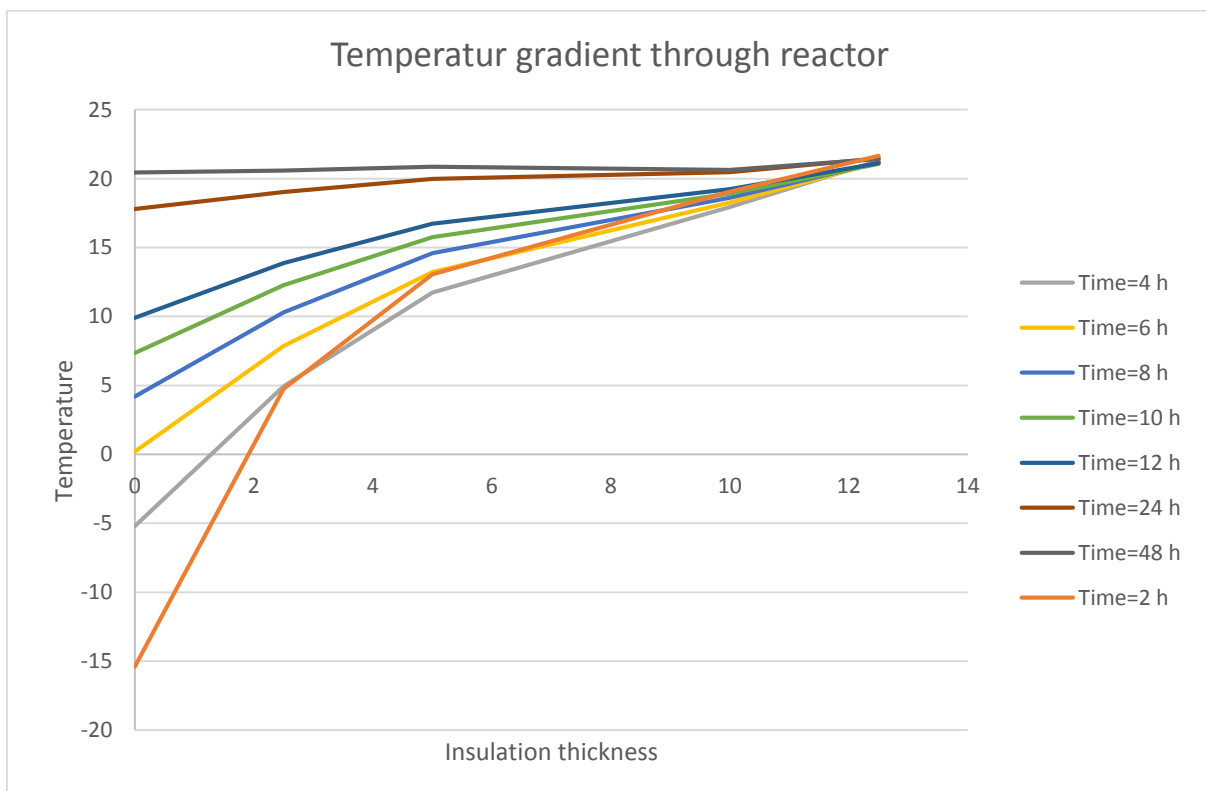
Figure 32 Temperature gradient through insulation

5.1.3 Heat added by stirrer

The heat added from the stirrer is measured to be 0,01 W. The measurement gave a clear tendency of a linear temperature rise. This is positive as it indicates a steady stream of heat and no sources of other disturbances. Because of this, there is reason to believe the measurement is very accurate.

This test was only performed once, so there is no other results to compare it to. To increase the accuracy even more, the water could have been placed in the container a little while before the

test was performed. This way there would have been a zero difference between the system and surroundings, eliminating the heat leakage completely.

5.1.4 Regulation systems

The regulation system was not changed during the period of testing. When the initial settings was decided, there was no effort made to improve these. The only change made was the input of a minimum power of 3,8 W, which shortened the duration of the tests. There is little reason to believe that changes in the regulation will make a big difference to the accuracy of the measurements, other than saving time and reducing some of the impact of other sources of heat, as heat leakage and heat from the stirrer.

5.2 PART 2

5.2.1 Ice melting in pure water at room temperature

After 22 tests the accuracy of the tests is 93,5 % compared to theoretical values. There is a good correlation between the theoretical value and the measured value. The accuracy also increased with an increasing amount of snow, as shown by Figure 30. But still there is an error of 6,5 % to account for. The temperature sensor for the liquid was replaced after test 38, as there was some disturbances in the temperature measurement, which resulted in a too early closure of the program.

Every test shows a too low estimate of the energy added. This means there is some heat missing in the equation. These sources of heat can come from an underestimate of the heat leakage, heat from the stirrer or the ice heating up before it is inserted in the reactor. After analyzing the experiment for heat leakage, it is probable that the calculated heat leakage is too low. The amount of ice is limited, with a low heat capacity, which means the temperature decrease must be significant to have an effect on the result.

The only test that measured more than the theoretical value was test 58, with 1 % over the theoretical value. This test had a very short time duration, only 127 seconds compared to the average time that was 814 seconds. The also had some bigger fluctuations in the temperature than usual. This diverges from the other results, but as the input is the same there is no obvious reason for this irregularity.

The heat from the stirrer is not accounted for in the results of the experiments with ice melting. In room temperature, where the length of the experiments is less than 1000 s, this will add 10 joules and can explain approximately 0,1 % of the missing heat.

To achieve better results it is preferable to have as similar starting point as possible. If the set temperature and the ice temperature was more constant throughout the different tests, it may have been easier to detect smaller differences. Because the ice samples was made in a room that varied in temperature, the temperature of the ice samples also varied. If the input parameters are the same, the duration of the experiment should be more stable. The duration of the experiment is included in Table 5. The duration of the experiment varied most with the tests performed with only one syringe; this indicates the time aspect of the experiment will be more stable if a higher amount of ice is used.

5.2.2 *Ice melting with salt solution*

In total there was performed seven experiments but only three of them was carried out completely. The reason that four experiment failed was that there was no drop in temperature, which led to a prematurely closure of the program.

The first experiment conducted was a fail. The ice had sintered too much, and the ice crystals had become an ice block, due to storage in freezer. Therefore, it was assumed that the little surface area led to a slower reaction and that was why the temperature did not drop. To be certain there would be a temperature drop some improvements was made before the next experiment:

- More ice was inserted (looser)
- Higher start concentration

Still after making some improvements, the next experiment, experiment 2, also failed. As a consequence the minimum power was changed from 3,8 W to 0 W. In experiment 3 the temperature was monitored thoroughly through the experiment and it was observed an unexplainable increase in temperature immediately after the cooling system was turned off. Neighter the contribution from heater nor the draining of the cooling liquid could explain this, since the power was 0 W and the liquid was not drained.

The time it took to finish experiment 3 was over an hour, so the the next experiment was performed with a minimum heat leakage of 3,8 W.

Experiment 4 was also a success, with a total time of 40 minutes. To get more results to compare, two more of the same experiment was performed with approximately the same initial conditions, which both failed. In experiment 6 the salt had not dissolved and lay frozen to the bottom of the reactor. To save time, the salt and the water was mixed in the reactor in some of the experiments. Realizing that the salt may not have dissolved in the reactor, the procedure of the other experiment had to be reviewed. Every experiment where the salt had been mixed in the container the experiment had failed, i.e. experiment 1, 2, 5 and 6. It was earlier presumed the salt had dissolved in the water, since the temperature had dropped below zero.

The last experiment was made with salt solution and less snow to reduce the length of the experiment. The length of the test was 12 minutes, but the accuracy was very low.

The difference between this test and the one performed at room temperature is:

- Heat leakage
- The cooling process
- Salt

Since we know the accuracy of the calorimeter is good, the change has to come from one or more of these sources. It is observed that the salt solution should be made in advance. If this factor is in order, it has to be the heat leakage and the cooling process that effects the accuracy of the measurements. It was performed an additional test to examine the cooling process, as this was a point of uncertainty. The test was performed to see how much time it took to cool the insulation, as well as the liquid inside. The result is displayed in Figure 33.

In the experiment with the heat leakage, there was a noticeably increase in temperature the first minutes after turning the cooling apparatus of. The same happened when testing with saltsolution. The first time it was assumed that this was caused by removing the cooling liquid from the tubes around the reactor, which induced air with room temperature into the system. However, this effect also happened when the cooling liquid was kept in the system.

The test was performed by cooling down a salt solution with a consentration of 14,7%. From the figure it is possible to see:

- It takes approximately 20 minutes too cool down the cooling liquid
- The temperature in the reactor is warmer than the cooling liquid
- It takes approximately 90 minutes to cool down the reactor and insulation
- There is an sudden increase in the temperature after the cooling liquid is turned off
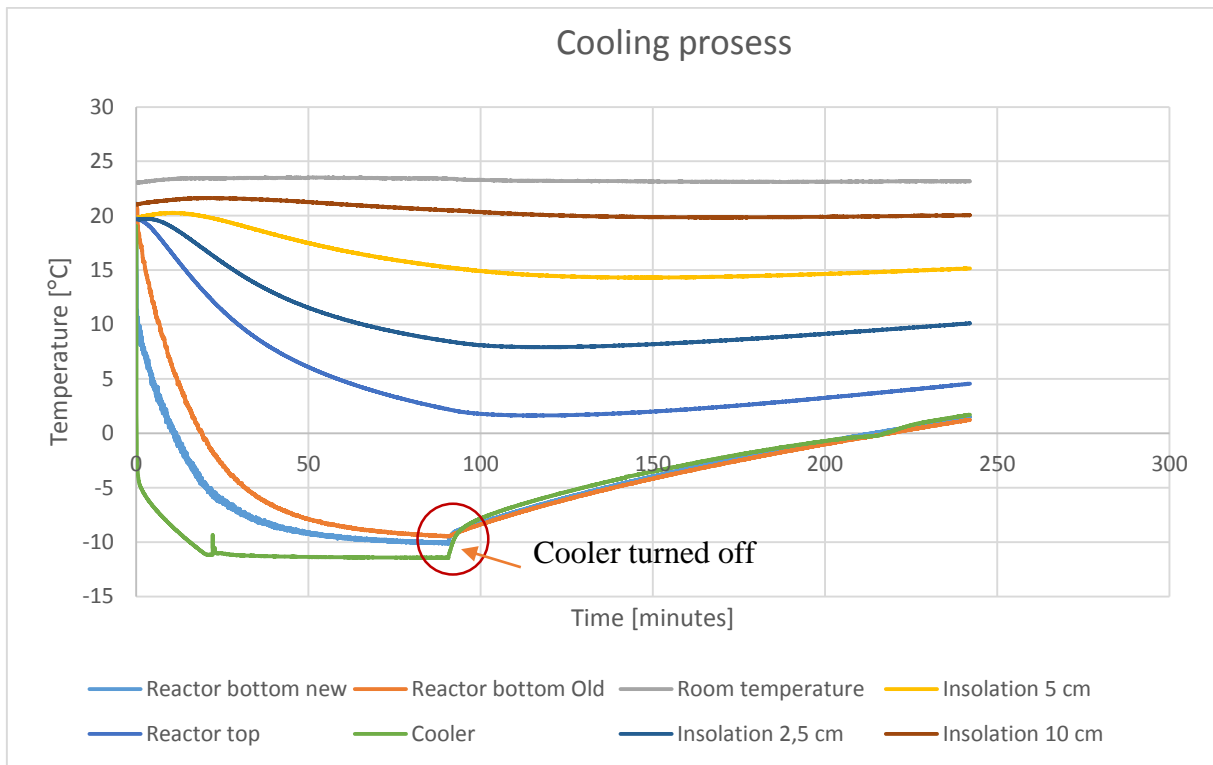
Figure 33 Temperaure development during cooling process

From the temperature gradient in the insulation, it is not sure 90 minutes is enough time too cool the insulation enough. It is still a big difference between the temperature in the liquid and the insulation at 2,5 centimeters at 90 minutes. But the latent heat left in the reactor can not be big enough to fully explain the sudden rise in temperature. From the green line, which shows the temperature of the cooling liquid, we see that the temperature rises quickly. This indicates there is some heat introduced to the system, even though the tubes with liquid is not drained.

A possible solution to reduce this impact is to cool the liquid down below the wanted set point. This way there is time to wait for the temperature to stabilize before the experiment is executed. This allows the rise in temperature to be more steady.

5.3   COMPARISON TO OTHER EXISTING TESTS

The test have some advantages compared to other existing test. There is no reason for removing the ice from the solution. This is positive, because the biggest source of error in the other tests are the removal of the liquid from the ice. The two main problems with this are: First, it is hard to collect all the water on the surface of the ice, and secondly, the removal introduces heat to the system and increases the melting speed. On the other hand, it has proved difficult to give an account for the all the heat in the calorimeter too. However, if the changes suggested is implemented and the accuracy improves, the calorimeter may still be a good alternative to the existing tests.

All the tests used in melting capacity, measures the melted ice at different times. Since the duration of these test often end after 60 minutes, there is no guarantee the total melting capacity has been accounted for. This makes it harder to compare the results from the existing test with the test performed in the NTNU Calorimeter. The DSC is the most similar test, but here the sample is very small (10 micrograms), and the interaction between the ice and solution is not examined. The test is only performed with the deicer, and a warming cycle is used to obtain the most accurate results. The calorimeter is more comparable to the real situation on the road, and the calorimeter is a mix between the DCS and the SHRP test is combined.

The advantage of only develop an existing test further, is that it gives a better foundation to compare results with the original test. In this laboratory test the measured values is with the theoretical values of melting capacity for NaCl. If the existing test also is compared with the theoretical values, for test performed with NaCl, it is possible to compare the accuracy of these tests and the test developed in this thesis.

5.4   OTHER APPLICATIONS

If the accuracy of the calorimeter becomes consistent enough, it may be applied to measure both the speed of melting and determine the freezing curve for new deicers.

The speed of melting is an important property when salt is used to remove ice from the road. As the situation between an icy road, until the ice is melted away the situation is unfavorable. In the process of melting the ice, the salt solution produces melting water which on top of the ice, makes the road even slipperier than it was in the beginning. The speed of melting is also possible to determine during the experiment. If the input parameters are the same, amount of ice, set temperature and concentration of the solution, the time it takes to perform the

experiment is comparable with different kind of deicers. If the deicer melts the ice rapid, the temperature will drop more quickly. This leads to more effect from the heater, leading to the experiment to end quicker. This will only be an indicator on how effective the deicer is, as the experiment is only an idealized situation, and does not actually describe field performance.

The calorimeter makes it possible to define a freezing curve, without knowing something about the chemical. The only information necessary is the amount of chemical in the solution and the energy added to the system. This means the calorimeter is not only useful for deicing purposes. The depression of the freezing point is an important aspect regarding anti-icing also. As the climate in Norway varies a lot, the line between what is ant-icing and deicing is blurry. There will be use for information on all aspects of the winter maintenance, even tough the most desired methods is the proactive measures.

6. CONLUCIONS

Throughout this thesis the accuracy of the calorimeter to predict the melting capacity for deicers was tested. The calorimeters accuracy to measure amount of snow was measured both with and without heat leakage. Based on the results the main findings was:

- At room temperature the general correlation between the measured and theoretical values was revealed to be good. The amount of melted snow was predicted with an 93,5% accuracy, the remaining 6,5 % still seems to be an systematic error. This indicates that $Q_{electric}$ can be measured reasonably well. The accuracy of the measurements improved when at least 45 g ice was used.

- Test with salt solution at low temperature had a significantly less accuracy. This gives little basis of comparison to other experiments. The main differences between this and the previous test, were the heat leakage and the cooling of the reactor. This gave an indication that the heat leakage may not be determined correctly and that the method of cooling the liquid has a potential of improvement.

- It is a potential to measure the melting capacity with the NTNU calorimeter, because the accuracy of the measurements in room temperature is promising.

7. FURTHER WORK

With background in the data collected, I would like to suggest a procedure to increase the accuracy of the measurements for testing melting capacity in a deicer solution.

Surroundings

The calorimeter should be placed in a cold room, which hold the same temperature as the desired set temperature. This way the heat leakage is minimal, even at low temperatures. The ice sample and the salt solution should be stored in these surroundings prior to testing. This will contribute to a more consistent temperature.

Before testing: measure the heat leakage and the contribution from the stirrer, as these may have changed.

Ice samples

The ice samples can be made with the same procedure as described in section 3.3. To increase the accuracy of the amount of ice, the ice could be measured to 25 g ice before it is compressed in the syringe. The syringes still has to be measured before and after insertion in the reactor, as ice may fall out during compression. If the temperature of the ice is very cold, the syringes with ice could be placed in room temperature for 30 seconds, to let the ice melt a bit. If this is done, it is important that the ice is cooled down sufficiently before testing.

Solution

The solution should be made in advance. The salt dissolves more quickly in room temperature, so it is profitable to make them a day before and let the solution cool in the cold room until testing. The concentration of the solution, should be based on the set temperature and the amount of snow inserted. When it is an unknown deicer, with unknown freezing curve, the values in table X can be a good starting point. If all the ice melts, reduce the concentration. If no ice melts, increase the concentration.

Procedure

1. Set the temperature of the cold room in advance
2. Prepare minimum three syringes with snow (75 g)
3. Make a solution with a concentration according to Table 9
4. Use 200 mL of solution
5. Weigh the beaker before and after the liquid is poured in the reactor

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6. Pour the solution in the reactor with care, minimizing droplets of solution on the reactor wall.

7. Cool down the reactor with solution

8. After the temperature has been stable in the container for 10 minutes, turn the cooler off without draining the tubes.

9. Wait 2 minutes before the samples of ice is inserted

Table 9 Calculated start concentrations based on NaCl

Set temperature [°C]	C_{end} [%]	C_{start} [%]	$m_{melted\ ice}$ [g]
-3	5	6,25	50
-5	8	10	50
-10	14	17,5	50
-15	18,8	23	48,7

The reason for the different start concentrations is to perform the test with the same ratio between solution and amount of snow inserted. If this is implemented, in addition to less temperature difference between the ice and solution, the foundation of comparing results could be better.

I would also suggest to start with performing 3-5 tests at the same temperature. This ensures a good basis of comparison to check if the precision is good. If there is large differences between the results, the reason for this must be investigated further.

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Fakultet for ingeniørvitenskap og teknologi
Institutt for bygg, anlegg og transport

MASTEROPPGAVE
(TBA4945 Transport, masteroppgave)

VÅREN 2014
for
Linda Betten

Måling av smeltekapasitet med kalorimetri

Bakgrunn

Det finnes en rekke typer salt, kjemikalier og tilsetningsstoffer som brukes i vinterdrift av veger. For å kunne forstå hvordan disse kjemikalier virker, og kunne sammenligne egenskapene er det viktig med gode testmetoder. En viktig egenskap av en kjemikalie er sin smeltekapasitet, altså hvor mange gram is man kan smelte per gram kjemikalie.

Det finnes flere testmetoder for å måle smeltekapasitet, men hovedproblemet av disse at man må fysisk skille is fra smeltevann for å kunne måle hvor mye is har blitt smeltet. Dette er vanskelig å gjennomføre uten å introdusere noe varme. På NTNU jobbes det med å utvikle en ny type måleinstrument hvor smeltekapasiteten måles ved hjelp av kalorimetri.

Målet

Målet med oppgaven er å videreutvikle og teste kalorimeteren og undersøke om smeltekapasiteten kan bestemmes ved hjelp av kalorimetri.

Oppgaven

Oppgaven inneholder følgende deloppgaver:

1. Beskrive teorien bak kalorimetri
2. Utføre tester for å bestemme nøyaktigheten av kalorimetriske målinger av smeltekapasitet
3. Utvikle en måleprosedyre som maksimaliserer nøyaktigheten
4. Sammenlikne smeltekapasitetsmålinger av ren NaCl med teoretiske verdier for smeltekapasitet

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GENERELT

Oppgaveteksten 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 bearbeidingen 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 rapportskriving 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 godkjennelse 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.

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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 ekskursjoner, 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

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: Alex Klein-Paste

Institutt for bygg, anlegg og transport, NTNU
Dato: 10.01.2014, (revidert: 29.04.2014)

Underskrift

A Klein Paste

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Faglærer

Appendix 1

This all the graphs for Test "Ice Melting in pure water at room temperature"

Explanations for the graphs:

Temperature reactor – This is the temperature of the liquid

Power – This is the contribution of the heater, referred to as $\dot{Q}_{electic}$ in the equations

Energy – The accumulated energy over time, referred to as $\int \dot{Q}_{electic} + \dot{Q}_{heat\ leakage}\ dt$ in the equations. The contribution from the stirrer, $\int \dot{Q}_{stirrer}\ dt$, is calculated and added after the experiment is finished.

Test 27

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 28

Temperature container

Power [J/s]

Energy [J]

Test 34

Temperature reactor

Power [J/s]

Energy [J]

Test 35

Temperature reactor

Power [J/s]

Energy [J]

Test 36

Temperature reactor

Power [J/s]

Energy [J]

Test 38

Temperature reactor

Power [J/s]

Energy [J]

Test 40

Temperature reactor

Power [J/s]

Energy [J]

Test 41

Temperature reactor [°C]

Power[J/s]

Energy [J]

Test 42

Temperature container

Power [J/s]

Energy

Test 43

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 44

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 47

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 48

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 49

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 51

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 53

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 55

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 56

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 57

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 58

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 59

Temperature reactor [°C]

Power [J/s]

Energy [J]

Test 60

Temperature reactor [°C]

Power [J/s]

Energy [J]

Appendix 2

This all the graphs for Test "Ice Melting with salt solution"

Explanations for the graphs:

Temperature reactor – This is the temperature of the liquid

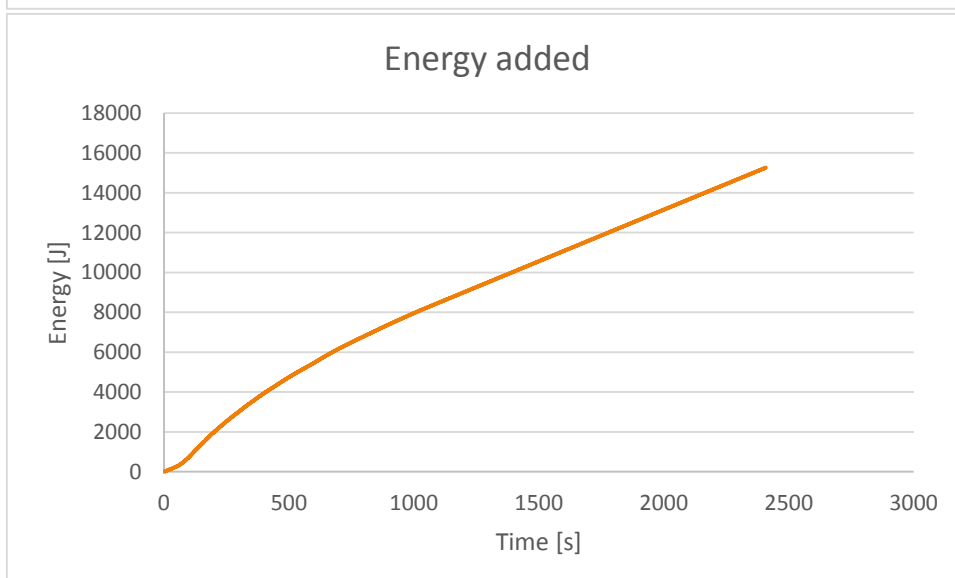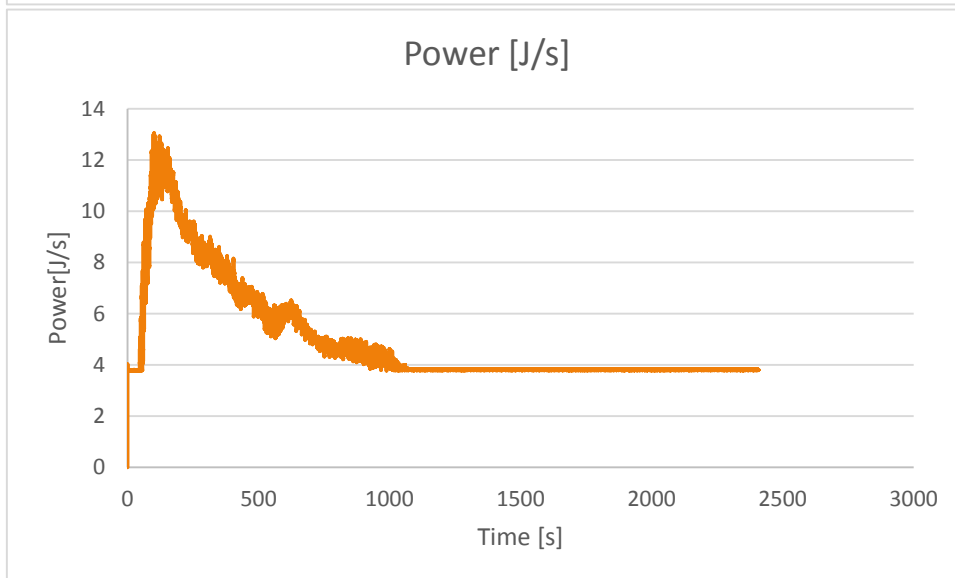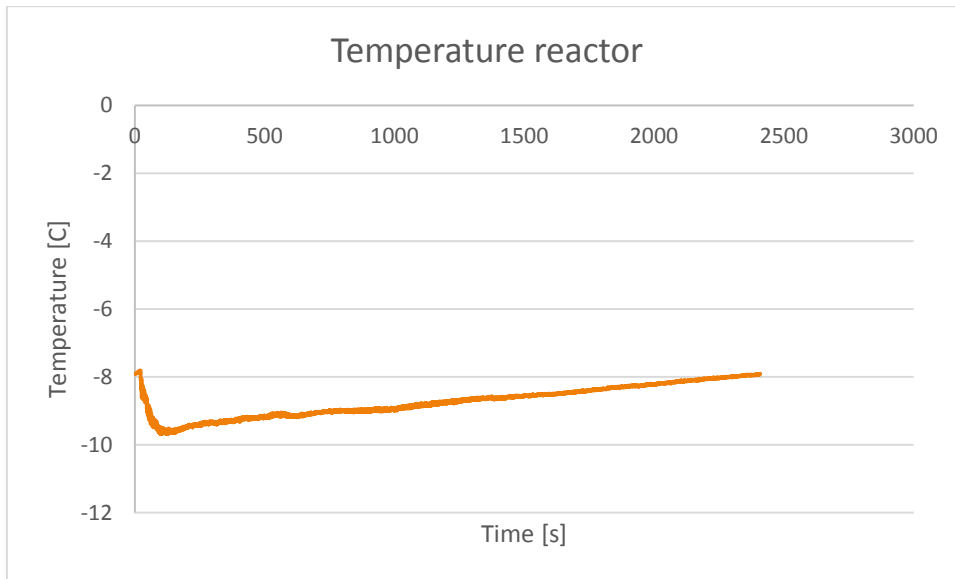Power – This is the contribution of the heater, referred to as $\dot{Q}_{electic}$ in the equations

Energy – The accumulated energy over time, referred to as $\int \dot{Q}_{electic} + \dot{Q}_{heat\ leakage}\ dt$ in the equations. The contribution from the stirrer, $\int \dot{Q}_{stirrer}\ dt$, is calculated and added after the experiment is finished.

Test 69

Temperature reactor

Power [J/s]

Energy added

Test 71

Test 75

Temperature reactor

Power [J/s]

Energy added