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Melting ice with salt - a thermodynamic model

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Abstract:

Road salting forms an essential element in the winter maintenance of roads. With salt usage increasing there is a need for an optimizing of salt practices. This master thesis is focused on the melting of ice below 0°C with use of salt (the de-icing process). The use of dissolved salt (Sodium Chloride) is considered only, and the melting process that takes place in an adiabatic system. The increased understanding of the physics of ice melting will hopefully contribute into optimizing de-icing operations.

The thermodynamics of ice melting by salt has been studied by developing a calculation model, which can be used to predict the final temperature of an “ice-salt solution” system and the amount of melted ice, for a given salt solution.

Five solutions with different salt concentrations (5, 10, 15, 20 and 23 w%) have been experimentally tested to determine the temperature change inside the reactor caused by adding of a certain amount of ice to the solution.

The calculated and experimentally determined values of final temperature (T_f) have been further compared to identify the discrepancy in obtained results and to which extent the developed model is theoretically applicable. The comparison between the model and experiments has shown that the model was able to predict the final temperature of the “ice-salt solution” system with high precision throughout the investigated temperature range between -16°C and 0°C. In 89% of the cases the error between the determined results lies within temperature interval ± 1°C. The model has showed to have a better performance and gives lower level of discrepancies between the calculated and measured results when the solution has reached its ice melting capacity, i.e. when unmelted ice fractions are present in salt solution.

In order for decrease the level of existent uncertainties and obtain more accurate results, it is recommended to incorporate the omitted value for heat loss in the developed model and to conduct all experiments in a cold room under constant, low temperature conditions.

Keywords:

1. Salt solution - Saltløsning
2. Melting of ice - Issmelting
3. Thermodynamic model – Termodynamisk modell
4. Final temperature – Den endelige temperaturen

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Norsk tittel
Smelting av is med salt – en termodynamisk modell

Engelsk tittel
Melting ice with salt – a thermodynamic model

Bakground

In the colder regions of the earth, large efforts are undertaken to prevent or remove ice depositions from road surfaces. Besides the mechanical removal of snow/ice, salts are often used to assist the removal. With salt amounts increasing and a growing environmental concern on impacts of road salt, there is a need for optimizing salt practices. In order to do so, more knowledge is needed about how salt physically works.

The melting of ice with salt is a complex process that involves heat flow, mass transport, dissolution and the phase transition from ice to water. In order to study this complex process it is needed to simplify the interaction, for example by studying the melting by dissolved salt, rather than solid salt. Another simplification that can be made is to study the melting in an adiabatic system, hence not allowing any heat flow from the surroundings. With these simplifications it is possible to study the thermodynamics of the reactions involved. In a later stage, the heat flow from the environment can be incorporated.

Master thesis

The objective of this master thesis is to study the thermodynamics of ice melting by salt by developing a thermodynamic model. The scope of the thesis is limited to only one type of salt (Sodium Chloride), the use of dissolved salt only, and the melting takes place in an adiabatic system.

The candidate shall:

1) Describe the different physical processes that are involved during the melting, based on a literature survey.

2) Develop a model to calculate the final temperature and the amount of melted ice, for a given salt solution.

3) Conduct laboratory experiments to verify the outcome of the model

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Dato: 06.12.2011

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Alex Klein-Paste

Preface

This master thesis is the last element of the two-year master degree program which completes Civil and Environmental Engineering studies at the Norwegian University of Science and Technology. The project was performed at the Faculty Engineering Science and Technology, Department of Civil and Transport Engineering in cooperation with the Norwegian Public Roads Administration. This thesis has been completed during 20 weeks between January and June in spring semester 2012.

I would like to use this opportunity to thank my supervisor, associate professor Alex Klein-Paste, for excellent response, support, inspiration and help especially during the execution of laboratory experiments. I would also like to thank PhD Candidate Johan Wåhlin for help with providing relevant information, articles and response concerning the topic of this master thesis. Additionally, I would like to thank the Norwegian public Roads Administration for the financial support of this work.

Summary

Road salting forms an essential element in the winter maintenance of roads. With salt usage increasing there is a need for an optimizing of salt practices. The motivation of this study is the lack of information, experimental data and calculation methods that predict the change of the temperature and the ice melting capacity for the “ice-salt solution” system. The increased understanding of the physics of ice melting will hopefully contribute into optimizing de-icing operations. This master thesis is focused on the melting of ice below 0°C with use of salt (the de-icing process). The use of dissolved salt (Sodium Chloride) is considered only, and the melting process that takes place in an adiabatic system.

Such mechanisms as heat flow, phase transition and decreasing of freezing point in the “ice-salt solution” system have the greatest impact on salt and water interaction when the melting process occurs in the closed adiabatic system. The thermodynamics of ice melting by salt has been studied by developing a calculation model. This developed model can be used to predict the final temperature of an “ice-salt solution” system and the amount of melted ice, for a given salt solution.

Experimentally part of this study has been performed in order to verify the outcome of the model. Five solutions with different salt concentrations (5, 10, 15, 20 and 23 w%) have been experimentally tested to determine the temperature change inside the reactor caused by adding of a certain amount of ice to the solution.

The calculated and experimentally determined values of final temperature (T_f) have been further compared to identify the discrepancy in obtained results and to which extent the developed model is theoretically applicable. The comparison between the model and experiments has shown in general a good correlation between the calculated and experimental results. The model was able to predict the final temperature of the “ice-salt solution” system with high precision throughout the investigated temperature range between -16°C and 0°C. In 89% of the cases the error between the determined results lies within temperature interval ±1°C. The model has showed to have a better performance and gives lower level of discrepancies between the calculated and measured results when the solution has reached its ice melting capacity, i.e. when unmelted ice fractions are present in salt solution.

In order for decrease the level of existent uncertainties and obtain more accurate results, following recommendations has been given:

- incorporate the omitted value for heat loss in the calculations in order to improve the developed model
- use of a better isolation of the reactor in order to decrease a negative impact of heat loss on the measured results
- conduct all experiments in a cold room under constant, low temperature conditions in order to improve experimental procedure by reducing the temperature gradient throughout the experiment and as a result avoiding melting of ice

Sammendrag

Veisalting er et viktig element i vintervedlikehold av veier. Med økende bruk av salt er det behov for en optimalisering av saltepraksis. Bakgrunnen for denne studien er at det mangler informasjon, eksperimentelle data og beregningsmetoder som kan hjelpe til å forutsi endring av temperatur og issmeltekapasitet for et is- og saltløsningssystem. Bedre forståelse av de fysiske prosessene som forekommer ved issmelting vil forhåpentligvis bidra til å optimalisere avisingspraksis. Denne masteroppgaven er fokusert på issmelting under 0 °C ved bruk av salt (avisingsprosess). Oppgaven er avgrenset til å se på bruk av oppløst salt (natriumklorid), og smelteprosesser som foregår i et adiabatisk system.

De mekanismene som har størst innvirkning på interaksjonen mellom salt og vann når smelteprosessen foregår i et lukket, adiabatisk system er varmestrøm, faseovergang og nedsettelse av frysepunkt i et is- og saltløsningssystem. Termodynamikk for issmelting med salt har blitt studert ved å utvikle en beregningsmodell. Den utviklede modellen kan brukes til å forutsi den endelige temperaturen (T_f) i et is- og saltløsningssystem og mengden av smeltet is, for en gitt saltløsning.

Den eksperimentelle delen av studien har blitt utført for å kontrollere utfallet av modellen. Fem løsninger med ulike saltkonsentrasjoner (5, 10, 15, 20 og 23 w%) har blitt testet for å måle temperaturendring inne i reaktoren etter tilføring av en viss ismengde til løsningen.

De beregnede og eksperimentelt bestemte verdiene av temperaturen (T_f) er videre blitt sammenlignet med hverandre for å finne mulige avvik i resultatene og se i hvilken grad modellen er teoretisk anvendbar. Sammenligningen mellom modellen og eksperimentene har vist et generelt godt samsvar mellom resultatene. Modellen var i stand til å forutsi den endelige temperaturen av is- og saltløsningssystemet med høy presisjon gjennom hele det undersøkte temperaturintervallet mellom -16 °C og 0 °C. I 89 % av tilfellene ligger avviket mellom ±1 °C. Modellen har vist seg å ha en bedre anvendelse og gir lavere nivå på avviket mellom de beregnede og målte resultatene for en saltløsning som har nådd sin issmeltingskapasitet, det vil si når usmeltede isfraksjoner er til stede i en saltløsning.

For å redusere usikkerhetsnivået og få mer nøyaktige resultater, er følgende anbefalingene gitt:

- inkludere den utelatte termodynamiske konstanten for varmetap i beregningene, for å forbedre den utviklede modellen
- bruke en bedre isolering av reaktoren for å redusere de negative konsekvensene av varmetapet på målte resultater
- utføre alle eksperimentene i et kjølerom under lave og konstante temperaturforhold for å redusere temperaturgradienten og unngå smelting av is i løpet av hele eksperimentforløpet

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Symbol	Explanation	Dimensions
c_{init}	initial concentration of salt solution	fraction
C_p	specific heat capacity	J/(kg×K)
$C_{p,ice}$	specific heat capacity of ice	J/(K×kg)
$C_{reactor}$	heat capacity of reactor	J/K
$C_{p,solute}$	specific heat capacity of solute	J/(K×kg)
$C_{p,solution}$	specific heat capacity of solution	J/(K×kg)
$C_{p,water}$	specific heat capacity of liquid water	J/(K×kg)
L	specific latent heat of fusion or vaporization	J/kg
m	mass	kg
$m_{ice,init}$	initial amount of ice	kg
$m_{ice,melted}$	amount of melted ice	kg
m_{solute}	mass of the solute in the solution	kg
$m_{solution}$	mass of solution	kg
$m_{solution,init}$	initial amount of salt solution	kg
m_{total}	total mass of salt solution	kg
m_{water}	amount of water	kg
S	entropy	J/K
T	arbitrary temperature/approached temperature	°C
$T_{solution,init}$	initial temperature of salt solution	°C
$T_{ice,init}$	initial temperature of the ice	°C
$T_{reactor}$	reactor temperature	°C
$T_{reactor,init}$	initial temperature of the reactor	°C
T_f	final temperature	°C

$T_{f,model}$	calculated final temperature	°C
$T_{f,exp}$	experimentally determined final temperature	°C
$T_{freezing}$	freezing temperature of salt solution	°C
T_{room}	room temperature	°C
ΔT	change of temperature	°C
Q	energy	J
Q_{melt}	energy required for melting a given amount of ice	J
$Q_{ice,cooling}$	energy released under cooling of ice	J
Q_{loss}	reactor heat loss	J
$\dot{Q}_{loss}$	reactor heat loss	Watt
$Q_{solution,cooling}$	energy released under cooling of salt solution	J
$Q_{reactor,cooling}$	energy released under cooling of reactor	J
$Q_{reactor}$	energy absorbed by reactor	J
Q_{water}	energy released from cooling of water	J
U	internal energy	J
w	weight fraction of salt solution	-
W	work	J

1 Introduction

1.1 Background

In the colder regions of the earth, large efforts are undertaken to prevent or remove ice depositions from road surfaces. Besides the mechanical removal of snow/ice, salts or other chemicals are often used to assist the removal. Road salting forms an essential element in the winter maintenance of roads. It is applied to prevent freezing (anti-icing), melt ice or snow (de-icing) or to prevent the formation of compacted snow on road surfaces (anti-compaction and anti-adhesion). This master thesis is focused on the use of salt in a de-icing situation.

With salt usage increasing and a growing environmental concern on impacts of road salt, there is a need for optimizing salt practices. In order to do so, more knowledge and information is needed about how salt physically. While there have been published a numerous reports and studies about lowering of freezing point of water with salt applications, there is still a lack of information, experimental data and calculation methods that would help do predict the exact change of the temperature and the ice melting capacity for the "ice-salt solution" system. The study in this master thesis is undertaken on the background of the lack of relevant information.

The melting of ice with salt is a complex process that involves heat flow, mass transport, dissolution and the phase transition from ice to water. In order to study this complex process it is needed to simplify the interaction, for example by studying the melting by dissolved salt, rather than solid salt. Another simplification that can be made is to study the melting in an adiabatic system, hence not allowing any heat flow from the surroundings. With these simplifications it is possible to study the thermodynamics of the reactions involved. In a later stage, the heat flow from the environment can be incorporated.

1.2 Objective, scope and limitations

The objective of this master thesis is to study the thermodynamics of ice melting by salt by developing a thermodynamic model. The model is based on the energy balance of ice melting in an adiabatic system and verified by comparing with data collected in experiments.

The scope of the thesis is limited to only one type of salt (Sodium Chloride). The use of dissolved salt is considered only, and the melting process that takes place in an adiabatic system. The behavior of salt solutions at the temperatures below water's freezing point (0°C) is studied in this master thesis.

The main goals of this study are to:

1. Give the description of the different physical processes that are involved during the melting, based on a literature survey and explain the thermodynamic aspect and mechanism of these processes occurred when salt solution and ice are brought in a contact with each other inside a closed, adiabatic system.
2. Develop a model to calculate the final temperature and the amount of melted ice, for a given salt solution.
3. Conduct laboratory experiments to verify the outcome of the model.

1.3 Report outline

This master thesis consists of six main chapters and 2 appendixes. Chapter 2 describes the basics of thermodynamics and the different physical processes that are involved in the process ice melting both when it brings in a contact with pure water and, further, with salt solution. Chapter 3 describes the developed model to calculate the final temperature and the amount of melted ice. The results of laboratory experiments are presented in Chapter 4. The outcome of the model is compared with the laboratory experiments in Chapter 5. Chapter 6 concludes with the results obtained in this study and gives the suggestions for improvement of both developed model and experimental procedure.

2 Literature review

This chapter gives a brief introduction to thermodynamics and reviews its fundamental concepts and parameters. The basic understanding of the thermodynamic system, what processes occur in this system and other definitions that are further used in this master thesis are defined. The mechanism of ice and salt solution interaction is described in the second part of this chapter.

2.1 The basic concepts of thermodynamics

- ***Thermodynamics*** is the study of the transformations of energy. An important concept in thermodynamics is the *thermodynamic system*, a part of the universe in which we have a special interest. Everything in the universe except the system is known as the *surroundings*. Exchanges of *work*, *heat*, or *matter* between the system and the surroundings take place across systems boundary. *Work (W)* is the fundamental physical property in thermodynamics and means motion against an opposing force. The *energy (Q)* of the system is its capacity to do work. And, finally, when the energy of the system changes as a result of temperature difference between the system and its surroundings, the energy is being transferred as *heat* [1].

- ***Types of system.*** Even though a system is enclosed by a boundary, heat may be transferred between system and surroundings, and the surroundings may do work on the system, or vice versa. If matter can be transferred from the surroundings to the system, or vice versa, the system is referred to as an *open system*. Otherwise, it is a *closed system.* If the boundary around a system prevents any interaction of the system with its surroundings, the system is called *isolated system* (closed system with neither mechanical nor thermal contact with its surroundings) (Fig.1). An *isolated system*, in other words, is one that does not couple to the external world. While this is an idealization it can be very nearly approached in reality, by surrounding the system with perfect (adiabatic) walls [2].

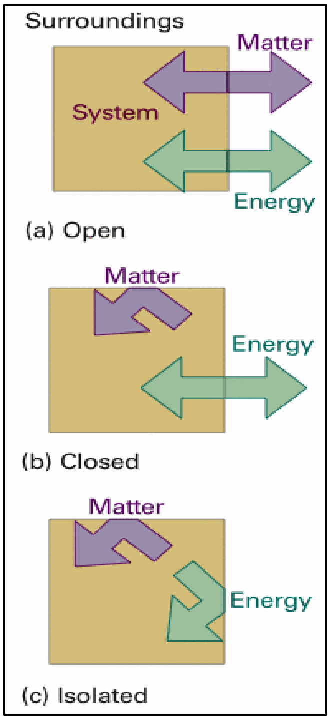


Figure 1 Types of system [1]

- ***Equilibrium.*** The two systems are said to be in *thermodynamic equilibrium* with each other when they are in mechanical, chemical and thermal equilibrium with each other. If two *closed systems* are brought together so that they are in thermal contact, changes may take place in the properties of both. Eventually a state is reached in which there is no further change (no net change in thermal energy), and this is a state of *thermal equilibrium.* If an *isolated system* is considered during a relatively long period, the thermodynamic variables will reach a steady value after some time and there will be no further change. This is the state of equilibrium [2].
- ***Adiabatic system*** is the system which can exchange neither heat nor matter with its surroundings [6]. A boundary is adiabatic (thermally insulated) if no change occurs even though objects have different temperatures. In such system with thermally insulating walls, changes in the environment from hot to cold, or cold to hot, do not cause any change in the equilibrium state of the system [1].
- ***First and second law of thermodynamics.*** In thermodynamics, the total energy of a system is called its *internal energy*, *U*. It has been found experimentally that the internal energy of a system may be changed either by doing work on the system or by heating it. This statement is also known as the *First Law of Thermodynamics* and can be expressed as follows [1]:

“The internal energy of an isolated system is constant” or in the form of an energy balance equation as:

$$\Delta U = Q + W \tag{1}$$

The law that is used to identify the direction of spontaneous change, *The Second Law of Thermodynamics*, may be expressed in terms of another state function, the *entropy (S). Entropy* is a thermodynamic property and can be defined as a measure of disorder in a system or as a measure of the amount of energy which is unavailable to do work [1]. The variation of the entropy *dS* may be written as sum of two terms [6]:

$$dS = d_eS + d_iS \tag{2}$$

Where d_eS is the entropy supplied to the system by its surroundings, and d_iS the entropy produced inside the system. *The Second Law of Thermodynamics* states that d_iS must be zero for reversible (or equilibrium) transformations and positive for irreversible transformations of the system:

$$dS \geq 0 \tag{3}$$

The entropy supplied, d_eS on the other hand may be positive, zero or negative, depending on the interaction of the system with its surroundings. Thus for an adiabatically insulated system S is equal to zero and it follows from (2) and (3) that [6]:

$$dS \geq 0 \tag{4}$$

This is a well-known form of *the Second Law of Thermodynamics.*

According to the theorem of Carnot-Clausius, following expression can be used for a closed system:

$$d_eS = \frac{dQ}{T} \tag{5}$$

Where dQ is the heat supplied to the system by its surroundings and T the absolute temperature at which heat is received by the system. From (2) and (3) it follows for the closed system that [6]:

$$dS \geq \frac{dQ}{T} \tag{6}$$

which is also a well-known form of *the Second Law of Thermodynamics*.

- ***Thermodynamic process*** is a process which occurs whenever a system changes from one state to another state. In many thermodynamic analyses, a single property, such as temperature, pressure, or volume, etc., is held constant during the process. Therefore following commonly studied thermodynamic processes are [7]:

- ✓ Isobaric process: occurs at constant pressure
- ✓ Isochoric process: occurs at constant volume
- ✓ Isothermal process: occurs at a constant temperature
- ✓ Adiabatic process: occurs without loss or gain of energy by heat.

In an adiabatic process no heat can pass across a boundary of the system. The first law of thermodynamics with Q=0 shows that all the change in internal energy is in the form of work done for an adiabatic process) [1].

- ***Phase transition.***

Matter can exist in three different phases: solid, liquid and gas states. In general, matter in one state can be changed into either of the other two states. Such transformations are called "phase transitions”. Phase transitions involving the breaking of intermolecular attractions (melting, vaporization, and sublimation) require an input of energy to overcome the attractive forces between the particles of the substance. Phase transitions involving the formation of intermolecular attractions (freezing, condensation, and deposition) release energy as the particles adopt a lower-energy conformation (Fig.2) [3].

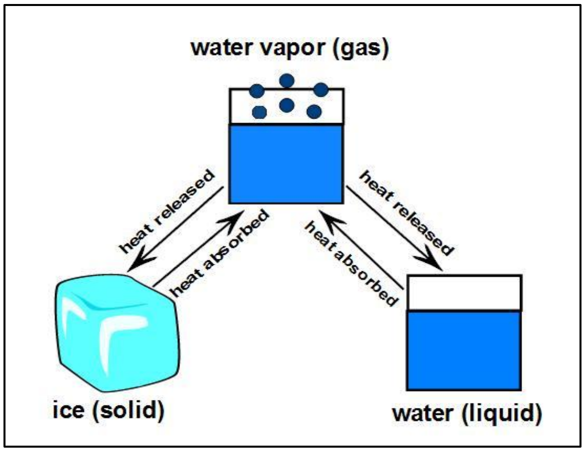


Figure 2 Phase transition

- ***Heat capacity/specific heat capacity.***

The *heat capacity* (C) of a substance is the experimentally determined amount of heat energy it must consume in order to raise its temperature by 1K or 1ºC (J/K) while the *specific heat capacity* (C_p) is the amount of heat required to raise the temperature of 1 kg of a substance by 1K or 1ºC, (J/kg/K) [4].

$$C_p = C \times m \tag{7}$$

Specific heat capacities provide a means of mathematically relating the amount of thermal energy gained (or lost) by a sample of any substance to the sample's mass and its resulting temperature change [4]. If Q is the quantity of heat transferred to or from the object, m is the mass of the object, C_p is the specific heat capacity of the material the object is composed of, and ΔT is the resulting temperature change of the object, the relationship between these four quantities can be expressed by the following equation:

$$Q = C_p \times m \times \Delta T \tag{8}$$

- ***Latent heat of fusion and vaporization.***

The *latent heat (L)* is the amount of heat transfer required to cause a phase change in unit mass of a substance at a constant pressure and temperature. The potential energy stored in the interatomic forces between molecules needs to be overcome by the kinetic energy the motion of the particles before the substance can change phase. When the phase change is from solid to liquid the *latent heat of fusion (J/kg)* is used, and when the phase change is from liquid to a gas, *latent heat of vaporization (J/kg)* expresses the amount of energy required to undergo this phase change [10].

If m is mass of the substance and L is the specific latent heat of fusion or vaporization, the energy Q required to change 1 kg of a solid into a liquid or 1 kg of a liquid into a gas can be expressed by the following equation:

$$Q = m \times L \tag{9}$$

- ***Heat loss***

The adiabatic system is theoretically assumed to be 100% isolated, but in practice there is an amount of heat that is either transferred out or into the system to/from the surroundings. The mechanisms that contribute to heat loss through the reactor wall can be listed as follows [15]:

1. Thermal conduction through reactor wall.
2. Thermal conduction through insulation (if reactor is insulated).
3. Convective heat loss to the surroundings from outer reactor wall (or) outer surface of insulation.
4. Radiation heat loss to the surroundings from outer reactor wall (or) outer surface of insulation.
5. Conduction through support structures, such as agitator or temperature sensor.

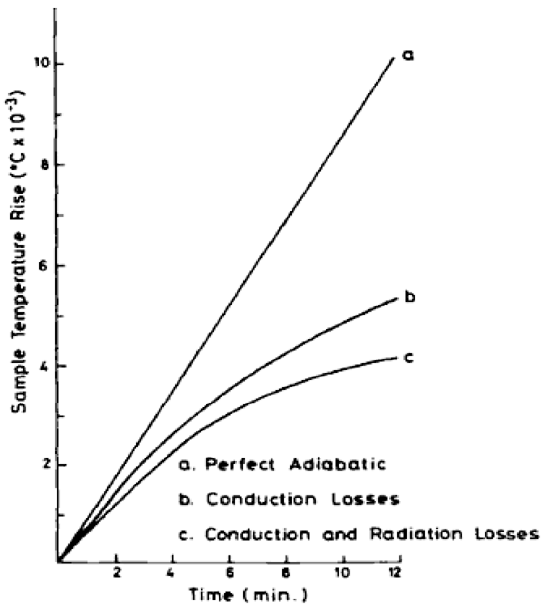


Figure 3 Heat loss by radiation and conduction [16]

Heat transfer by convection is, in general, only relevant in reactors with a large gas-filled region separating the controlled volume or sample and the surrounding medium. Thermal radiation heat loss is important where significant temperature differences exist between surfaces. It can be seen from Figure 3 that the heat loss by radiation is a significant fraction of the total heat loss even though the temperature differences are very small [16].

2.2 Melting of ice with salt below 0°C

Under normal conditions, ice melts at 0°C. For better understanding how ice is melted with salt at lower temperatures, it is important to see what actually happens in both "pure water-ice" and "salt solution-ice" systems on a molecular level. Using examples from earlier studies and researches [13] it is therefore first shown what happens when ice brings into contact with pure water and, further, the changes in this system after adding salt to it. The processes, such as heat flow, phase transition and depressing of freezing point are the main processes that one should expect in such system.

2.2.1 Decrease of the freezing point

Scott Koefod points out in his study [12] that the freezing point depression occurs when a deicer dissolves in water. This phenomenon is known as colligative property and it occurs if any foreign substance is dissolved in water. For every mole of foreign particles dissolved in a kilogram of water, the freezing point goes down by roughly 1.8°C [5].

It has been observed that the amount of freezing point depression is directly proportional to the concentration of total solvated molecules or ions (colligative particles) in solution. While all solutes will theoretically depress the freezing point about the same amount at a given colligative concentration, not all solutes are equally soluble in water [12]. Salt's solubility in water is relatively high compared to other chemicals, for example to sugar. Thus, for example, solubility of NaCl in water is 1/3, which means that approximately one part of salt can dissolve in three parts in water (saturated solution) [11].

Figure 4 shows the phase diagram for Sodium Chloride solution. The diagram is based on the values from Handbook of Chemistry and Physics [11]. The blue line on the diagram represents the effect of increasing amount of salt on the freezing point of water: as the concentration of Sodium Chloride increases, the freezing point of the solution goes down until the minimum is reached (23.3% NaCl salt solution at -21.1°C) [11]. This happens because while ice freezes out of the salt water, the fraction of water in the solution becomes lower, concentration increases, and the freezing point drops.

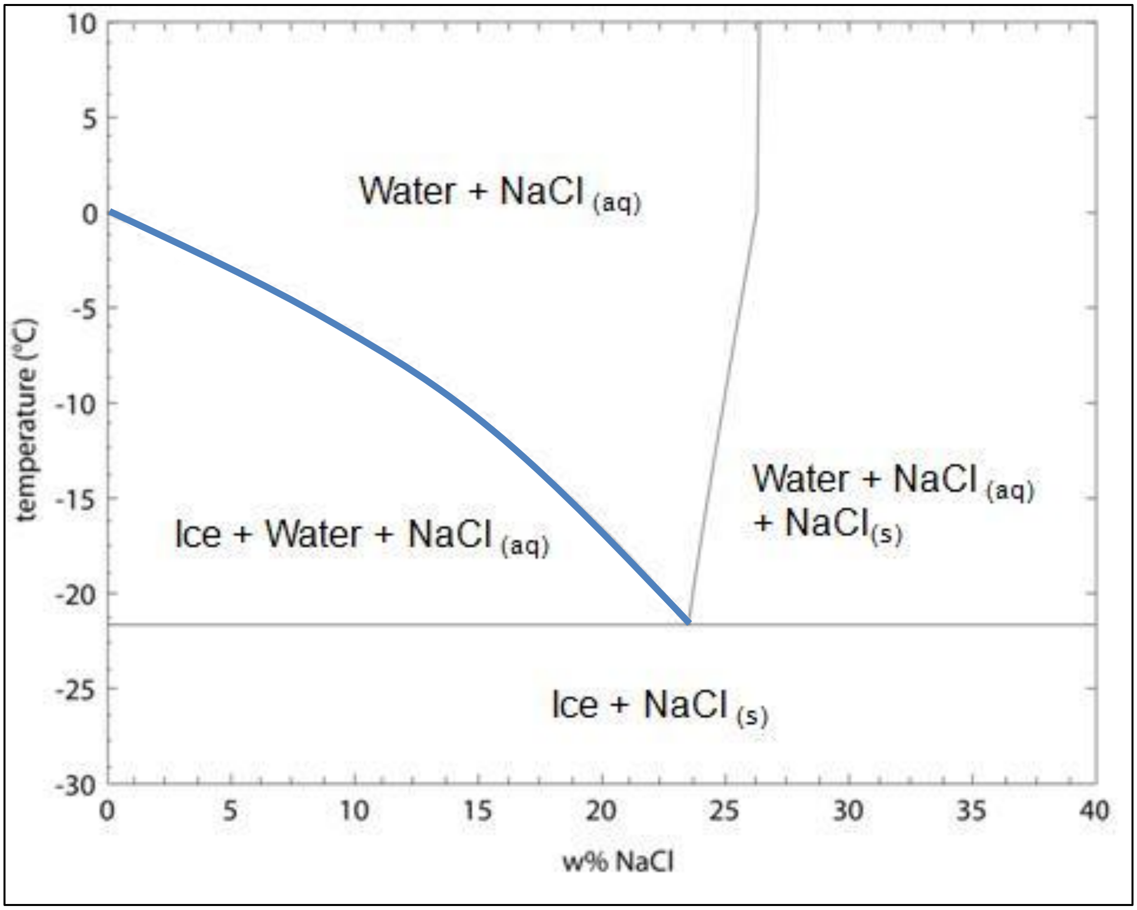


Figure 4 Phase diagram, water – NaCl [11]

2.2.2 Phase transition

The article published on a Worsley's School web-site, Alberta, Canada [13] is used in the two next sections of this chapter to describe the process of ice melting both in pure water and when salt is further added to it.

2.2.2.1 "Pure water – ice" system

1. If the *isolated* system which consists of pure water at 10°C and ice at 0°C is considered first (Fig. 5), the processes that occur in this system are following:

- Water molecules are constantly escaping from the solid ice into the liquid water (melting)
- At the same time, water molecules are being captured on the surface of the ice (freezing)

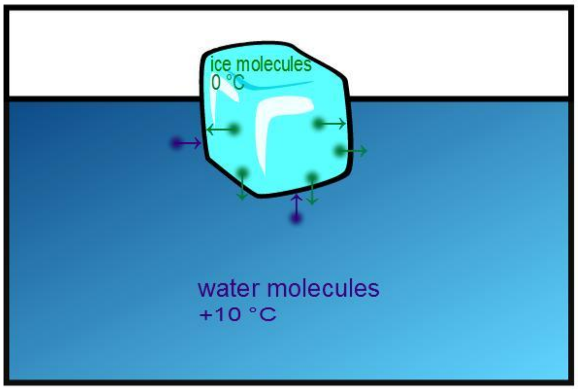


Figure 5 Pure water - ice system, +10°C

As the freezing point of water is 0°C [11] and the current temperature of water is 10°C, the water molecules in the liquid are still moving quickly and can't easily be captured by the surface of the ice, so not very many of them freeze. There are fewer water molecules being captured by the ice (being frozen) than there ice molecules turning to water. That means in other words that freezing occurs at a slower rate than melting here and the result will be that the amount of water increases while the amount of ice decreases.

At the same time, as the ice melts, the water temperature decreases. This happens because *energy is removed from the water to melt some of the ice.* In other words, the *"phase transition"* from a solid to a liquid extracts energy from the liquid.

2. When the water reaches 0°C (energy extracted from water leads to temperature drop in the system) and there is still some ice remaining in water, following processes occur in the system “pure water-ice” (Fig. 6) :

- Water molecules are still escaping from the solid ice into the liquid water (melting)
- Water molecules in the liquid are still being captured on the surface of the ice (freezing).

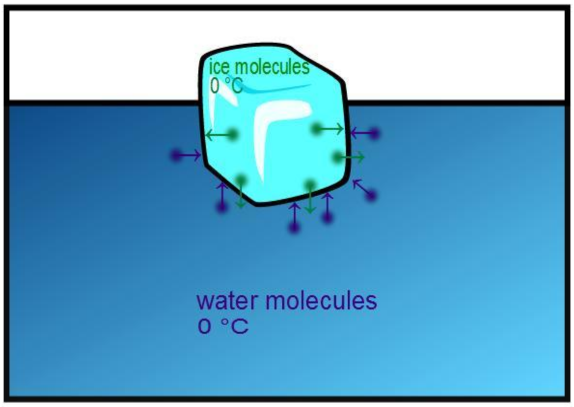


Figure 6 Pure water - ice system, 0°C

Now the rate of freezing is the same as the rate of melting: the amount of ice and the amount of water will not change anymore and, as a result, there will be no change in either quantity. The ice and water are said to be in *dynamic equilibrium* with each other. This balance remains as long as the system is *isolated* and no heat can be transferred to or out of this system.

2.2.2.2 "Salt solution - ice" system

1. Adding of salt to water at 0°C will *disrupt the existing equilibrium in the system*.

This happens because some of the water molecules will be replaced by salt molecules now (Fig. 7). This means that the total number of water molecules able to be captured by the ice (frozen) goes down, and, as a result, the rate of freezing goes down. The rate of melting of the ice is at the same time unchanged by the presence of the salt. Adding of salt to water at this stage results in faster ice melting than water (or here – salt solution) freezing.

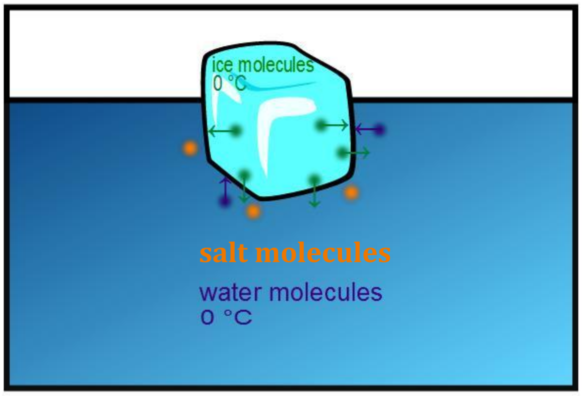


Figure 7 Salt solution - ice system, 0 °C

2. As ice melts, energy is extracted from the surrounding liquid, and the liquid cools as a result. As the internal temperature of the system decreases, liquid will continue to cool until the system returns to equilibrium, which means when the number of molecules of water that are freezing is equal to the number of ice molecules that are melting. The new freezing/melting point depends on the concentration of salt in solution: the higher the concentration is, the lower the temperature of the new freezing/melting point will be (Fig.8).

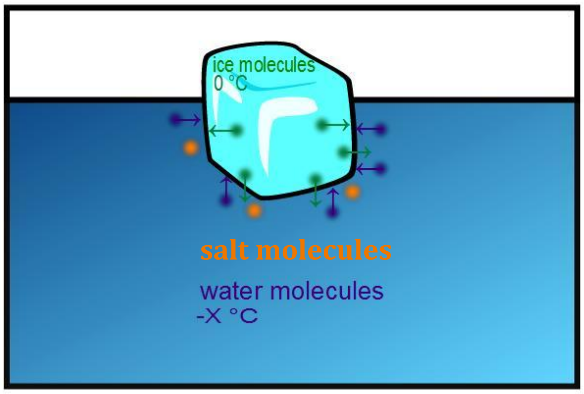


Figure 8 Salt solution - ice, -X °C

2.3 Summary

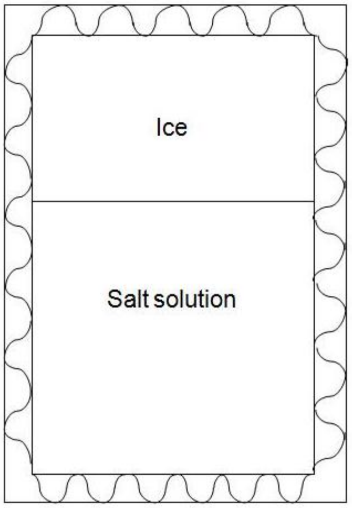


Figure 9 Isolated "ice-salt solution" system

When ice is introduced to a salt solution in an *insulated* container (Fig.9), a certain amount of heat is required to generate the process of ice melting. As the considered system is isolated, no external heat from the surroundings can therefore be transferred to it. This results in a temperature drop inside the container and the melting of ice starts. The melted water dilutes the salt solution and its concentration decreases. This results in an increase of the freezing point of the salt solution. The decrease of the temperature inside the reactor and increase of the freezing point occurs until the final temperature (T_f) is reached (Fig.10).

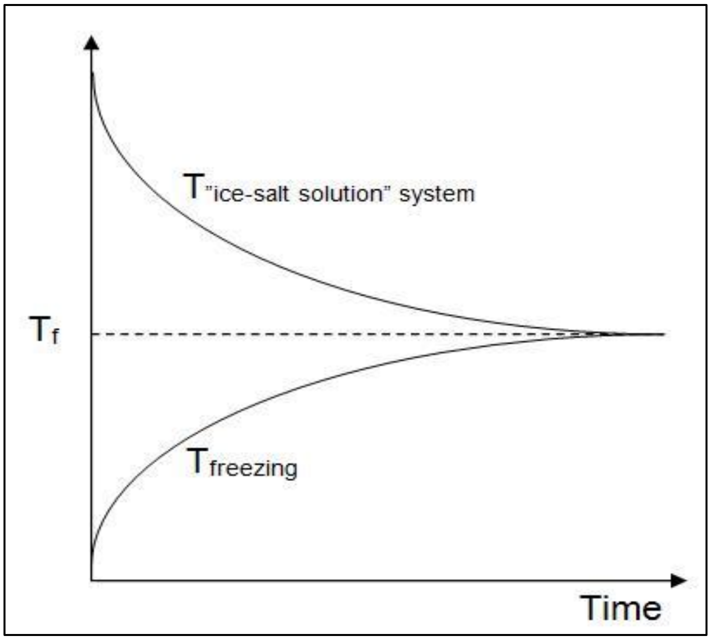


Figure 10 Temperature drop and increase of the freezing point of the solution inside the insulated container. Change in time

Depending on the amount of ice being added to the system, three following situations can occur:

- **Case 1.** The total amount of ice is greater than the amount which can be melted under the given conditions (ice excess). The process of ice melting and decrease of the temperature occurs until the equilibrium is reached, which means that the temperature of the system is equal to the freezing point of the salt solution of a given concentration. A certain amount of unmelted ice will still remain in the system.

- **Case 2.** The total amount of ice is less than the amount which actually can be melted under the given conditions (ice deficiency). This means that the system still has the potential to melt more ice if this were to be added.
- **Case 3.** Total amount of ice is equal to the amount that can be melted under given conditions. Neither ice excess nor ice deficiency occurs in the system. The equilibrium is reached once all given snow is added to the system.

Final temperature (T_f) is the temperature system gets after adding all available ice to the system, independent on the excess or deficiency of ice. In Case 2 and 3 the amount of melted ice equals the ice melting capacity at the final temperature.

3 Calculation model

The model developed for this study can be used to predict the final temperature of an “ice-salt solution” system and the amount of melted ice, for a given salt solution (Fig.11). All calculations in this model are performed for an *isolated*, *adiabatic* system, which means that no heat enters the system. The processes and changes that occur in this system are described in Chapter 2.3.

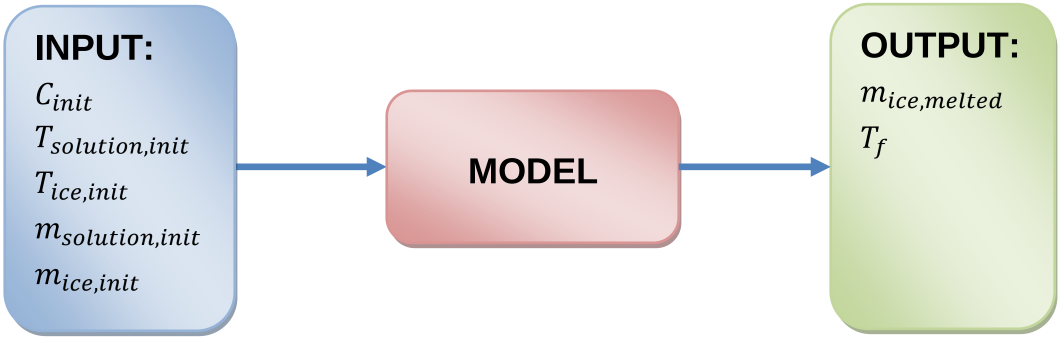


Figure 11 Calculation model

Input variables:

- initial concentration of the salt solution (C_{init}), weight fraction
- initial temperature of salt solution($T_{solution,init}$), °C
- initial temperature of the ice ($T_{ice,init}$), °C
- initial amount of salt solution ($m_{solution,init}$), kg
- initial amount of ice ($m_{ice,init}$) , kg

Physical constants:

- specific latent heat of ice (L), J/kg
- specific heat capacity of ice ($C_{p,ice}$), J/(K×kg)

Experimentally determined constants:

- heat capacity of reactor ($C_{reactor}$), J/K

Assumptions:

- no heat flow from the surroundings
- $T_{solution,init} = T_{reactor,init}$

Calculation model:

Numerical data analysis software MatLab has been chosen to perform all calculations. Other data analysis programs can also be used for this purpose.

The developed MatLab model takes into account all three cases, described in Chapter 2.3. These cases are combined into one algorithm in the calculations.
The energy extracted from cooling of ice, salt solution and reactor goes to melting of ice. The model is therefore based on the following energy balance:

$$Q_{melt} = Q_{ice,cooling} + Q_{solution,cooling} + Q_{reactor,cooling} \tag{10}$$

$$Q_{ice,cooling} = C_{p,ice} \times (m_{ice,init} - m_{ice,melted}) \times \left(T_{ice,init} - T\right) \tag{11}$$

$$Q_{solution,cooling} = C_{p,solution} \times (m_{solution,init} + m_{ice,melted}) \times \left(T_{solution,init} - T\right) \tag{12}$$

$$Q_{reactor,cooling} = C_{reactor} \times \left(T_{reactor,init} - T\right) \tag{13}$$

Before the final temperature of the "ice-salt solution" system can be calculated, the following variables have to be determined. Primarily: mass fraction of salt solution (w) for a given amount of melted ice, the specific heat capacity of liquid water ($C_{p,water}$), the specific heat capacity of solute ($C_{p,solute}$), the specific heat capacity of solution ($C_{p,solution}$) and the energy (Q_{melt}) required to melt a given amount of ice. Each of these variables will change as long as the ice melting process is taking place in the system. Heat capacity of reactor *($C_{reactor}$)* is determined experimentally (Chapter 4.2).

The calculations are performed incrementally, increasing the amount of melted ice by a certain constant value Δm until the final temperature is reached (Case 1, 2 or 3).

1. ***Mass fraction.*** Melting of ice leads to increase of water amount in the salt solution and, as a result, decreases the salt concentration.

The equation 17 is used to find the mass fraction w of salt solution for a given amount of water in a solution (sum of the initial amount of water in the solution and the amount of melted ice as a result of the melting process which occurs in the system):

$$w = \frac{m_{solute}}{m_{total}} \tag{14}$$

$$w = \frac{m_{solute}}{m_{solute} + (m_{water} + m_{ice,melted})} \tag{15}$$

$$w = \frac{m_{solution,init} \times C_{init}}{m_{solution,init} \times C_{init} + (1 - C_{init}) \times m_{solution,init} + m_{ice,melted}} \tag{16}$$

$$w = \frac{m_{solution,init} \times C_{init}}{m_{solution,init} + m_{ice,melted}} \tag{17}$$

Where:

$m_{solution,init}$ - initial mass of solution, kg

C_{init} - initial concentration of salt solution, weight fraction

$m_{ice,melted}$ - mass of melted ice, kg

2. *Specific heat capacity*

The heat capacity of both solid salt and liquid water is temperature dependent. The variation can therefore also be observed for salt solutions. To be able to calculate specific heat capacity of an arbitrary salt solution at the given temperature, the specific heat capacity of both liquid water and the solute should be determined first [14]:

2.1. ***Specific heat capacity of liquid water***. It has been experimentally determined that the specific heat capacity of liquid water at the temperatures below freezing point (between -15 and 0 °C) will decrease with increasing temperature [9]. The same dependence can also be observed further for temperatures between 0 °C and 45 °C. As the temperature continues to increase above 45 0 °C, and inverse dependence takes place: the specific heat capacity begins to increase again [14].

A third-order polynomial interpolation between known values of the specific heat capacities for temperature range from -15 °C to 15 °C is used in the developed model. The following function is therefore used to find specific heat capacities at arbitrary temperatures:

$$C_{p,water}(T) = f\left(C_{p,water,i}, T_i\right) \tag{18}$$

Where:

$C_{p,water}(T)$ – specific heat capacity of water (kJ/(kg×K)) at an arbitrary temperature T (°C)

$C_{p,water,i}$ – known specific heat capacity of water (kJ/(kg×K)) at temperature T_i (°C)

f – third-order polynomial function

Interpolation of data has been performed with help of numerical data analysis software MatLab. Known values for specific heat capacities can be found in various scientific publications, articles and directories. The specific heat capacities of water at different temperatures have been especially studied by Regnault [8]. For temperatures below freezing point (between -15 and 0) °C, the data for subcooled water from Archer is used [9].

2.2. ***Specific heat capacity of the solute.*** The following equation is used to calculate the heat capacity of the solute [14]:

$$C_{p,solute} = a_1 \times e^{\alpha} + a_5 \times (1 - w)^{a_6} \tag{19}$$

$$\alpha = a_2 \times T + a_3 \times e^{0,01 \times T} + a_4 \times (1 - w) \tag{20}$$

Where:

$C_{p,solute}$ – specific heat capacity of solute (kJ/(kg×K)) at an arbitrary temperature T (°C)

w – mass fraction of the solute (salt) for a given amount of water in solution

a_1, a_2, a_3, a_4, a_5, a_6 – dimensionless empirical coefficients

a_1 = - 0.06935597

a_2 = - 0.07821342

a_3 = 3.84798479

a_4 = - 11.2762109

a_5 = 8.73187699

a_6 = 1.8124593

2.3. ***Heat capacity of solution.*** At the next stage of calculations the heat capacity of the solution is estimated when the mass fraction, specific heat capacity of the water and solute are known. The following equation is used:

$$C_{p,solution} = ((1 - w) \times C_{p,water} + w \times C_{p,solute}) \times 1000 \tag{21}$$

Where:

$C_{p,solution}$ – specific heat capacity of solution (J/(kg×K)) at an arbitrary temperature T (°C)

$C_{p,water}$ – specific heat capacity of water (kJ/(kg×K)) at an arbitrary temperature T (°C)

$C_{p,solute}$ – specific heat capacity of solute (kJ/(kg×K)) at an arbitrary temperature T (°C)

w – weight fraction of the solute (salt) for a given amount of water in solution

Figure 12 shows the calculated specific heat capacities of 0, 5, 10, 15, 20 and 23 w% salt solutions at the temperatures between -20 °C and 0 °C:

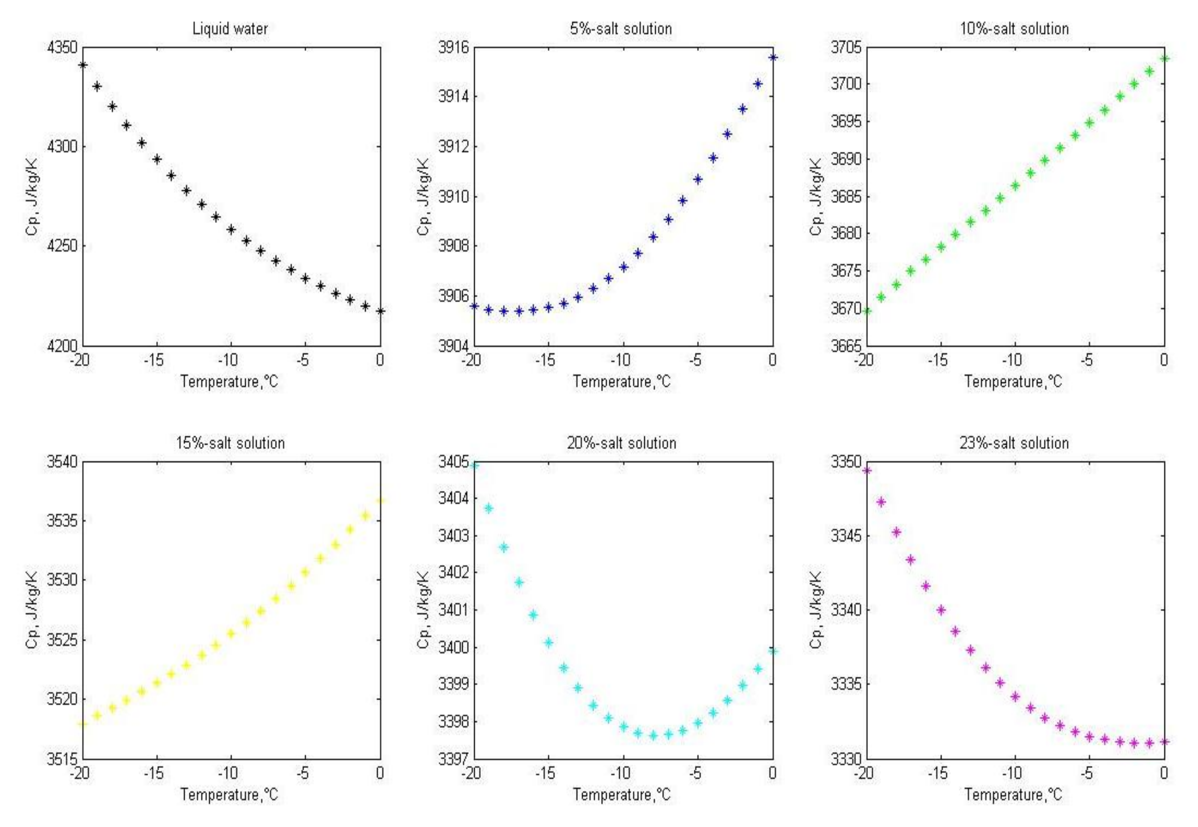


Figure 12 Calculated specific heat capacity. Variation with concentration and temperature

As one can see from the Figure 12, the variation of specific heat capacity with temperature is less than the variation with salt concentration. The $C_{p,solution}$ changes with about 20 J/(kg×K) over the temperature range from -20°C to 0°C. At the same time the variation of $C_{p,solution}$ is almost 1000 J/(kg×K) over the salt concentration range from 0 to 23 w% (Table 1).

Table 1 Calculated specific heat capacity. Variation with concentration for -20°C and 0 °C

	Salt concentration:					
Temperature:	**0%**	**5%**	**10%**	**15%**	**20%**	**23%**
-20 °C	4340.9	3905.6	3669.7	3517.9	3404.9	3349.4
0 °C	4217.0	3915.6	3703.4	3536.7	3399.9	3331.1

3. ***Energy*** required for melting a given amount of ice. The amount of heat required to melt 1 kg ice is equal to 334 000 J/kg [11], which is known as latent heat of fusion of ice, L (Chapter 2.1). Therefore the following equation can be used to calculate the energy needed to melt a given amount of ice (Chapter 2.1):

$$Q_{melt} = L \times m_{ice,melted} \tag{22}$$

Where:

L – specific latent heat of fusion, J/kg

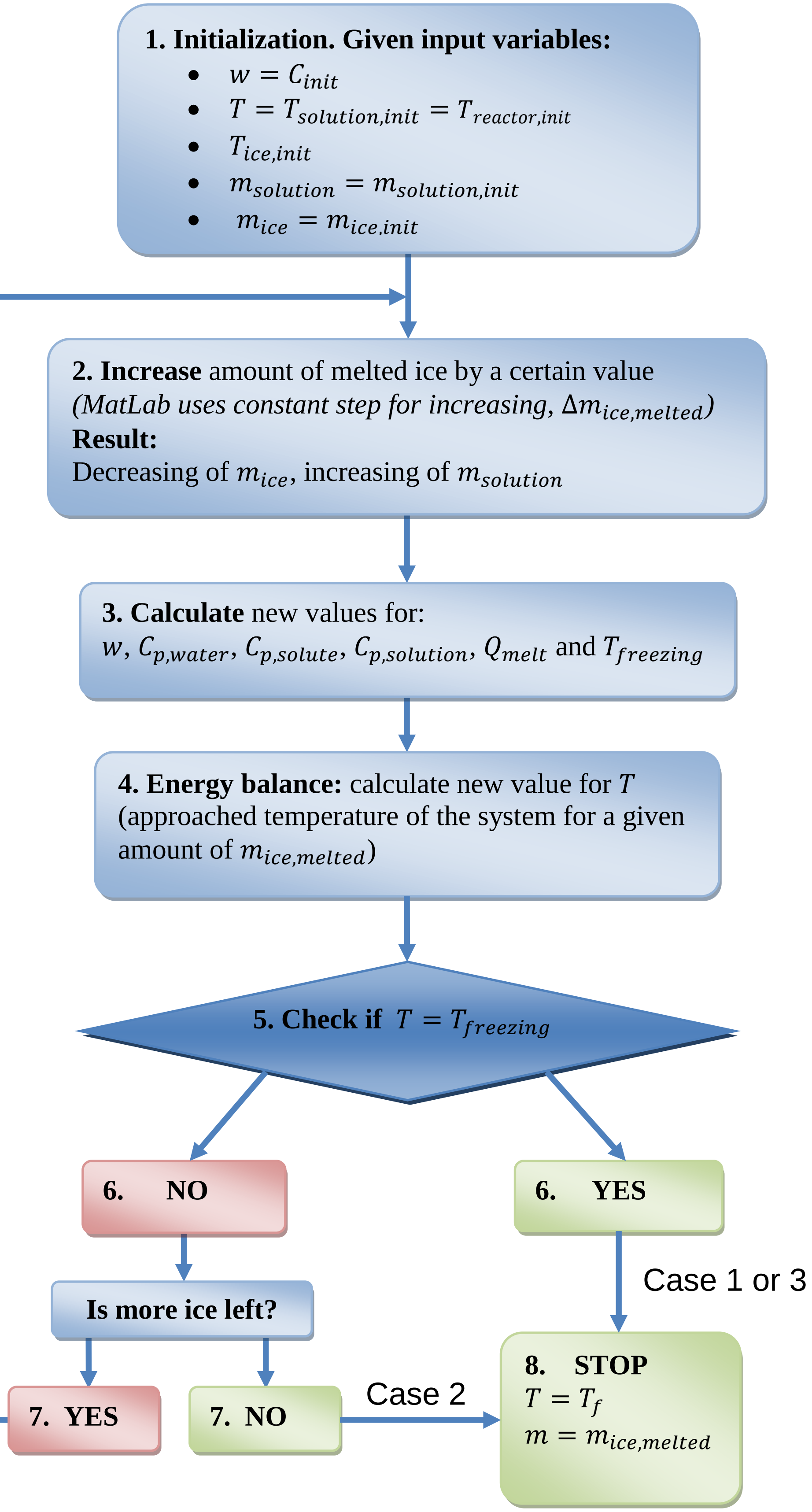
$m_{ice,melted}$ – amount of melted ice at a given moment, kg

4. ***Approached temperature.*** The temperature of the system for a given amount of melted ice is determined from the energy balance for the reactor described in Equations 10, 11, 12 and 13. From these equations follows that the final temperature of the system can be expressed as:

$$T = \frac{C_{p,ice} \times (m_{ice,init} - m_{ice,melted}) \times T_{ice,init}}{C_{p,ice} \times (m_{ice,init} - m_{ice,melted}) + C_{p,solution} \times (m_{solution,init} + m_{ice,melted}) + C_{reactor}}$$
$$+ \frac{C_{p,solution} \times (m_{solution,init} + m_{ice,melted}) \times T_{solutiom,init}}{C_{p,ice} \times (m_{ice,init} - m_{ice,melted}) + C_{p,solution} \times (m_{solution,init} + m_{ice,melted}) + C_{reactor}}$$
$$+ \frac{C_{p,reactor} \times T_{reactor,init} - Q_{melt}}{C_{p,ice} \times (m_{ice,init} - m_{ice,melted}) + C_{p,solution} \times (m_{solution,init} + m_{ice,melted}) + C_{reactor}} \tag{23}$$

5. ***Result: final temperature.*** The iterations are stopped once the final temperature T_f is reached (Case 1, 2 or 3). The temperatures at which equilibrium is reached ($T_{freezing}$) can be found with help of the phase diagram (Chapter 2.2.1). In the developed MatLab model a function that determines equilibrium freezing point for different salt concentrations is given.

The chart below shows in a logical order short summary of all steps of the calculation algorithm.



4 Laboratory experiments

This chapter gives a description of equipment utilized in this study, experiment procedure and results obtained during laboratory experiments. These results are further verified and compared with the values calculated in MatLab model.

4.1 Equipment

Reactor used in the experiments has been designed for this study at the Norwegian University of Science and Technology. The reactor consists of following units (Fig.13):

1. Vacuum flask*, capacity: 1,5 liter
2. Stirrer connected to rotation system
3. Temperature sensor connected to data logging software PicoLog
4. Lid of insulating material with a hole

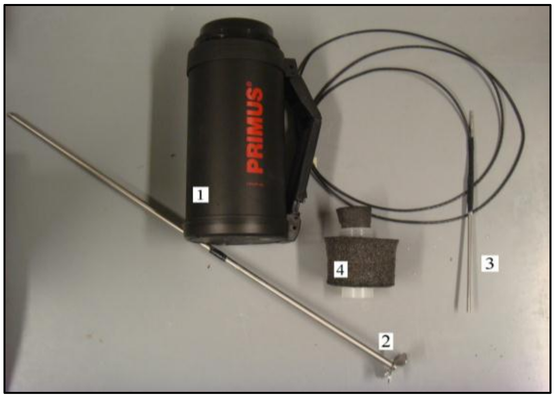


Figure 13 Reactor

4.2 Heat capacity of reactor

The heat capacity of the reactor ($C_{reactor}$) should be known before the calculation model can be used for estimation of the final temperature of the "ice - salt solution" system. Three experiments have been conducted and the heat capacity has been calculated as an average of obtained results.

The reactor at temperature T_1 was filled with hot water at temperature T_2 . The water was cooling down while the reactor was heating up, until they both got to the same final temperature T. Therefore two thermodynamic processes occur here:

Cooling of water:

$$Q_{water} = m_{water} \times C_{p,water} \times (T_2 - T) \tag{24}$$

Heating of reactor:

$$Q_{reactor} = m_{reactor} \times C_{reactor} \times (T - T_1) \tag{25}$$

* *A vacuum flask is considered as an approximation to an adiabatic container*.

At the equilibrium, the energy released from cooling of water is equal the energy absorbed by reactor:

$$Q_{water} = Q_{reactor} \tag{26}$$

$$m_{water} \times C_{p,water} \times (T_2 - T) = C_{reactor} \times (T - T_1) \tag{27}$$

$$C_{reactor} = \frac{m_{water} \times C_{p,water} \times (T_2 - T)}{(T - T_1)} \tag{28}$$

Heat capacity of water ($C_{p,water}$) at the experimental temperature is found using Eq.18. The average of T_2 and T is used as the experimental temperature in this equation. Results of measured and calculated parameters are presented in Table 2.

Table 2 Experimentally determined reactor heat capacity.

	m_{water}, kg	T_1, °C	T_2, °C	T, °C	$C_{p,water}$, J/(kg×K)	Q_{water}, J	$C_{reactor}$, J/K	$C_{reactor,average}$, J/K
1	0.3479	20.514	58.940	53.555	4181.300	7833.421	237.082	251.041
2	0.2358	21.574	62.440	54.207	4182.100	8118.884	248.794	
3	0.2317	20.694	62.863	53.747	4182.100	8833.336	267.248	

4.3 Ice melting experiment

Five solutions with different salt concentrations have been tested to determine the temperature change inside the reactor caused by adding of a certain amount of ice to. The following salt solution concentrations have been chosen for laboratory tests in this study: 5, 10, 15, 20 and 23 w%.

Six ice samples of approximately the same mass were added to the solution in each test. The decision to divide all ice for each experiment into 6 smaller samples has been done in order to be able to observe a temperature change inside the reactor gradually. Additionally, this also makes it easier to detect the state of reached equilibrium inside the reactor. A steady or increasing temperature with adding of more ice is the proof that the equilibrium has been reached.

For solutions with 5, 10, 15 and 20 w% salt concentrations the test has been conducted one time, which means that final temperature has been measured 6 times in each experiment. For

23% -salt solution the same test has been conducted 5 times, which gives 30 values of measured final temperatures. All in all this gives 54 readings of T_f.

4.3.1 Experiment procedure

1. ***Preparation of a salt solution***.

The required amount of solid Sodium Chloride was dissolved in distilled water (Fig.14). Table salt without any additives has been used for experiments in this study. To get the desired salt concentration, a certain amount of solid NaCl (Table 3) was first weighed and then distilled water was added to the beaker with salt so that the total weight of both NaCl and water was 1000 g.

The mass of salt solution used in each ice melting experiment was about 500 g.

Figure 14 Salt solution

Table 3 Mass of solid NaCl in solutions of different concentrations

Concentration, %:	5	10	15	20	23
Mass of solid NaCl, g:	50	100	150	200	230

2. ***Cooling the salt solution.***

The objective of this study is to test the behavior of salt solutions at the temperatures below water's freezing point, which is 0 °. Therefore each salt solution was cooled down to approximately -5°C in a thermos flask with help of cooling system before adding this solution to the reactor (Fig.15).

The freezing point of salt solutions is lower than for pure water and drops as the concentration increases (Chapter 2.2.1). Thus it is important to avoid cooling the solutions down to the temperatures that are lower than the actual freezing point of the considered solution in order to prevent ice formation on the cooling system.

Figure 15 Cooling system

3. *Preparation of ice samples.*

Ice samples for each experiment were prepared in the cold room under low temperature conditions (-5°). Granulated, long-term stored snow was used for experiments in this study (Fig.16). 2 mm snow fraction was chosen as an optimal for the experiments. This snow fraction gives larger surface area than pure ice cubes and makes the melting process faster. A faster melting is desired in order to minimize the effect of the heat loss through the reactor walls.

Figure 16 Ice samples

The lower the salt concentration is, the less ice a certain amount of this salt solution is able to melt before the equilibrium is reached. To get the first approximation of how much ice can be melted by 500 g salt solution of different concentrations, the ice masses were calculated with help from the developed model. Based on the calculations, following sample masses were used in the experiments (Table 4):

Table 4 Ice masses, first approximation

Concentration, %	5	10	15	20	23
Total ice mass in 6 samples, g	18	40	180	180	180
Mass per sample, g	3	6.5	30	30	30

4. *"Reactor – salt solution" equilibrium temperature*.

After the three previous preparation steps were fulfilled, the experiments to measure the temperature changes inside of the reactor were started. Logging of data (temperature vs.

time) started at the same moment as a cooled salt solution is poured inside reactor. A stirring rate of 600 rpm was employed throughout the experiments.

The first temperature change is caused by a temperature difference between the cold salt solution and the reactor. This temperature change was observed until the reactor and solution come to equilibrium with each other, i.e. the further measured temperature remains constant with time ($T_{solution,init} = T_{reactor,init}$).

5. ***Final temperature measurements***.

When the steady-state was reached inside the reactor, the prepared ice samples were added one by one to the solution through the hole in the insulating lid (Fig.17). As long as the melting capacity was not reached, the temperature inside the reactor dropped after addition of each ice sample. Decreasing of the temperature continues until the final temperature (T_f) is reached, i.e. further measured temperature values remain constant. Each next ice sample is added after this final temperature is obtained.

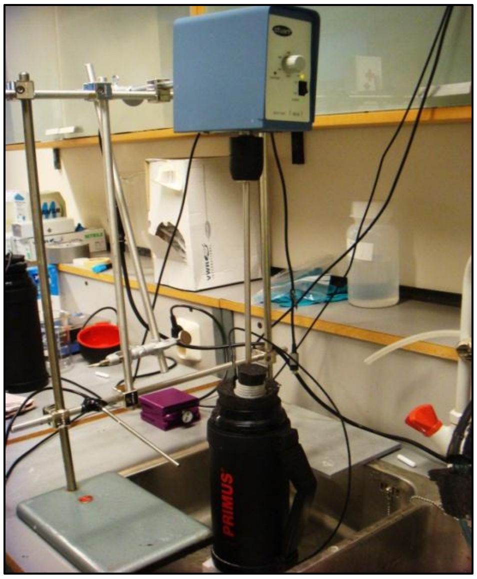


Figure 17 Temperature measurements inside the reactor

4.3.2 Results

Measuring of temperature vs. time has been done with one minute interval. The logged data has been further processed to determine the final temperature (T_f) of the “ice-salt solution” system after adding each ice sample to the solution. Both initial parameters for each experiment and the results of experimentally determined and calculated final temperatures are listed in tables in Appendix 1.

A typical temperature vs. time graph is shown in Figure 18. Adding of the first 4 samples caused a temperature drop inside the reactor. Sample 5 had almost no influence on the temperature change, which indicates that the ice melting capacity of the solution has been reached. At the same time the temperature started to slightly increase again after adding of sample 6.

Logging of data has been continued over approximately 5 minute time intervals after the final temperature has been reached and before each ice sample has been added to the solution. Measured temperatures inside the reactor will theoretically remain constant over this time interval. However, a small temperature increase has been observed in each experiment (Appendix 1). This can especially be seen in the graphs for 5% and 10% salt solutions. The heat generated by the stirrer during the experiment along with heat flux from the surrounding (heat loss) causes these small temperature changes. The value of the final temperature (T_f) has been detected as the lowest one on the horizontal section of the graph.

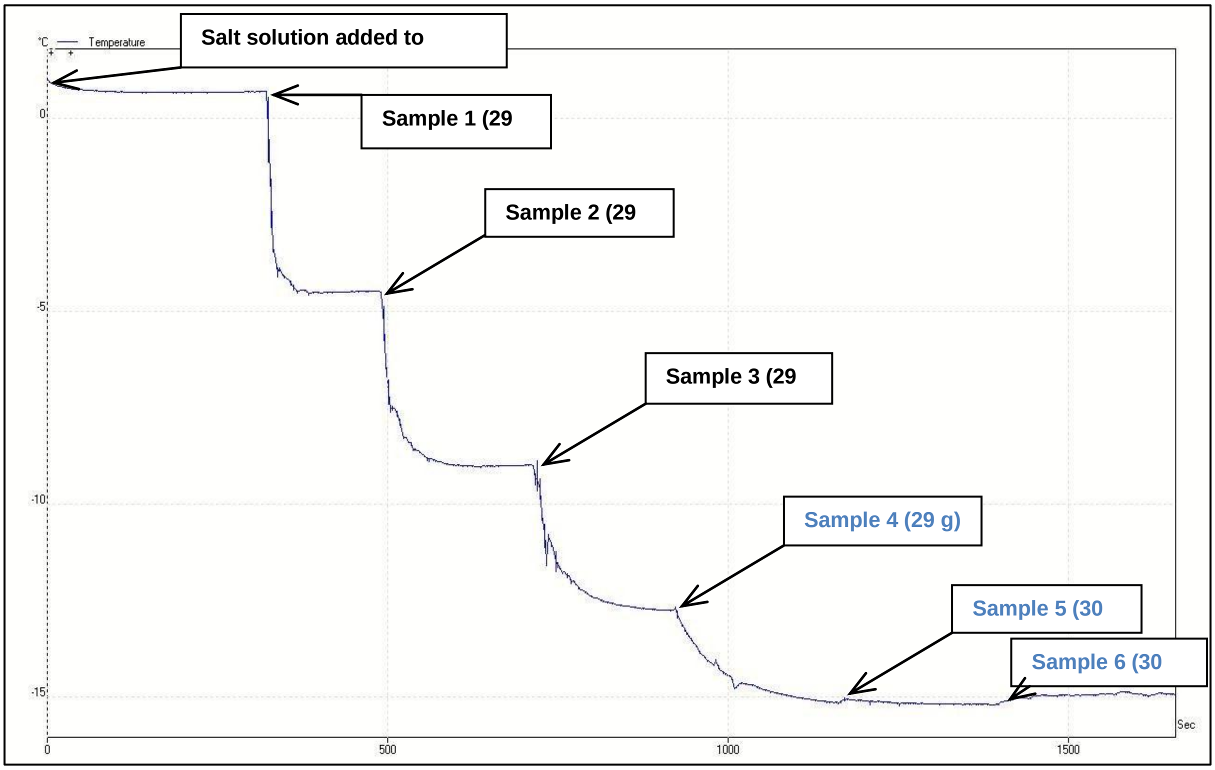


Figure 18 Experimental data, temperature vs. time. 23% salt solution, test 4

The initial parameters and the results of this test are presented in Table 5. The mass values that indicate reached ice melting capacity of the solutions are highlighted with blue color*.

**In some experiments (Appendix 1) the visually detected unmelted ice fractions does not correlate with the calculated results. The discrepancy has been caused either by melting of stored ice during the experiment, difficulties with visual detecting of remaining ice or inaccuracy in following of the experiment procedure due to technical problems occurred during the experiment.*

Table 5 Experimental and calculated results. 23% salt solution, test 4

# 1	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	23,30 %	0,508	0,727	0,727	-0,200	0,029	0,029	-3,943	-4,470	0,528
2	23,30 %	0,508	0,727	0,727	-0,200	0,058	0,058	-8,204	-8,992	0,788
3	23,30 %	0,508	0,727	0,727	-0,200	0,087	0,087	-11,992	-12,747	0,756
4	23,30 %	0,508	0,727	0,727	-0,200	0,116	0,113	-15,053	-15,169	0,116
5	23,30 %	0,508	0,727	0,727	-0,200	0,146	0,115	-14,966	-15,209	0,243
6	23,30 %	0,508	0,727	0,727	-0,200	0,176	0,117	-14,873	-14,947	0,074

At the state of equilibrium the system reaches its ice melting capacity and additional adding of ice samples results in a presence of unmelted ice fractions in the solution. Both calculated and measured values of the final temperature start to increase again after the state of equilibrium is reached. This temperature increase is caused by adding the warmer ice to cold solution.

The total amount of melted ice under given conditions has been calculated in a MatLab model and results are presented in tables in Appendix 1. The masses of the unmelted ice are difficult to measure experimentally, thus the presence of unmelted ice fractions has been detected by visual observation in the experimental part of this study.

4.4 Heat loss through the reactor wall

The adiabatic reactor in practice is not 100% insulated. The heat loss through reactor wall can lead to a certain inaccuracy in the results of all experimental measurements. To test the assumpttion, the heat loss has been experimentally determined.

The experiment to estimate the reactor heat loss has been carried out continuously during 6000 minutes. Following parameters has been measured:

- change of the temperature inside the reactor with time after the cold 23% salt solution (approximate solution temperature -10 °C) has been poured inside the reactor
- room temperature during the whole experiment

Substantial noise or imprecision is present in experimental data (Figure 19). Measured values of temperature signals have therefore been smoothened before the data could be preceded further. The fifth degree polynomial interpolation of data has been used to reduce the temperature unevenness. Interpolation has been carried out with help of numerical data analysis software MatLab.

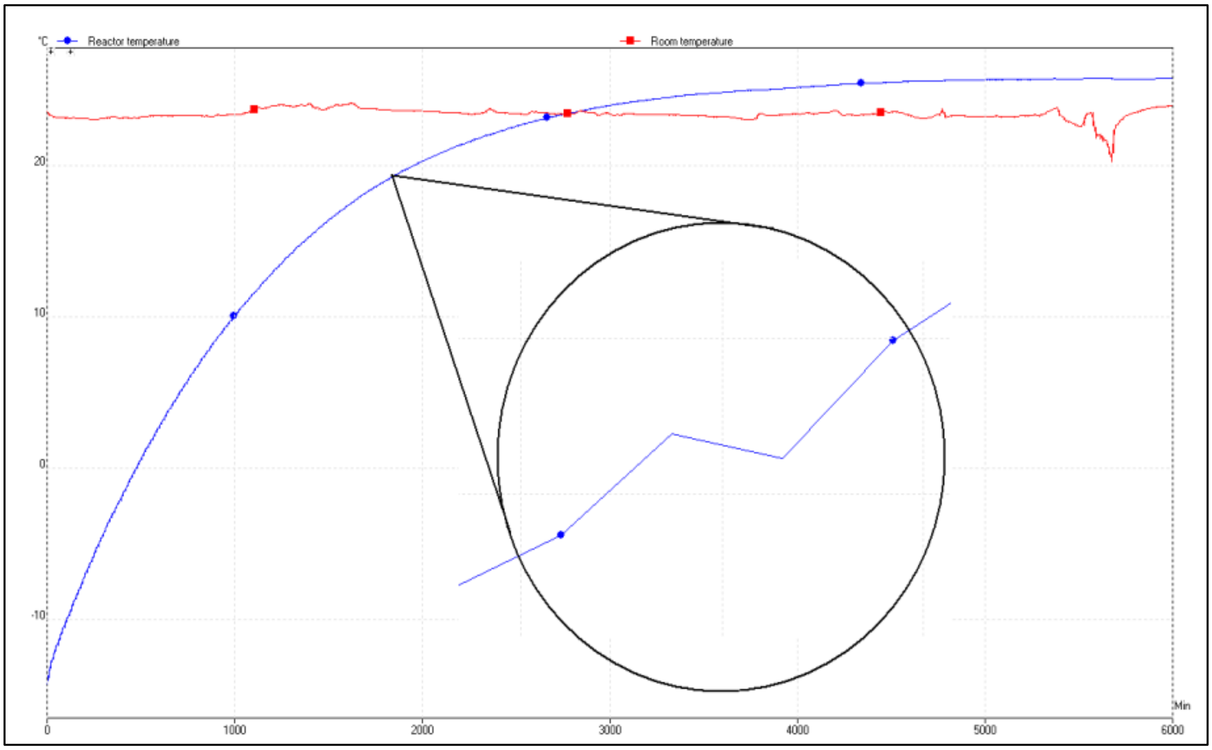


Figure 19 Temperature disturbances

The heat transfer mechanism such as conduction through reactor wall, convection and radiation occur due to the temperature difference inside the reactor ($T_{reactor}$) and the temperature of surroundings (T_{room}, assumed to be constant in this experiment and equal to 23°C). Theoretically the increase of the temperature inside the reactor would stop once it reaches the same temperature as room temperature (23 °C). As can be seen from Figure 19, this doesn't happen and a further increase can be observed. The heat generated by the stirrer during the experiment causes this further temperature change.

The total heat loss for the reactor can be expressed by the following equation:

$$Q_{loss} = m_{solution} \times C_{p,solution} \times \Delta T + C_{reactor} \times \Delta T \quad (29)$$

$$Q_{loss} = m_{solution} \times C_{p,solution} \times (T_{reactor} - T_{room}) + C_{reactor} \times (T_{reactor} - T_{room}) \quad (30)$$

$$Q_{loss} = (m_{solution} \times C_{p,solution} + C_{reactor}) \times (T_{reactor} - T_{room}) \quad (31)$$

Logging of temperature during the experiment has been done with one minute time intervals. To find how the temperature changes with time, the following equation has been used:

$$\frac{\partial Q_{loss}}{\partial t} = (m_{solution} \times C_{p,solution} + C_{reactor}) \times \frac{\partial \Delta T}{\partial t} \tag{32}$$

$$\dot{Q}_{loss} = (m_{solution} \times C_{p,solution} + C_{reactor}) \times \frac{\partial \Delta T}{\partial t} \tag{33}$$

The developed MatLab model has been used to calculate the total reactor heat loss (Appendix2). Mass of the salt solution used in the experiment is equal to 0.5018 kg. The results show that the variation of heat loss with temperature change lies between 0 and 1 Watt (Fig.20). The average heat loss of the reactor is 0.5 Watt and the contribution of the stirrer to the total heat loss is 0.0848 Watt.

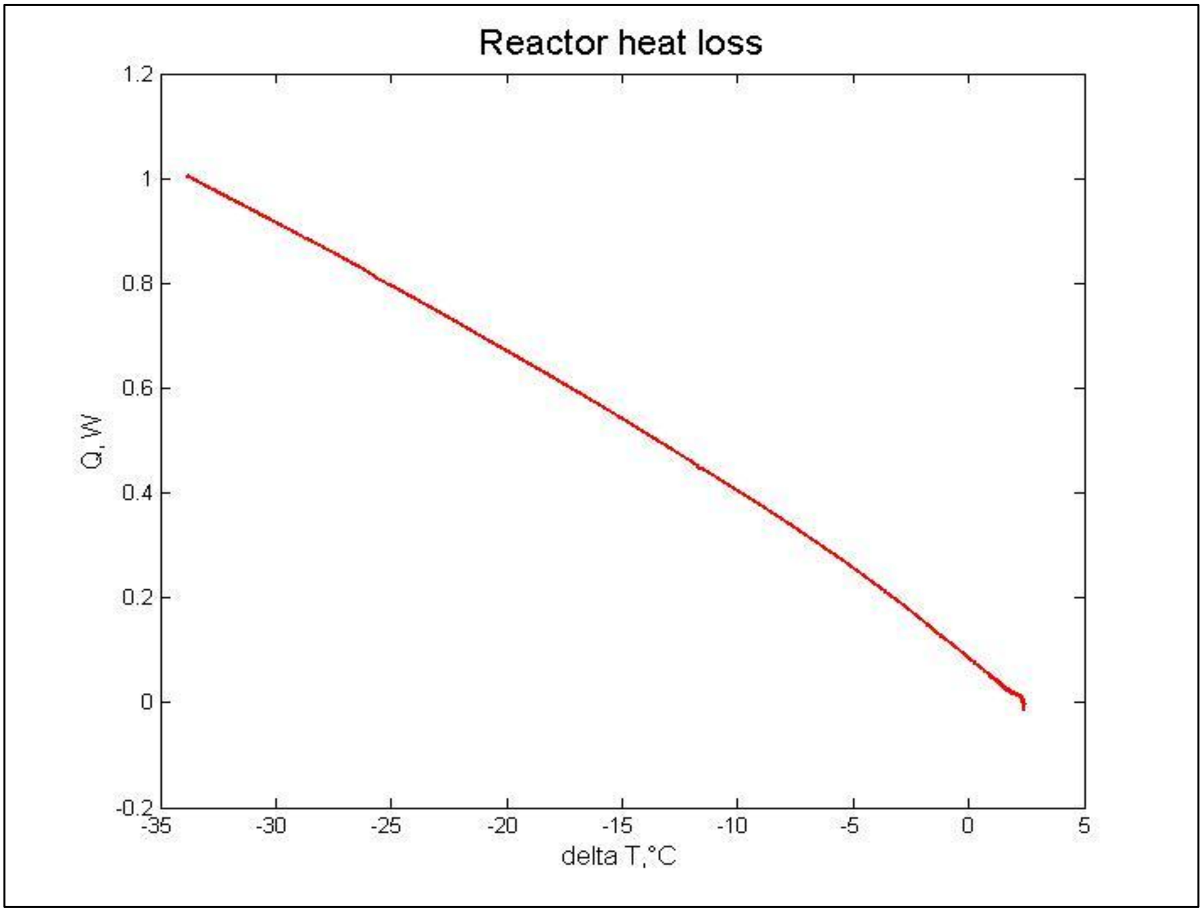


Figure 20 Reactor heat loss, Watt

5 Analysis and discussion

5.1 Comparison between model and experiment

5.1.1 Comparison between all measured and calculated results

The calculated and experimentally determined values of final temperature (T_f) are compared in Figure 21. Comparison includes all 54 determined final temperature values, regardless if the equilibrium in the system has been reached or not. The dashed line on the graph depicts the ideal correlation between measured and calculated results. From Figure 21 can be seen that the results generally fit this correlation well.

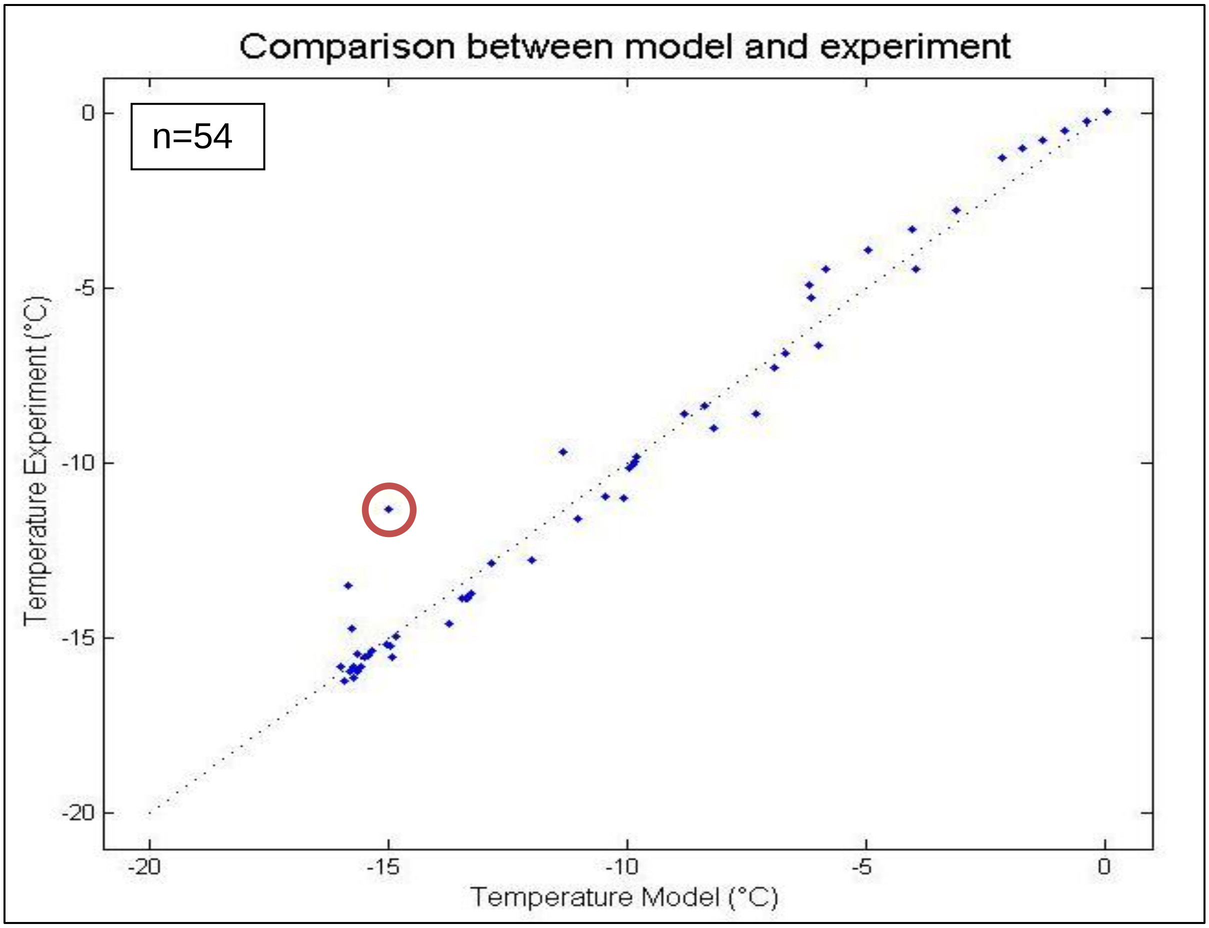


Figure 21 Calculated final temperature vs. experimentally determined final temperature. Result for 54 determined values

The difference between all 54 calculated and measured results is plotted in Figure 22. The error for the 48 out of 54 determined final temperatures (T_f) lies in the temperature interval between -1°C and 1°C. 13 determined temperatures give the error of only 0.25°C. The discrepancy in determined temperatures for 4 other values is between 1°C and 2°C, and only 1 result gives a temperature difference equal to 3.7°C.

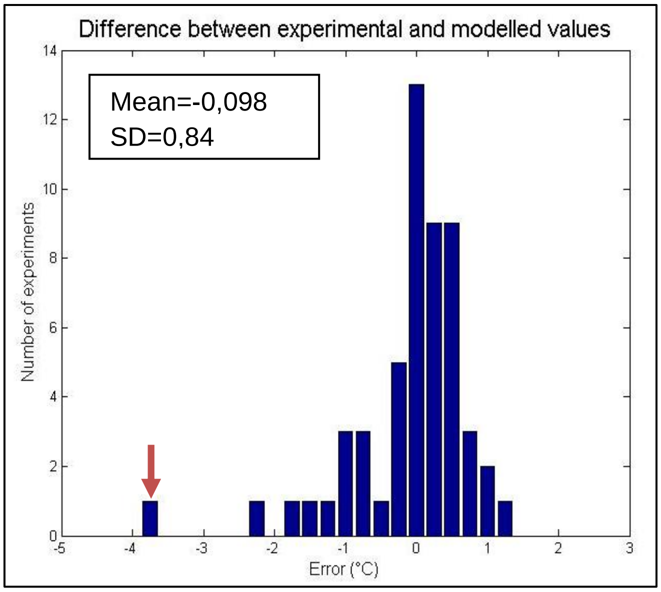


Figure 22 Error (°C) vs. number of experiments. Results for 54 determined values

It has been observed that the positive temperature difference occurs when $T_{f,model} > T_{f,exp}$ (situation A). This dependence has been revealed in 6 out of 9 experiments. The negative temperature difference is present is 3 out of 9 experiments when $T_{f,model} < T_{f,exp}$ (situation B). Table 6 presents the results of this observation.

Table 6 Positive and negative temperature difference between calculated and measured results

	Number of readings	
	Positive:	**Negative:**
5% salt concentration	1	***5***
10% salt concentration	0	***6***
15% salt concentration	***5***	1
20% salt concentration	***6***	0
23% salt concentration (test 1)	***6***	0
23% salt concentration (test 2)	1	***5***
23% salt concentration (test 3)	***6***	0
23% salt concentration (test 4)	***6***	0
23% salt concentration (test 5)	***5***	1

Summary:

- Comparison analysis reveals a generally good correlation between calculated and measured results throughout the tested temperature interval (Fig.21).
- 89% of compared temperatures are consistent within ±1 °C.

- The temperature readings within each experiment lie either over or under the ideal correlation, i.e. the difference between calculated and measured results gives either a positive or negative error.

5.1.2 Comparison of final temperatures before and after ice melting capacity is reached (Case 2 vs. Case 1 and 3)

To see if there are any better performance for the model before the state of equilibrium is reached (Case 2), or vice versa, when unmelted ice fractions are present in the solution (Case 1 or 3), the results have been further compared separately for these cases. The state of reached equilibrium in this comparison is referred to the values calculated in the MatLab model.

The state of unreached equilibrium indicates that all ice added to a solution has been melted. The ice melting capacity has not been reached and the salt solution still has a potential to melt more ice (Case 2). Comparison results of 27 determined final temperatures at this state are presented in Figure 23.

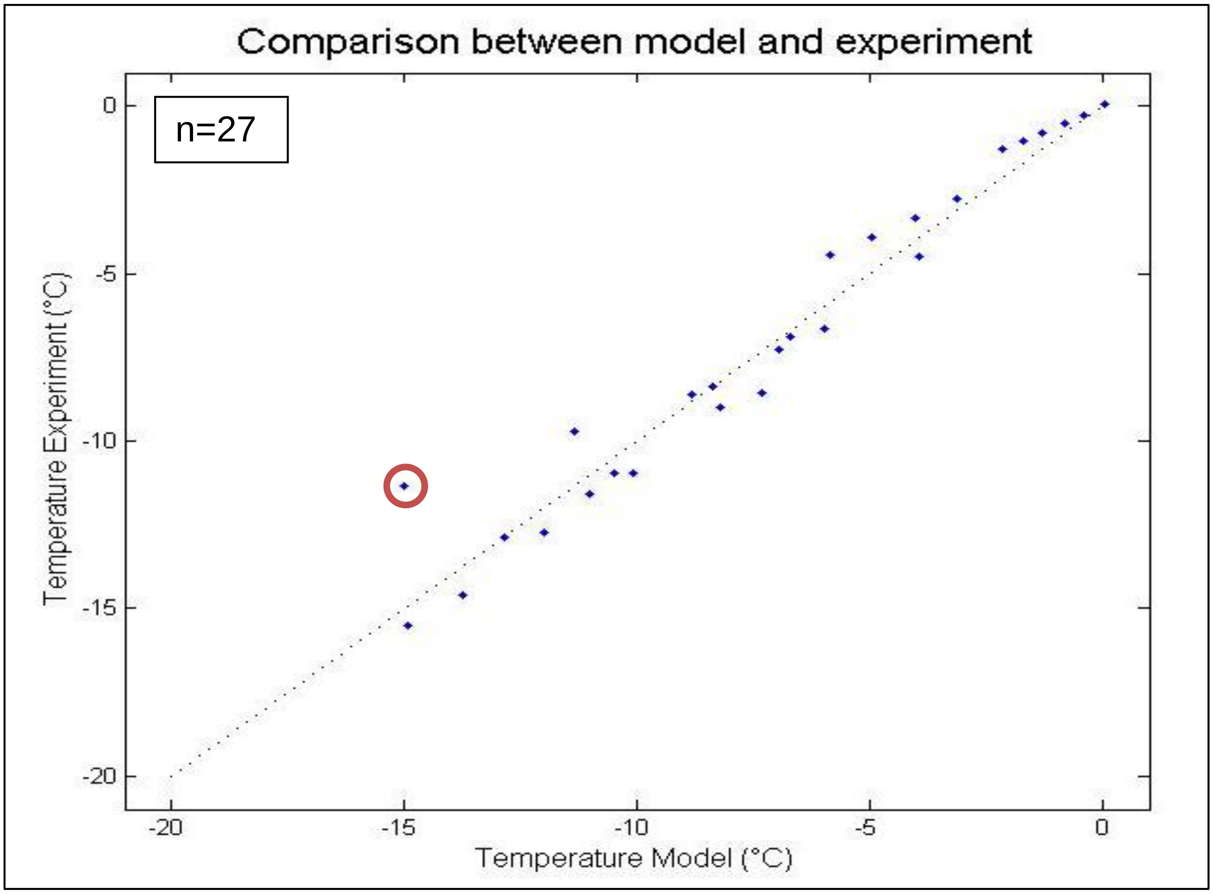


Figure 23 Calculated final temperature vs. experimentally determined final temperature. Before the melting capacity is reached

The difference between these 27 results is plotted in Figure 24. The error for 23 out of 27 values lies in the temperature interval from -1°C to 1°C. 4 values en error of only 0.25 °C and 3 compared results diverge from each other by less than 2 °C. The difference between measured and calculated final temperature for the 23% salt solution (test2) gives an error of 3.7°C.

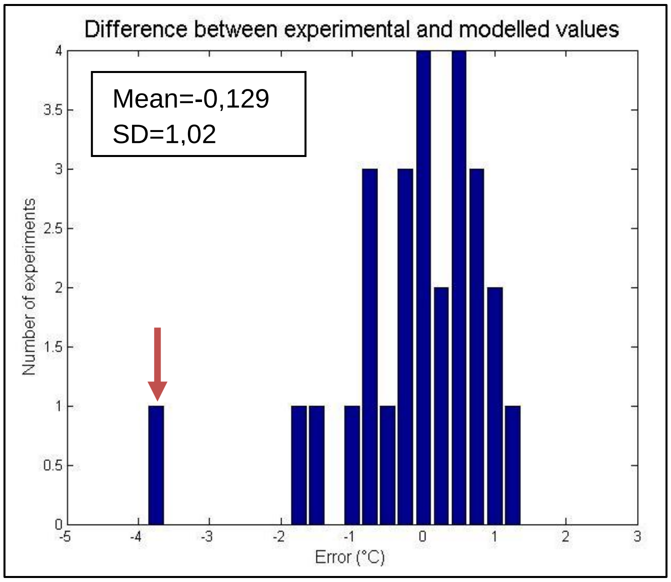


Figure 24 Error (°C) vs. number of experiments. Before the malting capacity is reached

After the salt solution has reached its ice melting capacity, further adding of ice samples has resulted in a presence of unmelted ice fractions in the system (Case 1 or 3). Comparison between 27 determined temperatures is presented in Figure 25.

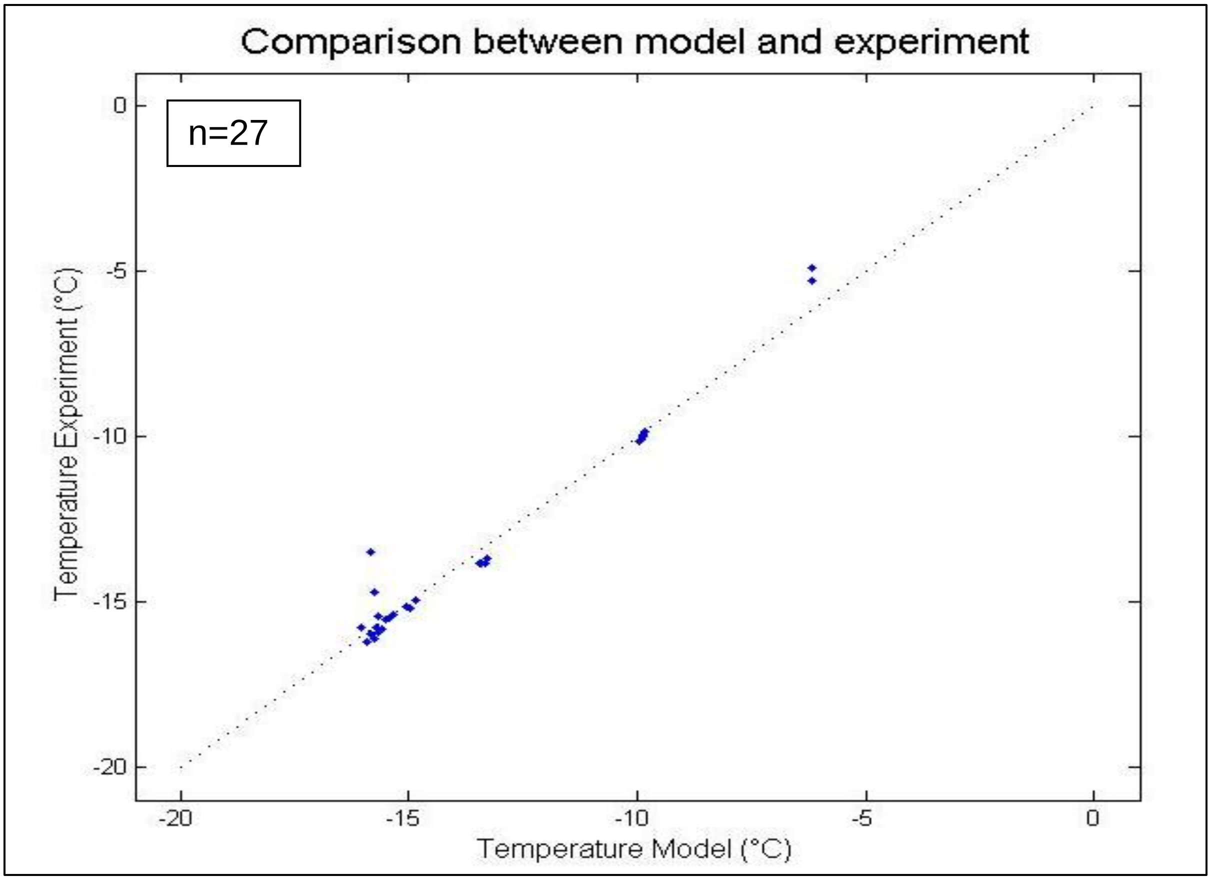


Figure 25 Calculated final temperature vs. experimentally determined final temperature. After the melting capacity is reached

The difference between these 27 results is plotted in figure 26. The comparison results for 25 out of 27 values give an error of ±1°C. 9 values of final temperature diverge from each other by 0.25°C. The maximum discrepancy (2.4 °C) in obtained results has been calculated for 23% salt solution (test 2).

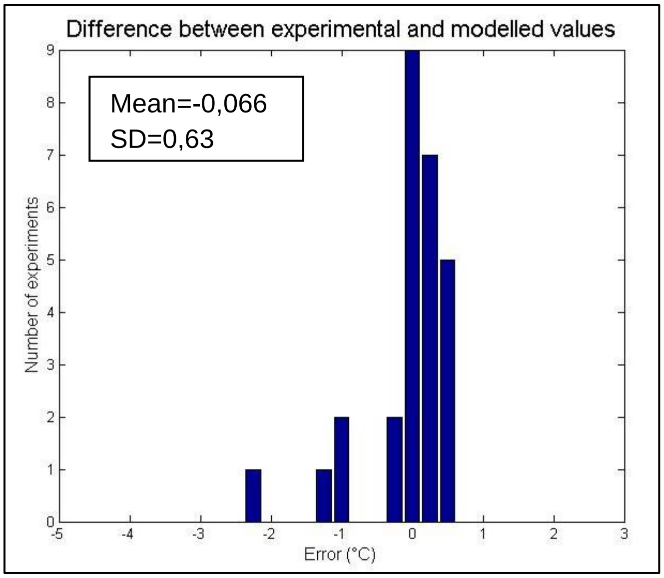


Figure 26 Error (°C) vs. number of experiments. After the melting capacity is reached

The heat required for melting of ice (Case 1 and 3) is higher than the heat released from cooling of unmelted ice fractions (Case 2). This results in a higher temperature drop inside the reactor after adding of 1 extra g ice to a solution that has not reached its ice melting capacity. The total impact on compared results is therefore higher for Case 1 and 3 than for Case 3 (Table 7):

Table 7 The difference between calculated final temperatures on example of 23% salt solution, test 4

Case 1 or 3:	**29,5 g ice added**	**30,5 g ice added**	ΔT
T_f:	-4.0809	-4.2340	-0.1531
Case 2:	**179,5 g ice added**	**180,5 g ice added**	ΔT
T_f:	-14.8621	-14.8619	0.0002

Summary:

- In both compared situations the error is systematic within each experiment and lies either over or under ideal correlation.
- The degree of uncertainty is lower for Case 1 and 3 when the unmelted ice fractions are present in the solution than for Case 2 where all ice has been melted.

5.2 Possible reasons for discrepancies between the experimentally obtained and calculated results

This discrepancy between measured and calculated final temperatures is caused by factors and uncertainties either in experimental part of work or in calculation model. The positive (Situation A) or negative (Situation B) impact of uncertainties on the difference between measured and calculates values of final temperature is considered in the comparison analyses.

5.2.1 Experimental uncertainties

The following reasons that can explain the discrepancy between results are considered:

- **Uncertainty in weighting of $m_{solution,init}$ and $m_{ice,init}$**

The accuracy of weighing scales utilized in the experimental part of work is 0.1 g. The uncertainty caused by weighing error can lead to both positive and negative difference between the obtained results depending on if the weighted values were lower or higher than the actual masses. The calculations verified with MatLab show that higher mass of solution results in a lower temperature change inside the reactor, while higher masses of ice samples cause a higher temperature drop. The uncertainty in weighting of $m_{solution,init}$ gives a systematic error within each experiment. The uncertainty in weighting of $m_{ice,init}$ results at the same time in inaccuracies that vary from reading to reading.

- **Uncertainty in temperature measurement ($T_{solution,init}$, $T_{react,init}$, $T_{ice,init}$)**

The accuracy of temperature measurements is ±1°C. The calculations verified with MatLab show that lower initial temperature of salt solution (reactor) leads to higher temperature drop inside the reactor, while lower initial temperature of ice results in a lower change of the temperature. The inaccuracy in measured $T_{ice,init}$ leads to both positive and negative difference between the obtained results which varies with temperature readings. The inaccuracy in measured $T_{solution,init}$ results in a systematic error within each experiment.

- **Uncertainty in C_{init} of prepared salt solutions**

The concentration of each salt solution has been measured before each experiment with help of an optical reflectometer in order to verify if concentration corresponds with the value used in MatLab calculations. In 8 out of 9 experiments the measured concentration is either slightly higher or lower than the desired value. Assuming that the reflectometer is 100%

accurate, some of the discrepancies between the experimentally determined and calculated results can be explained by the difference between the actual salt concentration and the one used in calculations. A lower concentration results in a lower temperature drop after adding a certain amount of ice. In test 3, 4 and 5 with 23% salt solution the measured concentration is higher than the value of 23% used in calculation (Appendix 1). This inaccuracy leads to a positive difference between determined temperatures (situation A). At the same time in tests with 5% and 10% salt solutions the measured concentrations are lower than the values used in calculations. Therefore the experimentally determined temperature drop inside the reactor is some lower than the calculated value (situation B). Generally, the impact of this uncertainty leads to a systematical error (either positive or negative) for all measurements within each experiment.

- **Uncertainty in experimentally determined $C_{reactor}$**

The inaccuracy in experimentally determined value of reactor heat capacity can lead to both positive and negative difference between determined final temperatures. The error is systematic, i.e. gives the same impact on determined temperatures within each experiment.

- **Melting of ice prior to the experiment**

All the ice samples have been prepared in a cold room under constant, low temperature conditions, while experimental determination of final temperatures has been performed in the technical laboratory under room temperature conditions (23°C). The duration of each experiment varies between 35-50 minutes. The ice samples during each experiment have been stored in an insulated container in order to minimize heat transfer between surroundings and ice samples, and, therefore, avoid melting of ice. However, is has not been capable to keep a constant temperature inside the container during the whole experiment, and melting of ice occurred as a result. The actual mass of some ice samples added to solution has therefore been lower than the values listed in Appendix 1. From Eq.19 follows that the less ice is added to solution ($m_{ice,init}$), the lower temperature drop it causes. Negative temperature difference (situation B) can therefore be explained by this experimental uncertainty. Melting of stored ice has the largest effect on results of test 2 for 23% solution, where the difference between measured and calculated final temperatures is equal 3.7°C (Table 8).

Table 8 Discrepancy between calculated and measured final temperature caused by melting of ice samples

mass_ice,kg	T_final (model),°C	T_final (experiment),°C
0,0573	-11,334	-9,690
0,0859	-15,008	-11,330

The impact of this experimental uncertainty varies within each experiment. The recommendation to execute both the preparation stage and the experimental part of the laboratory tests in the cold room is suggested in order to reduce the temperature gradient during the whole experiment, avoid the melting of ice and, therefore, reduce the level of discrepancies in obtained results.

5.2.2 Uncertainties in the model

- **Heat loss**

Heat loss of the reactor is perhaps the most serious source of errors in calorimetric measurements [15]. Therefore the value for heat loss has to be essentially included in the calculation model in order to obtain more accurate results. The total heat loss of the reactor (Watt) is the function of time which means that one more additional unknown variable should be added in calculation of final temperature (T_f) of the “ice-salt solution” system. This leads to certain difficulties and makes the model more complicated both for use and common understanding. Therefore it has been decided not to include this physical constant in the developed model. However, the total heat loss of the reactor is experimentally determined (Chapter 4.4) to get the insight in to what extent the results of all other experiments are affected by it.

The estimated average heat loss of the reactor utilized in this study equals to 0.5 Watt. The results of similar study of the Adiabatic Dewar Calorimeter can be used as example for comparison with the results obtained in this study. For 250 and 500 ml glass Dewar Calorimeter fitted with corks and thermocouple pockets heat loss factors have been measured as 0.077 and 0.03 Watt/L/K respectively [17]. With respect to the results of this study, the values of the total heat loss of the reactor are slightly higher, but still lie within acceptable limits. Discrepancies between the experimentally obtained and calculated values of final temperature (situation B) are partially caused by omitted heat capacity value in the calculation model.

The impact of this uncertainty leads to a systematical error (either positive or negative) for all measurements within each experiment. This systematical error can be reduced either by using better isolation of the reactor or by including this thermodynamic constant in the developed model.

- **Calculation of $C_{p,solute}, C_{p,water}$**

Calculation of some of the thermodynamic variables in the developed model does not give 100% accurate results. For instance, the specific heat capacity of water has been estimated using a third-order polynomial interpolation of data. The solute heat capacity has at the same time been empirically determined. The results of these calculation methods do not always 100% correlate with the actual values. This results in uncertainties in the output results and gives either positive or negative difference between the determined values of final temperature. The error varies with temperature measurements within each experiment.

- **Latent heat of fusion, L**

Granulated, long-term stored snow has been used for experiments in this study (Chapter 4.3.1). The latent heat of fusion for ice (334000 J/(kg×K)) has been used in calculations in developed MatLab model. The latent heat of fusion for snow may be equal or less than that for ice, depending on the amount of liquid water in snow [18]. Discrepancies between the measured and calculated values of final temperature can be caused by this possible error. The impact of this uncertainty leads to a systematical error (either positive or negative) for all measurements within each experiment.

6 Conclusion and recommendations for future work

The thermodynamic model that predicts the final temperature (T_f) and the amount of melted ice ($m_{ice,melted}$) for a given salt solution in the adiabatic system has been developed. The outcome of the model has been compared with the results of experimental measurements.

The main findings of the study are as follows:

- in general, the good correlation between the calculated and experimental results has been revealed. The model was able to predict the final temperature of the "ice-salt solution" system with high precision throughout the investigated temperature range between -16°C and 0°C. In 89% of the cases the error between the determined results lies within temperature interval ±1°C. The difference between the calculated and measured final temperatures was almost symmetrical, with Mean=-0.098 and SD=0.84
- comparison analysis reveals lower degree of uncertainties when the solution has reached its ice melting capacity. The model has therefore a better performance and gives more accurate results (Mean= -0.066, SD=0.63) compared with the situation when the solution still has a potential to melt more ice (Mean= -0.129, SD=1.02)
- the possibility to improve the developed model is to incorporate the omitted value for heat loss in the calculations. The possibility to improve the experimental set up is to conduct all experiments in a cold room under constant, low temperature conditions in order to reduce the temperature gradient throughout the experiment and as a result avoid melting of ice. Use of a better isolation of the reactor can help to decrease a negative impact of heat loss on the measured results

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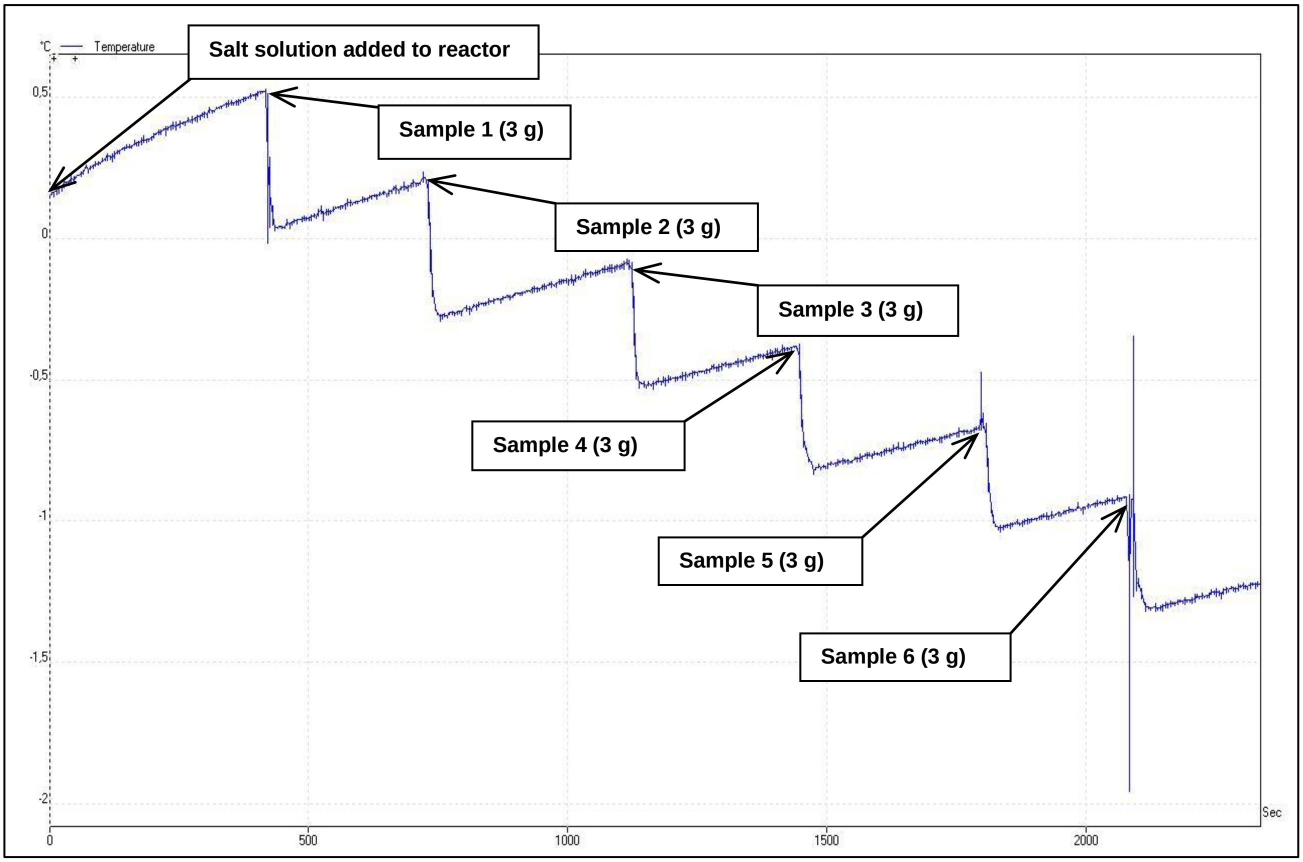
Appendix 1 – Final temperature of “ice-salt solution” system

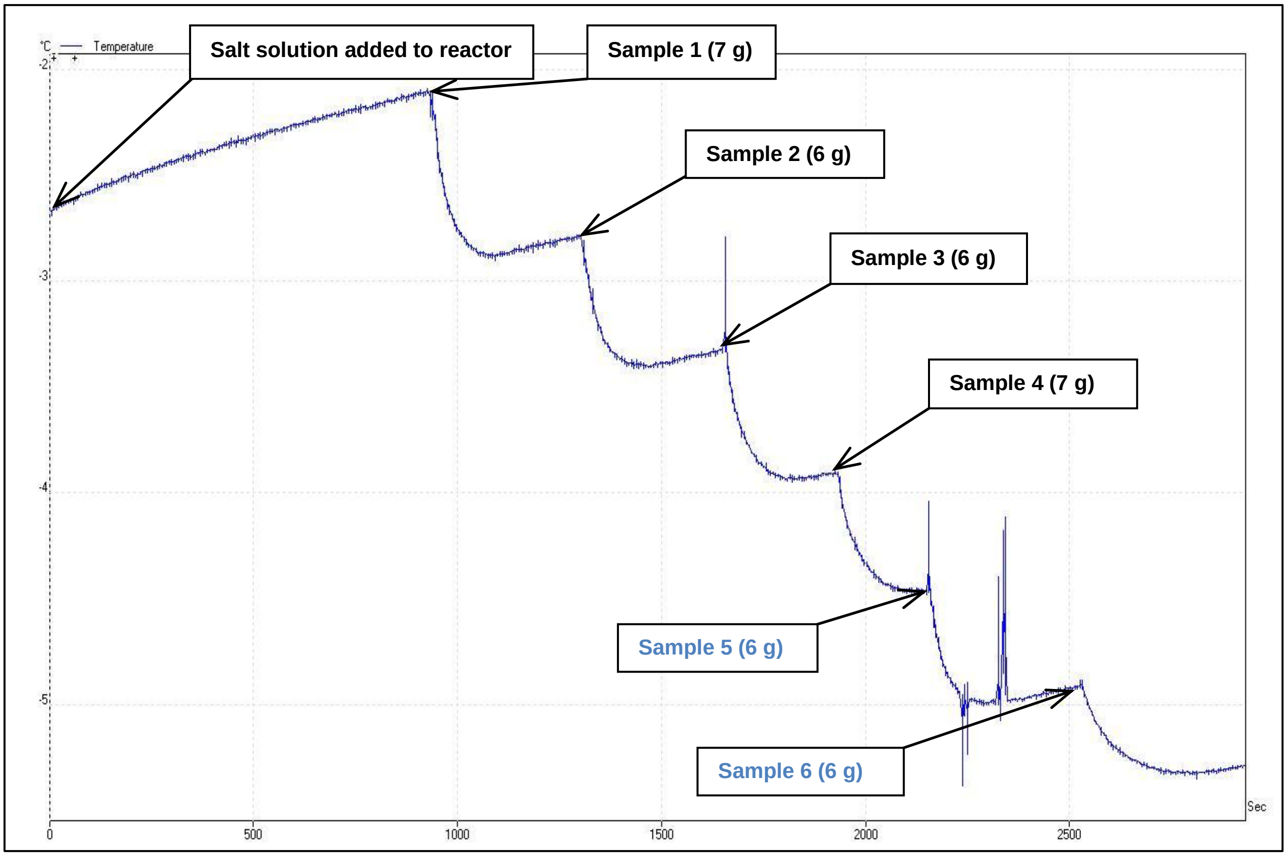
- 5 % - salt solution:

	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	4,50 %	0,488	0,517	0,517	-0,200	0,003	0,003	0,056	0,046	0,010
2	4,50 %	0,488	0,517	0,517	-0,200	0,006	0,006	-0,385	-0,263	-0,122
3	4,50 %	0,488	0,517	0,517	-0,200	0,009	0,009	-0,820	-0,514	-0,306
4	4,50 %	0,488	0,517	0,517	-0,200	0,012	0,012	-1,296	-0,812	-0,484
5	4,50 %	0,488	0,517	0,517	-0,200	0,015	0,015	-1,708	-1,030	-0,678
6	4,50 %	0,488	0,517	0,517	-0,200	0,018	0,018	-2,144	-1,300	-0,844



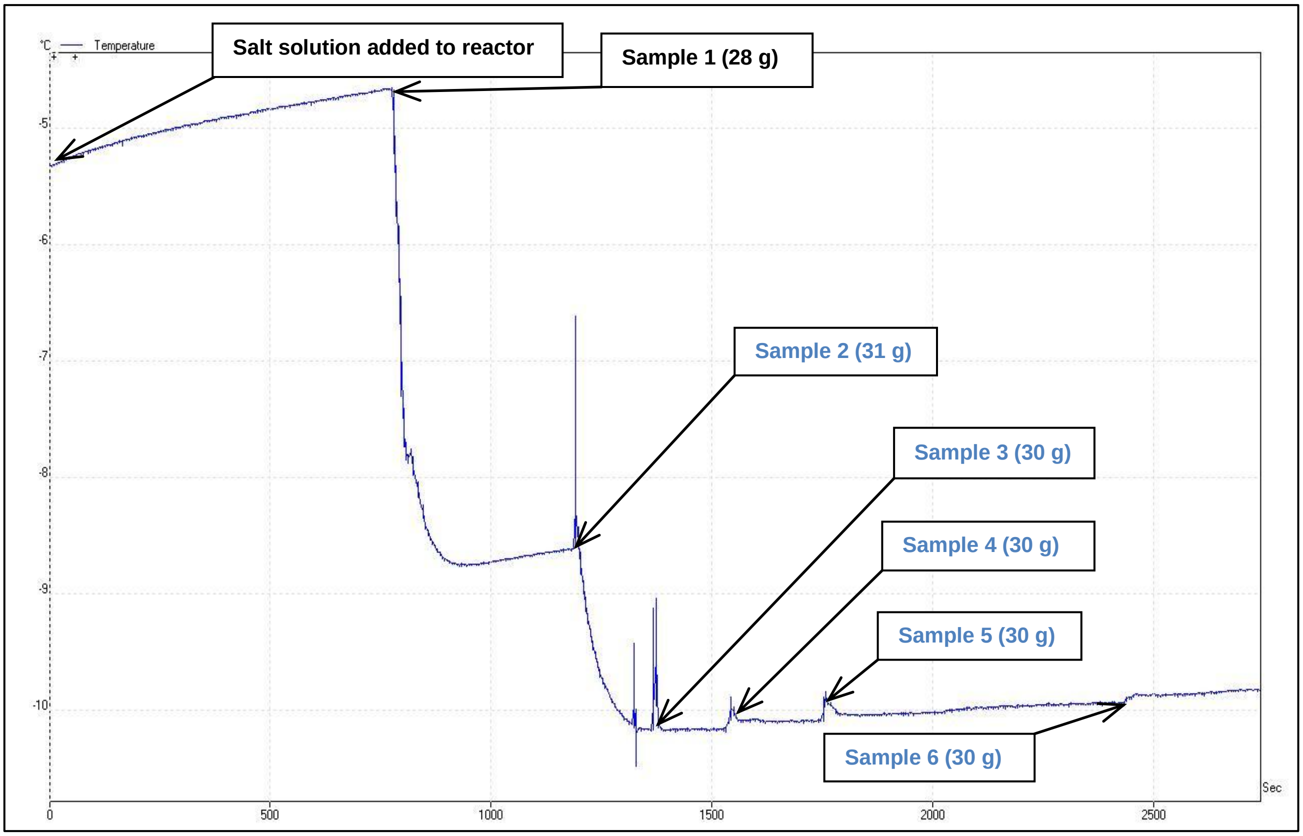
- 10 % - salt solution:

	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	9,80 %	0,527	-2,102	-2,102	-0,100	0,007	0,007	-3,122	-2,783	-0,339
2	9,80 %	0,527	-2,102	-2,102	-0,100	0,013	0,013	-4,045	-3,333	-0,712
3	9,80 %	0,527	-2,102	-2,102	-0,100	0,019	0,019	-4,905	-3,909	-0,996
4	9,80 %	0,527	-2,102	-2,102	-0,100	0,026	0,026	-5,887	-4,461	-1,426
5	9,80 %	0,527	-2,102	-2,102	-0,100	0,032	0,028	-6,169	-4,917	-1,252
6	9,80 %	0,527	-2,102	-2,102	-0,100	0,039	0,029	-6,173	-5,284	-0,889



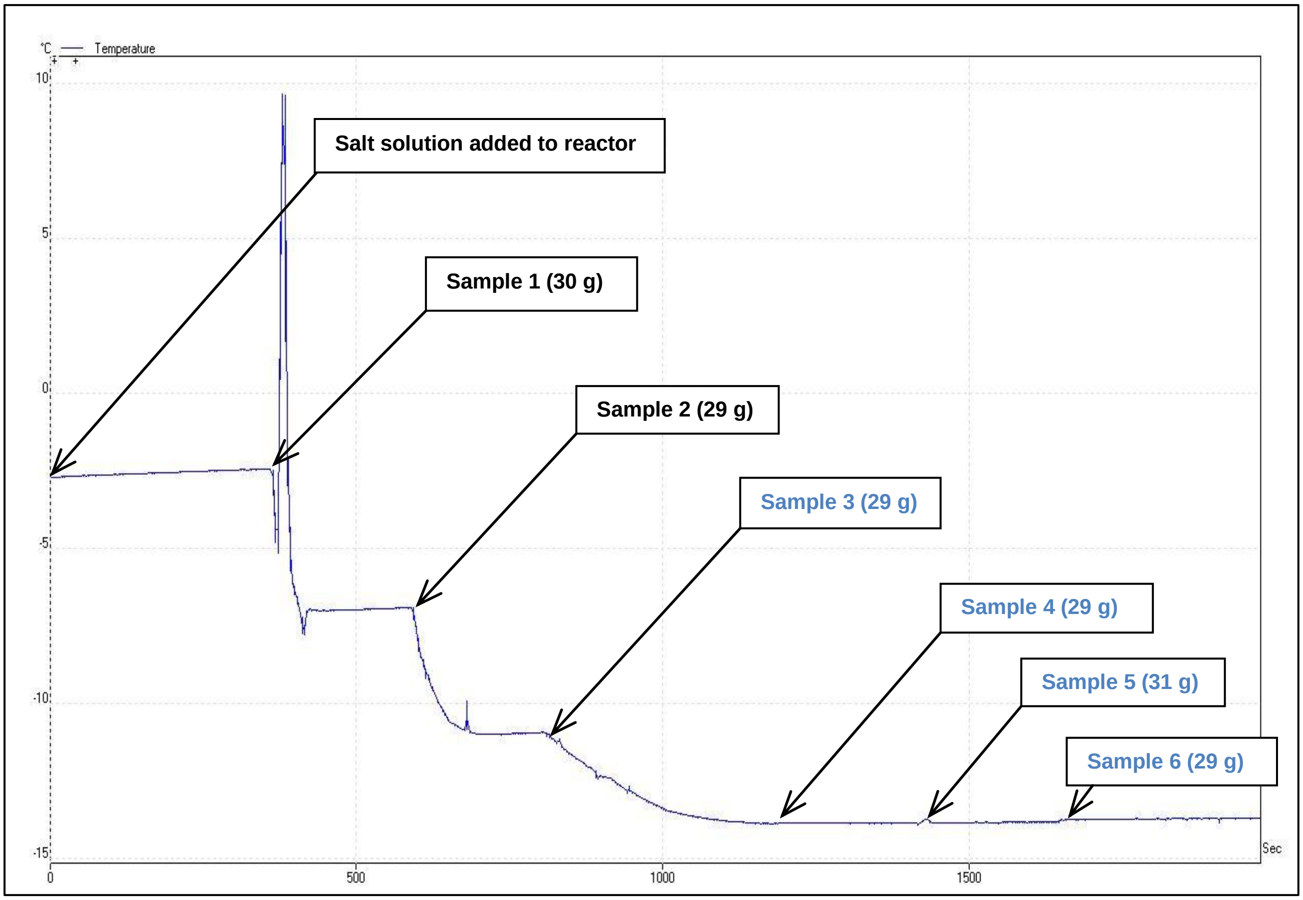
- 15 % - salt solution

	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	14,80 %	0,543	-4,658	-4,658	-0,100	0,028	0,028	-8,780	-8,606	-0,174
2	14,80 %	0,543	-4,658	-4,658	-0,100	0,059	0,038	-9,964	-10,154	0,190
3	14,80 %	0,543	-4,658	-4,658	-0,100	0,089	0,040	-9,926	-10,098	0,172
4	14,80 %	0,543	-4,658	-4,658	-0,100	0,119	0,041	-9,890	-10,023	0,133
5	14,80 %	0,543	-4,658	-4,658	-0,100	0,149	0,043	-9,856	-9,944	0,088
6	14,80 %	0,543	-4,658	-4,658	-0,100	0,179	0,045	-9,824	-9,832	0,008



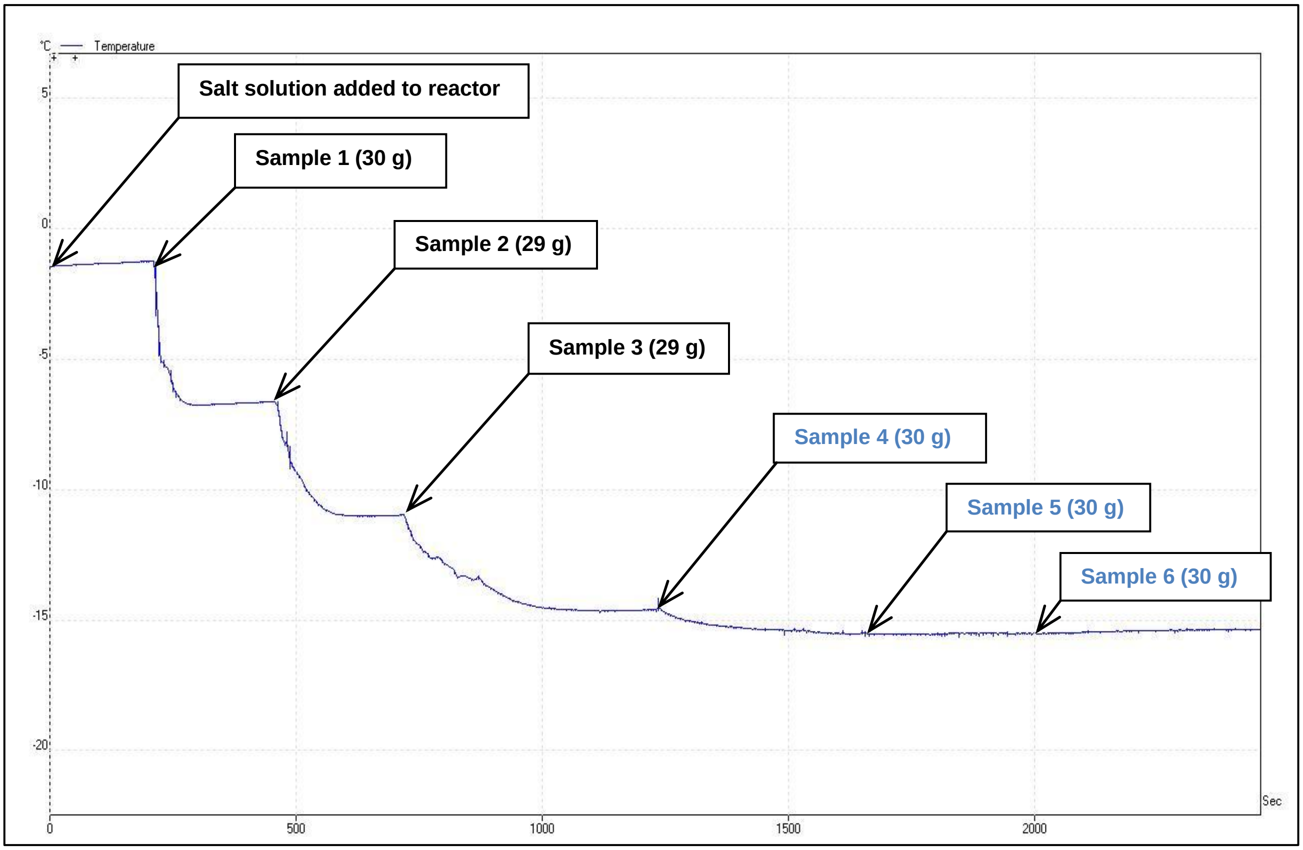
- 20 % - salt solution

	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	19,90 %	0,577	-2,421	-2,421	-1,400	0,030	0,030	-6,740	-6,892	0,153
2	19,90 %	0,577	-2,421	-2,421	-0,700	0,059	0,059	-10,497	-10,947	0,450
3	19,90 %	0,577	-2,421	-2,421	-0,200	0,088	0,084	-13,461	-13,845	0,384
4	19,90 %	0,577	-2,421	-2,421	-0,100	0,117	0,086	-13,403	-13,857	0,454
5	19,90 %	0,577	-2,421	-2,421	-0,100	0,148	0,089	-13,340	-13,839	0,499
6	19,90 %	0,577	-2,421	-2,421	-0,100	0,177	0,091	-13,277	-13,698	0,421



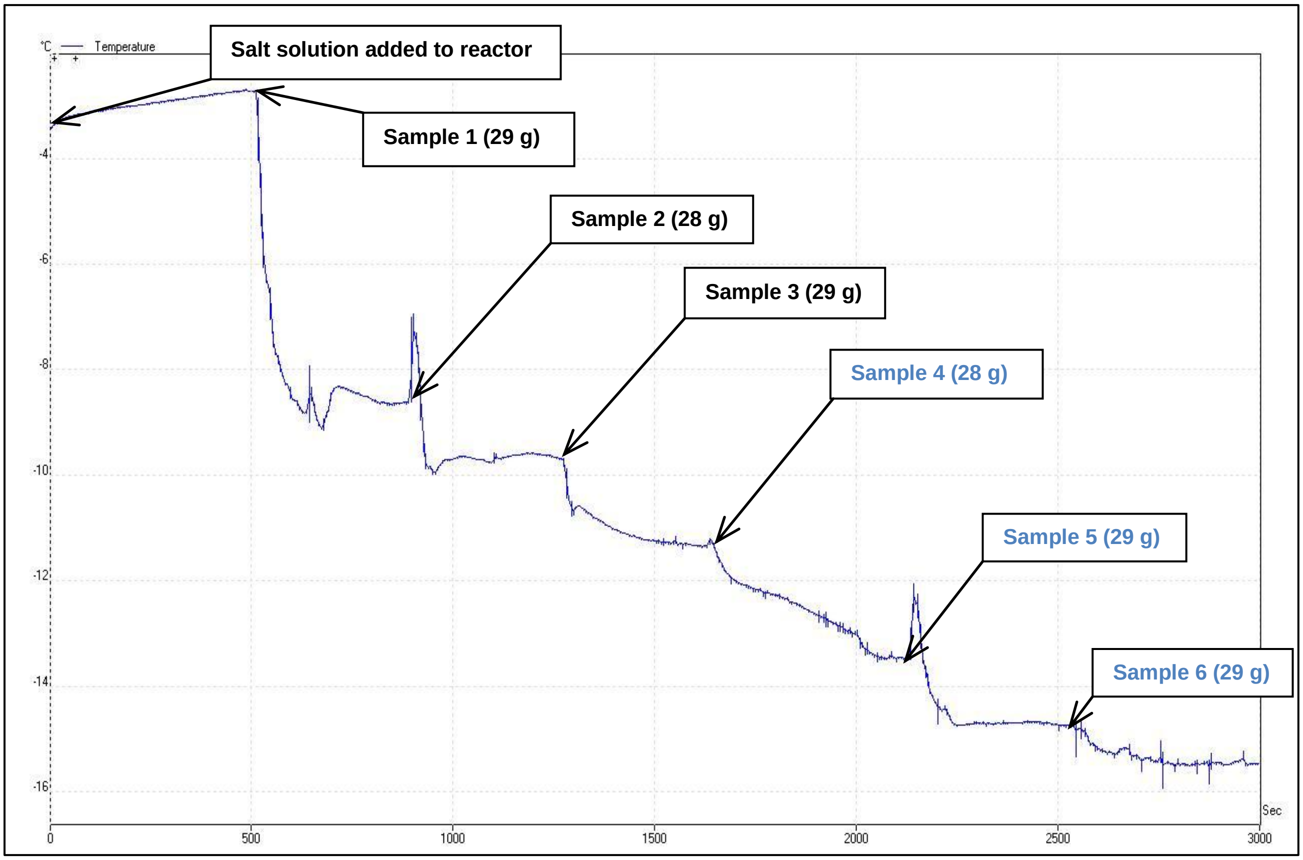
- 23 % - salt solution, experiment 1

# 1	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	22,70 %	0,528	-1,260	-1,260	-2,700	0,030	0,030	-5,991	-6,639	0,648
2	22,70 %	0,528	-1,260	-1,260	-2,700	0,059	0,059	-10,071	-10,982	0,911
3	22,70 %	0,528	-1,260	-1,260	-2,700	0,088	0,088	-13,725	-14,601	0,877
4	22,70 %	0,528	-1,260	-1,260	-2,700	0,118	0,104	-15,510	-15,533	0,023
5	22,70 %	0,528	-1,260	-1,260	-2,700	0,148	0,106	-15,445	-15,506	0,061
6	22,70 %	0,528	-1,260	-1,260	-2,700	0,178	0,108	-15,364	-15,369	0,005



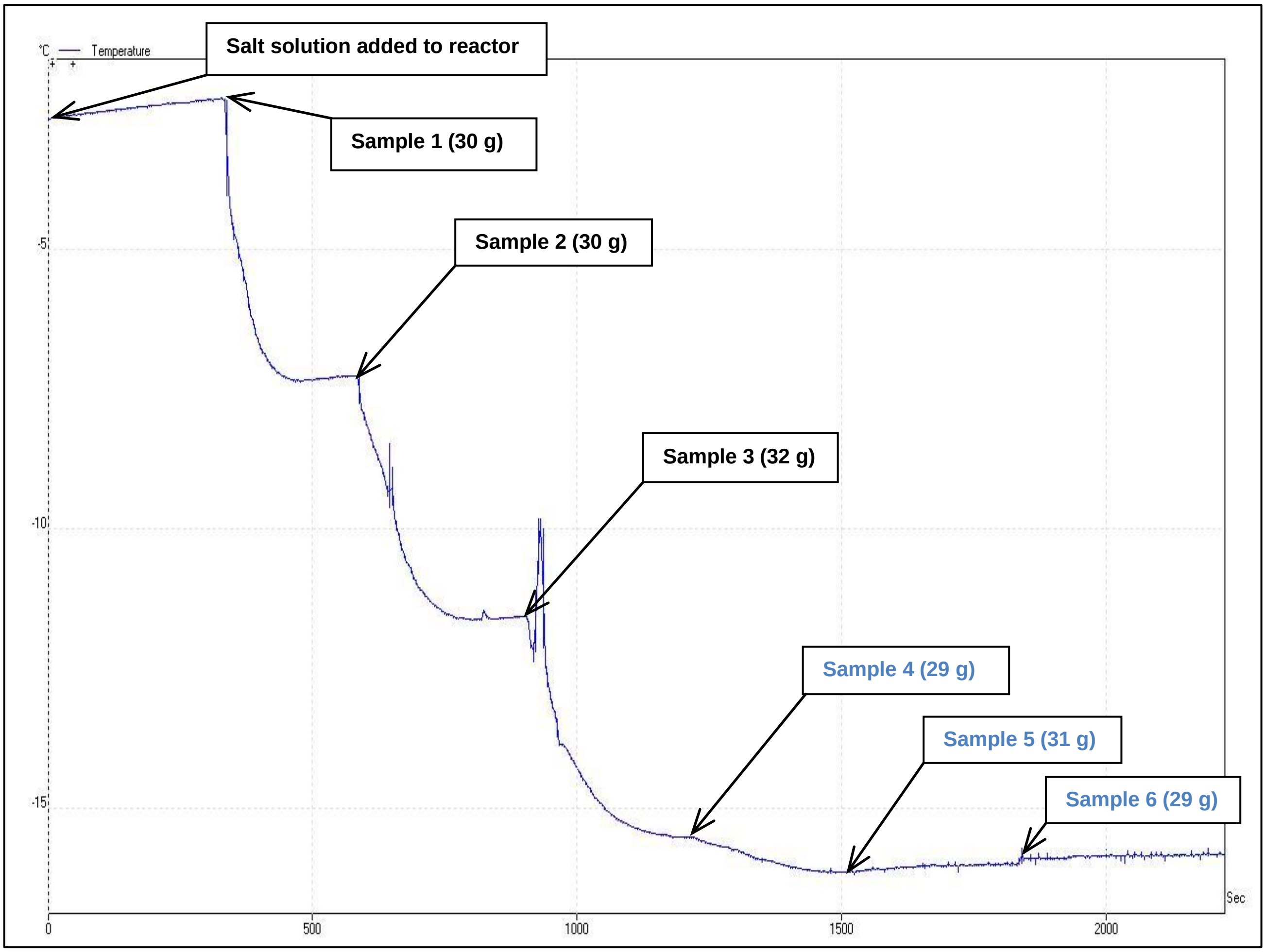
- 23 % - salt solution, experiment 2

# 2	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	23,00 %	0,528	-2,750	-2,750	-0,100	0,029	0,029	-7,304	-8,585	1,281
2	23,00 %	0,528	-2,750	-2,750	-0,100	0,057	0,057	-11,334	-9,690	-1,644
3	23,00 %	0,528	-2,750	-2,750	-0,100	0,086	0,086	-15,008	-11,330	-3,678
4	23,00 %	0,528	-2,750	-2,750	-0,100	0,114	0,095	-15,847	-13,486	-2,361
5	23,00 %	0,528	-2,750	-2,750	-0,100	0,143	0,098	-15,765	-14,730	-1,035
6	23,00 %	0,528	-2,750	-2,750	-0,100	0,172	0,100	-15,679	-15,462	-0,217



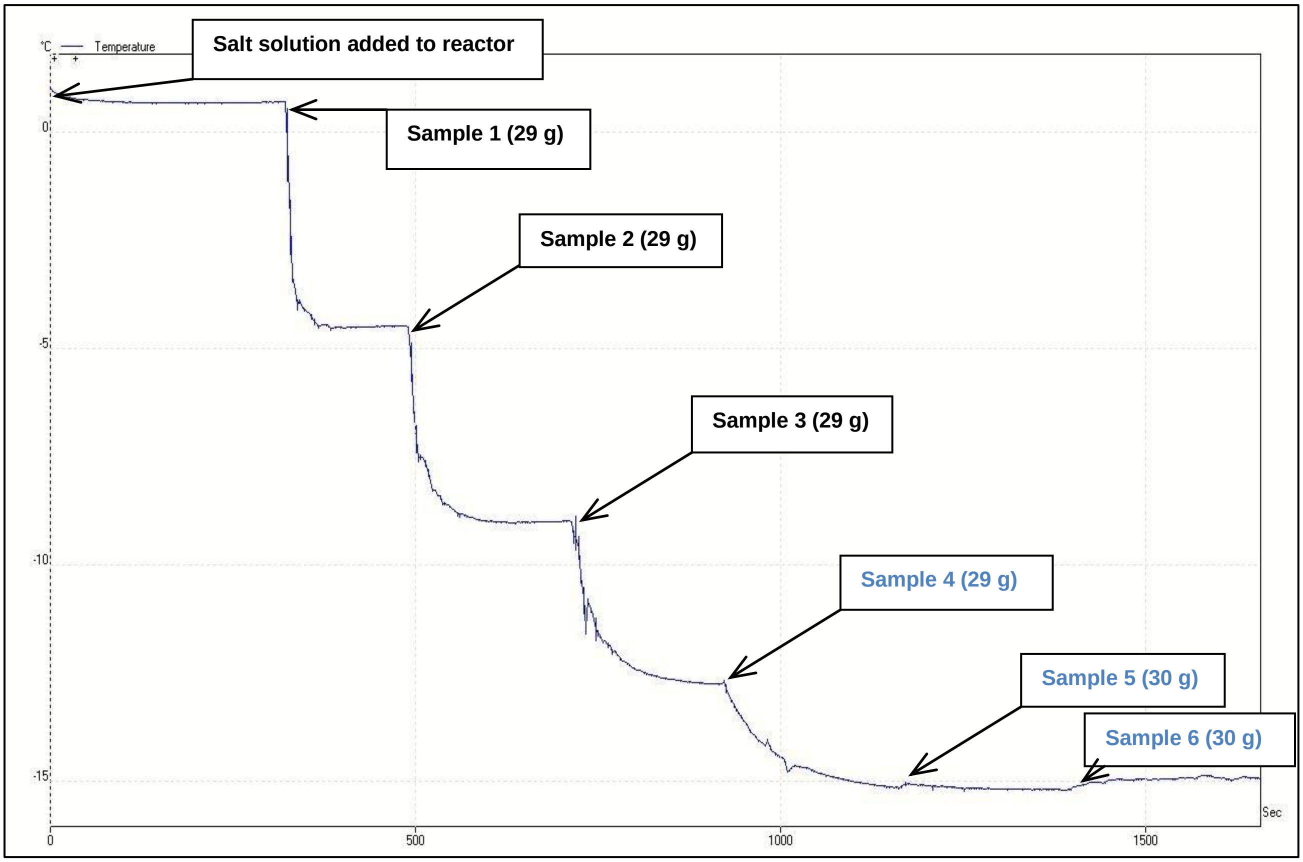
- 23 % - salt solution, experiment 3

# 3	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	23,30 %	0,544	-2,290	-2,290	-3,600	0,030	0,030	-6,934	-7,274	0,340
2	23,30 %	0,544	-2,290	-2,290	-2,800	0,060	0,060	-11,026	-11,569	0,543
3	23,30 %	0,544	-2,290	-2,290	-1,900	0,092	0,092	-14,939	-15,515	0,576
4	23,30 %	0,544	-2,290	-2,290	-1,000	0,121	0,101	-15,749	-16,132	0,383
5	23,30 %	0,544	-2,290	-2,290	-0,400	0,152	0,100	-15,664	-15,936	0,272
6	23,30 %	0,544	-2,290	-2,290	-0,100	0,181	0,106	-15,576	-15,813	0,237



- 23 % - salt solution, experiment 4

# 1	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	23,30 %	0,508	0,727	0,727	-0,200	0,029	0,029	-3,943	-4,470	0,528
2	23,30 %	0,508	0,727	0,727	-0,200	0,058	0,058	-8,204	-8,992	0,788
3	23,30 %	0,508	0,727	0,727	-0,200	0,087	0,087	-11,992	-12,747	0,756
4	23,30 %	0,508	0,727	0,727	-0,200	0,116	0,113	-15,053	-15,169	0,116
5	23,30 %	0,508	0,727	0,727	-0,200	0,146	0,115	-14,966	-15,209	0,243
6	23,30 %	0,508	0,727	0,727	-0,200	0,176	0,117	-14,873	-14,947	0,074



Salt solution added to reactor

Sample 1 (29 g)

Sample 2 (29 g)

Sample 3 (29 g)

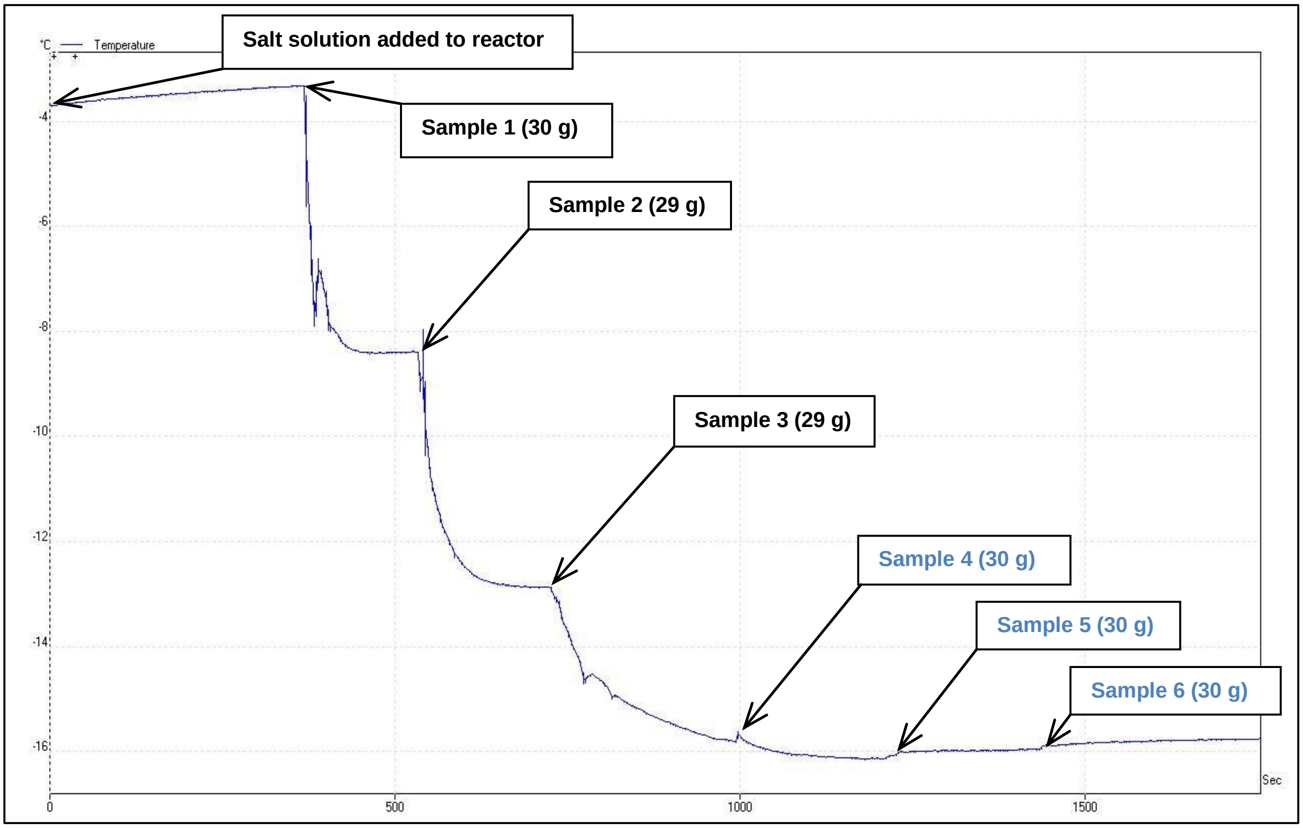
Sample 4 (29 g)

Sample 5 (30 g)

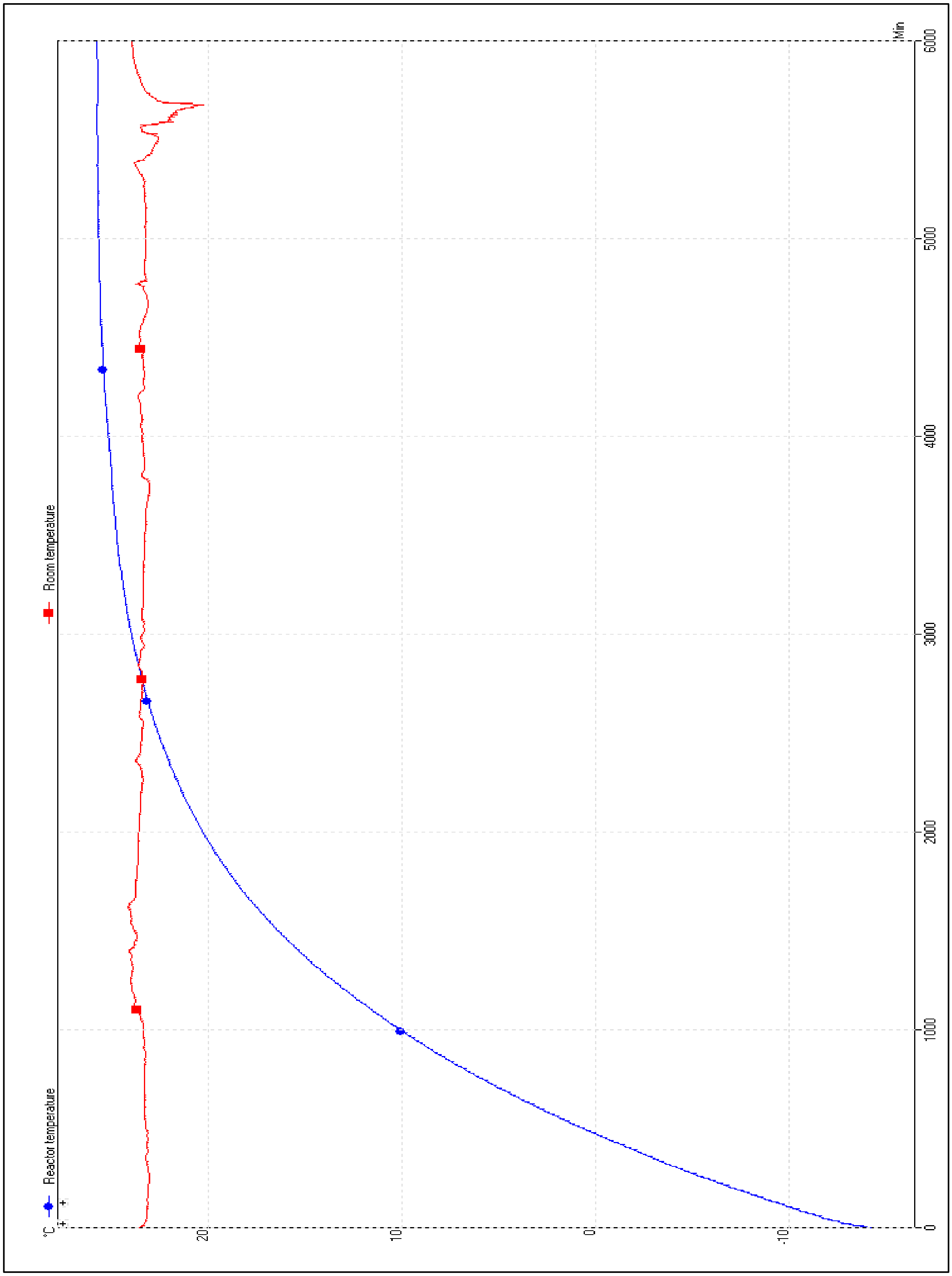
Sample 6 (30 g)

- 23 % - salt solution, experiment 5

# 5	Initial parameters:						Measured parameters:			
							Model:		Experiment:	Difference
sample #	c (measured)	m_solution,kg	T_solution,°C	T_reactor,°C	T_ice,°C	mass_ice,kg	m_ice_melted,kg	T_final,°C	T_final,°C	ΔT_final,°C
1	23,20 %	0,517	-3,310	-3,310	-0,100	0,032	0,032	-8,365	-8,387	0,022
2	23,20 %	0,517	-3,310	-3,310	-0,100	0,063	0,063	-12,832	-12,874	0,042
3	23,20 %	0,517	-3,310	-3,310	-0,100	0,094	0,089	-16,029	-15,792	-0,237
4	23,20 %	0,517	-3,310	-3,310	-0,100	0,124	0,091	-15,930	-16,198	0,268
5	23,20 %	0,517	-3,310	-3,310	-0,100	0,156	0,094	-15,836	-15,952	0,116
6	23,20 %	0,517	-3,310	-3,310	-0,100	0,188	0,096	-15,736	-15,787	0,051



Appendix 2 – Reactor heat loss, temperature vs. time


Reactor temperature
Room temperature
°C
20
10
0
-10
0
1000
2000
3000
4000
5000
6000
Min