



DLR

Deutsches Zentrum  
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in der Helmholtz-Gemeinschaft

ENSIAME

# Charakterisierung möglicher Kandidaten für die Anwendung von Flüssigsalzspeichern

**Confidential**

Gaétan HAMEL  
Engineering Student, 2A ME

Academic tutor: Mrs. Céline Morin, ENSIAME

Supervisor: Dr. Frau Nicole Pflieger, DLR

Institut für technische Thermodynamik,

Deutsches Zentrum für Luft und Raumfahrt e.V. in der Helmholtz-  
Gemeinschaft. Stuttgart, Deutschland.

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# I. Introduction

## A. German Aerospace Center, DLR

### 1. DLR at a glance

DLR is Germany's national research center for aeronautics and space. Its extensive research and development work in aeronautics, space, transportation and energy is integrated into national and international cooperative ventures. As Germany's Space Agency, the German federal government has given DLR responsibility for the forward planning and implementation of the German space program as well as international representation of Germany's interests. [1]

DLR's research portfolio ranges from fundamental research to innovative development of the applications and products of tomorrow. In this way, DLR contributes the scientific and technical know-how that it has gained, thus enhancing Germany's industrial and technological reputation. DLR operates large-scale research facilities for the center's own projects and as a service provider for clients and partners. It also promotes the next generation of scientists, provides advisory services to the German government and is a driving force in the regions centered on its various locations. [1]



Figure I.1: All 15 DLR sites in Germany

Approximately 6900 people work for DLR; the center has 32 institutes and facilities at 15 locations in Germany (Figure 1.1): Augsburg, Berlin, Bonn, Braunschweig, Bremen, Cologne (headquarters), Göttingen, Hamburg, Lampoldshausen, Neustrelitz, Oberpfaffenhofen, Stade, Stuttgart, Trauen and Weilheim. DLR also has offices in Brussels, Paris and Washington, D.C. [1]

### 2. DLR site Stuttgart

The German Aerospace Center (DLR) in Stuttgart consists of six research institutes conducting research into the areas of space, aeronautics, energy and transportation. The facility has its origins in the Research Institute of Jet Propulsion Physics (FPS) established in 1954 at Stuttgart airport. Since then the facility has moved to a site close to Stuttgart-Vaihingen University and currently employs a staff of around 590. DLR is close to the world of research in Stuttgart not



Figure I.2: Overview of the DLR site Stuttgart, DLR

just in geographic terms, but also in many other ways, through joint associations and special research projects, the training of undergraduate and doctoral students, as well as through the participation in teaching activities at the university itself. [2]

### **Institute of Structures and Design**

The research activities in the Institute of Structures and Design are concerned with the development and implementation of composite materials with polymer and ceramic matrix in innovative, high performance structures. The developments are not only for aeronautics and aerospace applications, but also for general technical applications within alternative energy technologies, transportation and mechanical engineering. Design and construction principles are hereby developed and validated, which under the given boundary conditions of the application, offer economical solutions with high reliability. [3]

### **Institute of Vehicle Concepts**

The Institute of Vehicle Concepts is a system-oriented institute, handling and coordinating research subjects related to traffic and transportation at the DLR location in Stuttgart. The activities at the Institute of Vehicle Concepts contribute to the sustainable development of technological systems for future generations of road and railway vehicles. The Institute of Vehicle Concepts' contributions range from concepts and feasibility studies to the construction, calculation, and simulation of research demonstrators, components, and vehicles, as well as their presentation. [4]

### **Institute of Technical Physics**

The Institute of Technical Physics is engaged in selected fields of optics and photonics. The work is primarily focused on aerospace issues and contributions to research in security and defense. The Institute is divided into four departments: Active Optical Systems, Solid State Lasers and Nonlinear Optics, Atmospheric Propagation and Effect, and Studies and Concepts. [5]

### **Institute of Combustion Technology**

The Institute of Combustion Technology carries out research and project work on the design principles of technical combustion processes. The main goals are: reducing the emissions of pollutants such as soot, nitrogen, unburned hydrocarbons and CO<sub>2</sub>; increasing reliability, especially regarding ignition, extinction and thermo-acoustic oscillation in transient combustion; promoting the effective and sustainable use of new, unconventional fuels; and developing and optimizing burner and combustion chamber systems. [6]

### **Institute of Solar Research**

The Institute of Solar Research of the German Aerospace Centre in Köln-Porz has further subdivisions in Stuttgart, Jülich and Almeria (Spain). On 1st of January 2011 it has been arisen from the DLR Institute of Thermodynamics as an independent institution. The institute is currently working on the development of concentrated solar systems for the generation of energy, heat and fuels. This contributes to a future sustainable energy supply based on renewable energies. [7]

### 3. Institute of Technical Thermodynamics

The Institute of Technical Thermodynamics at the German Aerospace Center does research in the field of the development of renewable energies and next generation energy conversion technologies with a staff of 150 scientific and technical employees, engineers and doctoral candidates. The spectrum of activities ranges from theoretical studies, to laboratory work for basic research and to the operation of pilot plants. [8]

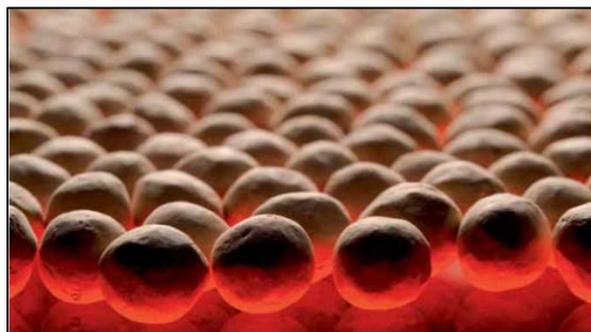
These experimental and theoretical studies are accompanied by systems analysis studies to analyze the associated technological, environmental, and economic potential, and situate it in a larger overall context of the energy economy by means of scenarios. In addition to these core activities in the DLR field 'Energy', the Institute of Technical Thermodynamics also works on selected subjects from the fields of 'Aviation' and 'Transportation', thus contributing to other focal points of DLR. These include developments to the use of fuel cells in aircraft and ground vehicles and to the generation and storage of hydrogen. [8]

Due to the fields of research, the institute acts as a bridge between basic research and industrial development, and thus often plays a key role in the introduction of new technologies. In addition to research and development, other important functions are advising political and business decision-makers, and advanced training of young scientists. [8]

With its strategic, long-term research and developmental work in the field of energy engineering, the institute makes a major contribution to ensuring power supplies that conserve natural resources and thus to sustainable development for our society. [8]

This institute is composed of three fields of activity:

- Systems analysis and technology assessment
- Electrochemical energy technology
- **Thermal process technology**



**Figure I.3: Ceramic spheres, DLR**

### 4. Thermal process technology

The overall objective of the Thermal Process Technology Department is to increase the efficiency of energy conversion and storage processes as a key element in reducing fuel consumption and protecting the climate. The department's work includes the development of advanced components, processes and system technologies in the field of thermal and chemical energy storage, heat management and fuel processing. [9]

The focal points of the department's work are:

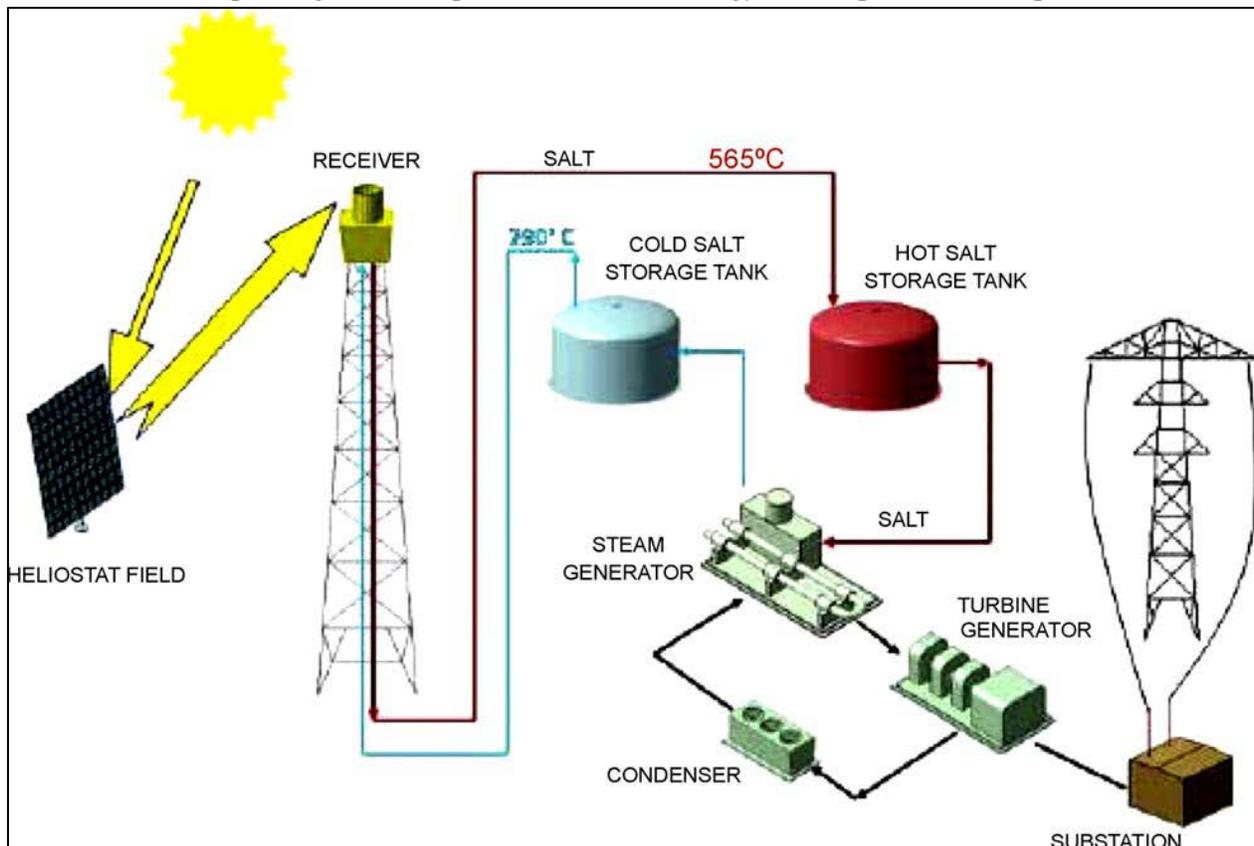
- High-temperature heat storage (up to 1000 °C) for solar thermal and conventional power plant technologies, cogeneration (combined heat and power) and industrial process heat (Figure 1.3).
- Thermo chemical storage of high-temperature heat for stationary and mobile applications.
- Hydrogen generation and storage for decentralized and mobile applications. [9]

## B. Molten salts theory

The molten salts theory describes molten salts : In what kind of technological installation they are used, what are their properties, what are they made of. In the following paragraphs will be given an overview of the state of the art of the molten salts.

### 1. Concentrated Solar Power (CSP) plants

According to a study, in 2010, 19.6% of the overall world consumption of energy was renewable energy [10]. As the demand is growing, it is necessary to find ways to produce energy and to produce it efficiently. To do so, it is either possible to create more power plants or to improve the already existing ones. But before explaining how to improve the CSP technology, let's explain what it represents.



**Figure I.4: Scheme of installation of a central tower power plant (Planta Solar Tres), with direct two-tanks and mineral oil like storage system**

In a concentrated solar power (CSP) plant, the energy is collected from sunlight. As the sunlight reaches a mirror device and reflects into a receiver, a molten salt flowing into a circuit gets heated. It is first driven to a hot salt storage tank to run a steam generator, running a turbine and creating electricity. Once cooled down, the salt goes to a cold salt storage tank. It will then wait for another cycle.

During night time, the hot salt that was stored drives the generator to provide the system with energy so that the system will always work. Thus, it is really important to find a salt with properties such as:

- Storing a lot of heat
- Releasing a lot of heat

Those two properties can be linked with the enthalpy. In addition, the enthalpy grows with a bigger  $\Delta T$ ; that implies that for a big  $\Delta T$ , the salt must have two properties:

- a low melting temperature
- a high thermal stability

These characteristics of the salt will be treated in the next paragraph.

## 2. Requirements of the salts

The purpose of my work is to study mixtures of salt consisting of the anions carbonates, sulfates and the cations lithium, sodium and potassium and supposed to be suitable for a use in a CSP plant. Therefore, this salt must have some particular characteristics in order to be used in a solar plant.

The studied salt must stay in a molten form during its whole use in the installation. That means that from the cold salt storage tank to the hot one, the salt must stay in the liquid form.

This means that this salt must have both a low fusion temperature and a high decomposition temperature which leads to a high enthalpy according to the formula below.

More than a temperature behavior, it is important to make sure that the salt is not corrosive or toxic and that it is easily available and not expensive.

The following table shows some very important properties of the salts.

Name	Sign	Unit
Enthalpy	$H=m \cdot C_p \cdot \Delta T$	J
Carnot	$h=1-T_f/T_c$	$\emptyset$
Cold temperature	$T_f$	K
Hot temperature	$T_c$	K
Heat capacity	$C_p$	J/K*g
Mass	m	g

**Table 1: Important properties of the molten salts**

With both a low fusion temperature and a high decomposition temperature, the salt can store a large quantity of heat and release it when it is cooled down.

To sum up, a molten salt is a mixture of anions and cations that must stay in the liquid form, it must have some properties which are:

- Low fusion temperature
- High decomposition temperature
- Available and affordable
- Not toxic or corrosive

All those points had to be considered during the research of a salt being suitable for a CSP plant.

As explained above, one of the most important points is to lower the melting temperature. To do so, several anions and cations can need to be mixed with an appropriate ratio. The dependence between the fusion temperature and the ratios can be shown on a phase diagram.

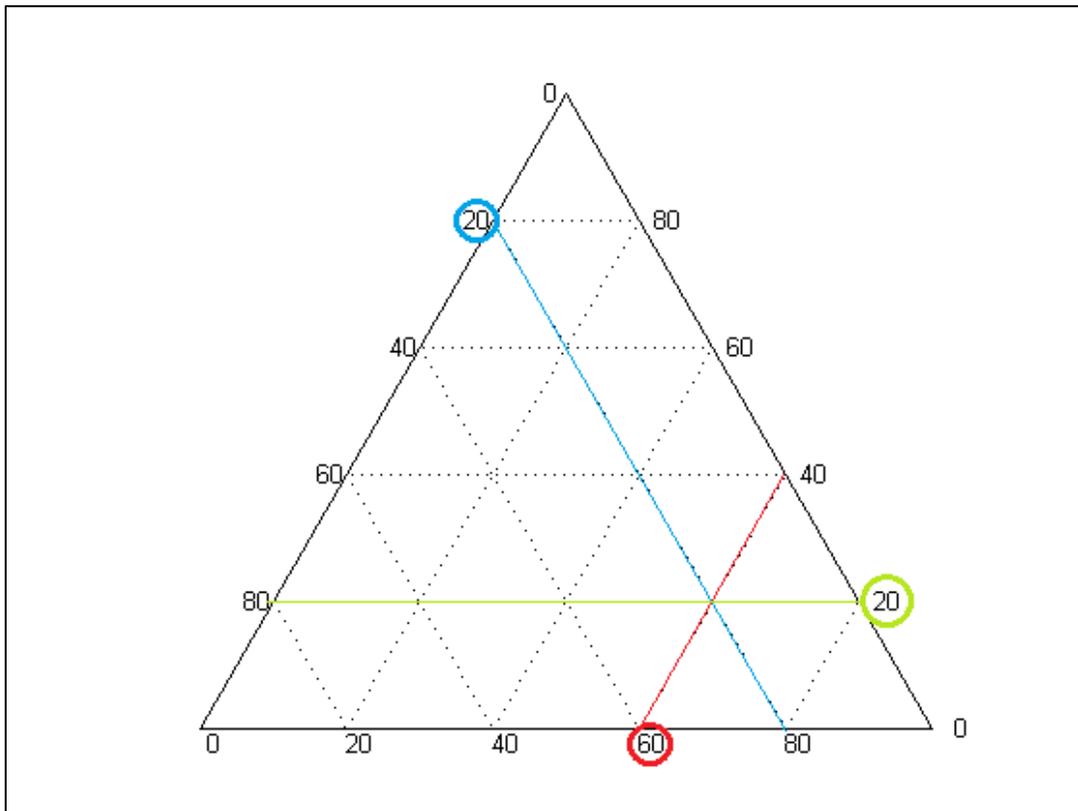
### 3. Phase diagrams

Phase diagrams are used to represent the temperature changes of a salt with its composition. Depending on the number of anions and cations, not the same phase diagram is used. As I worked with mixtures of at least three salts, I will introduce some phase diagrams starting the Ternary additive system.

a. Ternary additive systems

A ternary additive system is a system constituted of three cations or three anions in the same salt. If  $A^+$ ,  $B^+$  and  $C^+$  are three cations and  $X^-$  is an anion then  $A^+ B^+ C^+ // X^-$  is a ternary system. One can represent such a system on a triangular scale [Figure II.2]. The numbers on the lines refer to the ratios of the cations (or anions) so that we can find the ratios of a mixture on the intersection of three lines.

On the picture [Figure I.B.2], a system constituted with 60% of one element and 20% for the two others is represented. Once the two first ratios have been found, the third one can be deduced from the two others naturally.

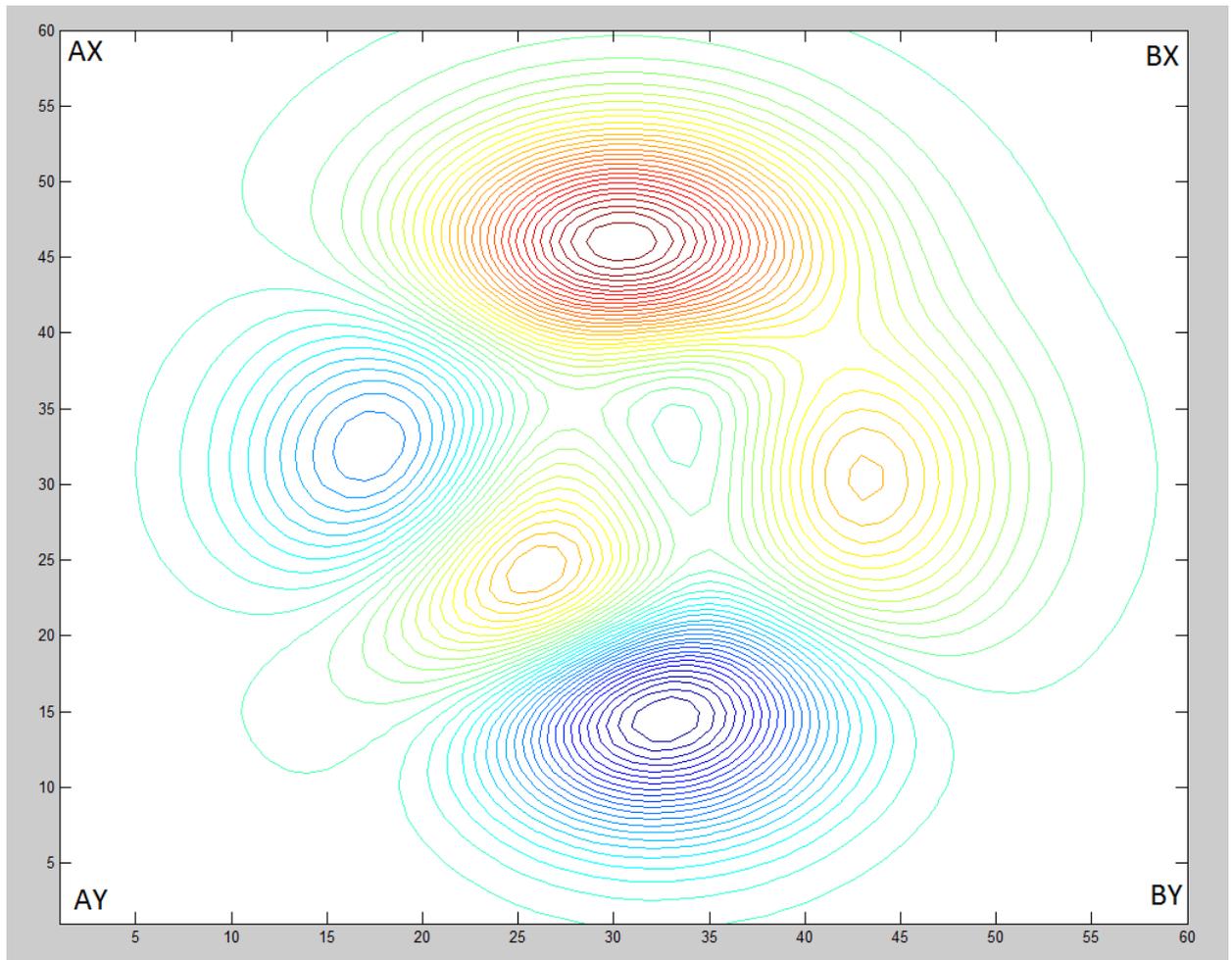


**Figure I.5: Ternary additive system diagram**  
(made by the author)

b. Ternary reciprocal systems

Type: A+, B+ // X- Y-

This system is constituted of two anions and cations and can be represented in a square where the concentrations are also on the borders.

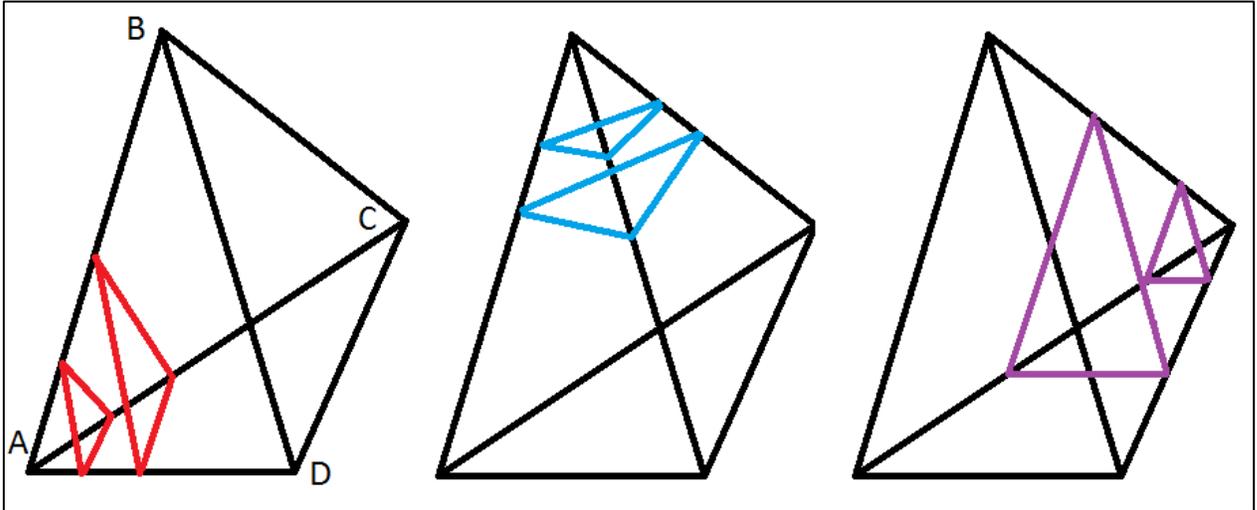


**Figure I.6: Ternary reciprocal system diagram** *(made by the author)*

c. Quaternary additive systems

Type:  $A^+$ ,  $B^+$ ,  $C^+$ ,  $D^+$  //  $X^-$

I didn't study such systems as I only used three cations and two anions maximum at the same time.

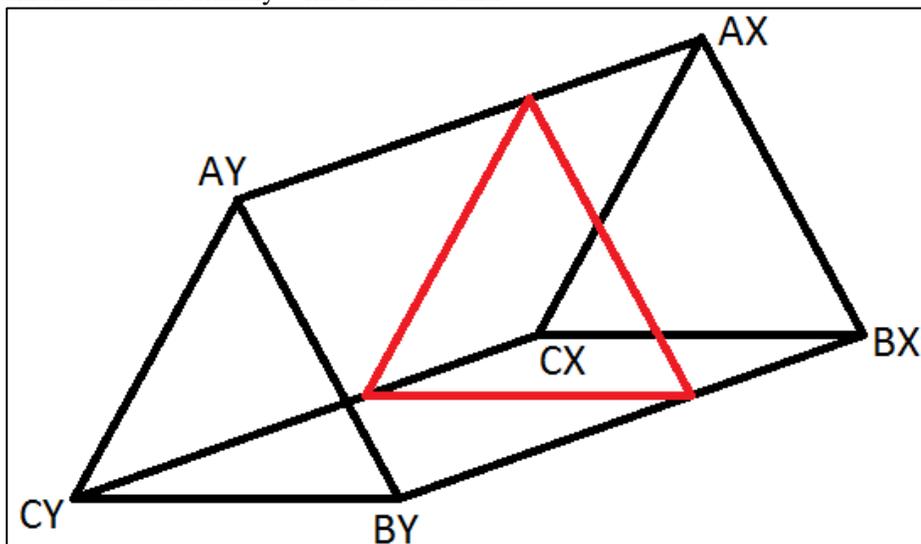


**Figure I.7: Quaternary additive system diagram** (made by the author)

d. Quaternary reciprocal systems

Type:  $A^+$ ,  $B^+$ ,  $C^+$  //  $X^- Y^-$

This is the kind of system that was the most interesting because it represents three cations and two anions which is exactly what I tried to mix.



**Figure I.8: Quaternary reciprocal system diagram** (made by the author)

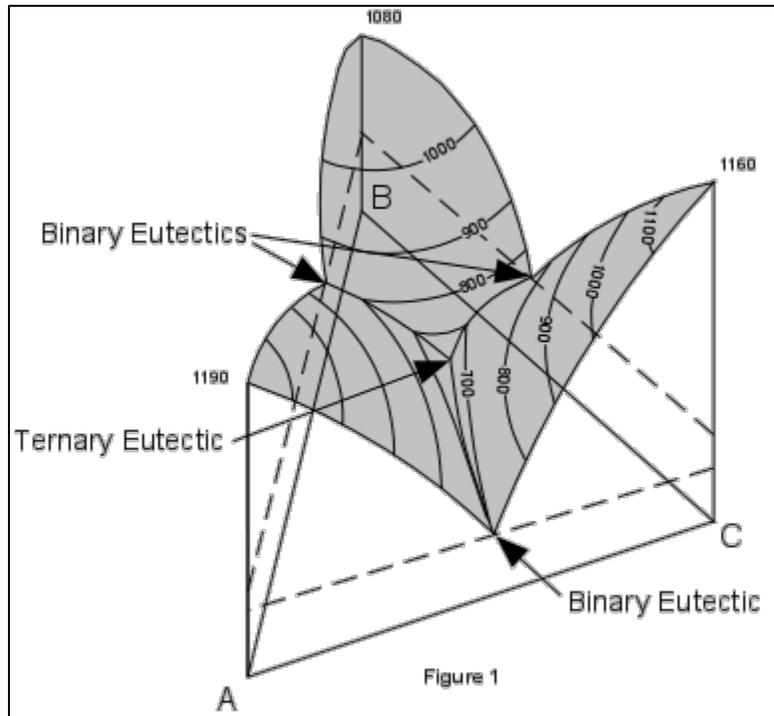
However, this system is complicated to represent so, in order to make things easier to read, I worked with the same percentage of Sulfates and Carbonates (50%). This way I am still working with a quaternary reciprocal system but as the ratio of anions is set, it looks like working with a ternary additive phase diagram where the concentration of the anions is read on the X-Y line. Focusing on one specific anions ratio is really useful because it would take a lot of time to make all the measurements for all the different ratios. Plus it was really convenient because later measurements showed that a ratio of 50% carbonates and sulfates gave good results concerning the fusion temperature of the samples.

For my study, I chose to work on mixtures of salt with 50% carbonates and 50% sulfates at first. One must know that, on average, the fusion temperatures of salts tend to decrease when we approach the middle of the triangle. That's why I started the experiments with several samples inside the triangle but not on the edges.

Plus, the lines on the border of the triangle represent a system with only two salts. Those systems have already been studied in the literature so it was not necessary to make samples with only two salts. Moreover, an interesting characteristic of a salt is that the more cations and anions it will be made of, the lower the temperature of fusion will be.

## 4. Eutectic Point

Eutectic is a word coming from the Greek *eutêksia* which means good melting. The eutectic point of a system represents the lowest temperature of melting [Figure II.3]. Equal temperatures for a ternary system are represented with a curve. On each line corresponding to a binary system, the lowest point is the Binary eutectic; it is the same in the middle of the figure, where the lowest temperature is the ternary eutectic. In the field of research of the molten salts, the eutectic point represents the most interesting part as it represents the lowest part of the temperatures.



**Figure I.9: Eutectic point on a ternary plot**

## II. Material and methods

### A. The laboratory devices

There are many laboratories inside of the DLR Stuttgart; I got to work in the chemical one where some state of the art machines are present. I used a few of them and as it is a starting point for my work, I will introduce them in the next paragraphs.

#### 1. The oven

The oven [Figure II.A.1] is a regular heating device, based on a heating with resistances in an ambient air atmosphere. It is able to heat above 1000°C but my experiments didn't lead me into needing such high temperatures. The oven is controlled by a control panel on its left [III.A.1] that allows it to follow instructions such as:

- Setting a couple of temperature ramps
- Setting isotherms

The oven is a device that needs to be used carefully with gloves and glasses because the very high temperatures reached may be harmful if not protected.

The experiments in the oven are an easy way to get information about the behavior of a salt.



**Figure II.1: Oven where the salts are heated**

## 2. The DSC

DSC stands for differential scanning calorimetry. It is a technique allowing to measure the temperatures and heat flow between a tested crucible and a reference one.

Two crucibles are put into the device, one is empty and is called the reference and one is filled with approximately 9mg of salt then heated to a temperature above the melting of the salt up to 1100°C. Then a program gives a graphic output with peaks corresponding to phase change.



**Figure II.2: A DSC device**

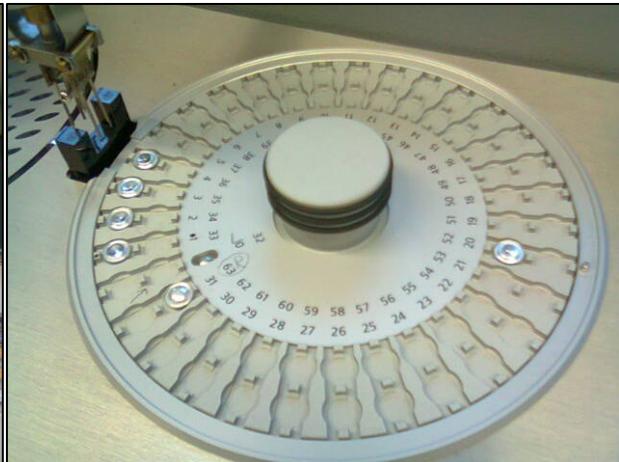


**Figure II.3: Zoom on a DSC device**

[Figure II.2&3] represent a DSC device. It is possible to see the oven as well as the place where the crucibles are put.



**Figure II.4: The NETSCH DSC 204 Phoenix F1**



**Figure II.5: The DSC sample changer**

I made several measurements with the DSC after fulfilling oven experiments. The model of the device is the NETSCH DSC 204 PHOENIX F1 and has the particularity to provide an automatic sampler changer and an incorporated cooler system. It means that up to 62 samples plus a reference can be put simultaneously and, when the macro program is set up, they will all be tested in a row with no human intervention. The macro program is a computer program that allows to set the heating of the tested crucibles. Basically, two cycles are made for every salt, during each cycle, the salt is heated with a temperature ramp (loss of water), then stays at this temperature for a while (incubation isotherm) then is cooled down. Finally the crucible is put out of the DSC and exchanged with another one.

It takes between three and five hours for a sample to be tested depending on the parameters of the macro program.

The crucibles I used for the DSC experiments are aluminum crucible that can be used up to 600°C. The amount of salt that can be put into such crucibles must be between 5 and 7 mg.

### 3. The thermogravimetry



**Figure II.6: The thermogravimetry device.**

The thermogravimetry device is constituted of two parts:

- The oven and mass balance [Figure II.A.4]
- The mass absorption spectrometer [Figure II.A.5]

The two parts are linked together by a black cable where the gas emitted during the decomposition flows through.

The whole system is also completed with a gas circuit so that it is possible to work with Argon and Nitrogen atmosphere and obtain better results.



**Figure II.7: The thermogravimetry device and the mass spectrometer (on the right).**

Several experiments with the thermogravimetry were made before choosing the salts because we wanted to make sure that they had high decomposition temperature. The samples that had already been used and known had a decomposition temperature around 650°C and we wanted to obtain even more stable samples. That's why we made thermogravimetry experiments at the beginning (confirmation of the stability) and at the end (compare the stability of samples).

## 4. Other materials

### a. Pro-Analyse Salts

The “Pro-analyse” salts have been used because their composition is 99.5% accurate and are a bit cheaper than the purest salts available.



**Figure II.8: Bottles containing the salts**

b. Crucibles

Many different crucibles were available in the laboratory. They can have different shapes, size and be composed of different materials. Depending on the use they are designed for, some crucibles are in porcelain, others in an aluminum-oxide. The material of a crucible gives it properties such as temperature stability.

That's why I only had to use porcelain crucibles that are cheaper and have a lower fusion temperature because the salt samples that I made had even lower fusion temperatures.



**Figure II.9: Porcelain crucibles used during the experiments**

c. Digital Analytical Balances

To measure the weight of salts, a balance with a precision of 0.001mg was used [Figure II.8]. This device is compulsory to use in order to obtain correct mixtures. Indeed, pouring too much of a salt and too few of another ends in a bad composition of a salt and cannot be used for further experiments. Therefore this device is always used to create the desired mixtures.



**Figure II.10: Numerical balance for weighing the salts**

The balance presented on the picture above is the one used to weigh the salts into the bigger porcelain crucibles.

When it comes to weighing the salts into smaller crucibles, it is necessary to use another balance which is even more accurate (0.0001 mg).

d. Heating plate

This device was used during the washing of the crucibles. As it was easier to get rid of the solid salts while heating them, it was possible to put the crucibles on this heating plate in order to raise the temperature to approximately 100°C and accelerate the process of washing.



**Figure II.11: Heating plate**

Every device was used during the measurements. Knowing the available devices is an important part of the work, it simplifies the experiments and allows to go further in the analyze.

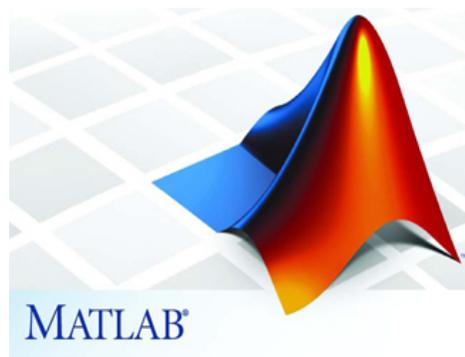
## B. Software

Once the experiments are done and after the data of the salts have been gathered, the data need to be further analyzed. With the use of a software, it is possible to make simulations and predictions on the properties and the behavior of a salt. The following paragraphs will introduce the software I used to proceed to simulations and data analysis.

### 1. Matlab R2007b

MATLAB is a technical computing software; it can be used for algorithm development, data analysis or visualization. It is a tool for building small programs called scripts, allowing the user to iterate operations easily. I created some MATLAB scripts in order to make my further analysis easier and faster. Therefore I programmed *Lowliquitern*, *Algointerpolation*, *Molarconverter* and *Masseversmol* in order to obtain a better overview of the results I obtained in the laboratory.

Matlab was really useful in order to gain time, prepare the quantity of the salts and drive the analysis further with interpolated data and fittings. The version I used was Matlab R2007b.



### 2. Netsch DSC software

The DSC device comes along with a DSC analysis software that allows the user to make many operations. The user can program heating cycles for numerous samples. It is possible to create heat ramps, isotherms and even cooling down the sample is possible.

### 3. Netsch thermogravimetry software

As the DSC software, the thermogravimetry device is provided with an analysis software to see both the output of the Thermogravimetry device and the mass spectrometer.

### III. Results

#### A. Literature research on the salts

The first step of this work was to study the literature. Thus, it is possible to know whether a salt has been already studied or not for example. Plus, researching the literature gives a better overview of a field of research. That's why it is so important to start with such a step as it will help being efficient with the incoming experiments.

For the experiments in the lab, it is possible to work with different devices, therefore it is important to choose the one that is designed for the experiments as well as the salts and the crucibles. Everything must be set before starting operations.

In addition, the use of a computer provides us with a powerful tool for simulations and making predictions. And in my case, to make sure that my program would work properly, I also had to make sure that the output of the experiments I wanted to make could be suitable for the program.

That's why I had to get the most data I could to either gain time on experiments, know what devices should be used or integrate them into a database for my program.

				T	%mol 1.	%mol 2.	%mol 3.	Source
<b>CO3</b>	Na2CO3	Li2CO3	#	497	46,7	53,3	#	[16]
	K2CO3	Na2CO3	#	710	?	?	#	[18]
	Li2CO3	K2CO3	#	482		~62	#	[17]
	Li2CO3	Na2CO3	K2CO3	397	43,5	31,5	25	Studienarbeit F.Knoll p69 in "KEN10"

				T	%mol 1.	%mol 2.	%mol 3.	Source
<b>SO4</b>	K2SO4	Na2SO4	#	823	?	?	#	[22]
	Li2SO4	Na2SO4	#	591	?	?	#	[19]
	K2SO4	Li2SO4	#	535	20	80	#	[20]
	K2SO4	Li2SO4	Na2SO4	512	8,5	78	13,5	[21]

				T	%mol 1.	%mol 2.	%mol 3.	Source
<b>CO3-SO4</b>	Li2CO3	Li2SO4	#	534	38,5	61,5	#	Studienarbeit F.Knoll p81 in "Ja81"
	Li2CO3	K2SO4	#	470	60	40	#	Studienarbeit F.Knoll p81 in "Ja81"
	Na2CO3	Na2SO4	#	825	39,8	60,2	#	Studienarbeit F.Knoll p81 in DLR
	K2SO4	K2CO3	#	901	0(??)	100(??)	#	tappi.org

**Table 2: Eutectic points found in the literature [15]-[21]**

## B. Programing and script writing

### 1. *Algo*interpolation program

*Algo*interpolation is the first script I developed. After searching the literature for informations about the stability of some salts, I had gathered many information but wasn't able to compare them. I had to write the coefficient of stability for every salt I found for every temperature I found. Out of all those data, I wanted to outline which were the best salts suitable for the CSP plants.

Indeed, some salts were already known and used (salts with nitrates for example) but our focus was on a salt that could be used on the specific part of a CSP plant: the tower where the light is concentrated.

That's why with such a program, we were able to find out that carbonates and sulfates were suitable with the association of lithium, potassium and sodium.

Finally, once the program was done and running, we had all the information we needed to start the experiments:

-which salts were going to be used

-up to which temperature is it possible to go until the salt decomposes

It was important for me to see how far it is possible to go in the development of a program. At first, the goal was only to find the temperature corresponding to the decomposition temperature. But during the writing of the code, I had to integrate many functions that allowed me for example to read the data of many salts and give the result for each one of them. Also, I faced so mathematical problems that I needed to solve in order to make the program work properly.

At the very end of the development of the program, I was able to obtain a shorter, faster and easier code that can be used by other people regarding there were no such program before.

This program is designed to work for the higher temperatures as it take as an input a matrix of decomposition coefficients corresponding to temperatures. This matrix is composed of columns, the first one representing the temperature and the other ones corresponding to the coefficients of decomposition. As the program runs, it gives for every column, the temperature corresponding to a specified decomposition coefficient.

Working with a specific coefficient is a convenient way to compare different samples data. Some elements don't have a lot of literature about their decomposition coefficient and in order to make sure that the program will run well, it can be useful to use a specific coefficient all elements have in common. This way it is possible to compare them more efficiently as the program works better with actual values than with the interpolated ones

With this program, it is possible to make a further analysis of the higher temperatures. It can be really convenient to compare the stability of salts before making experiments.

To make this program work, it is important to make literature researches before in order to gather the maximum amount of data concerning the different salts.

Once all the data are filled in the matrix, it is possible to find the optimum temperature corresponding to the specified decomposition coefficient.

The given decomposition coefficient is related to the concentration of the respective cation divide by the concentration of the second element.

*See the Appendix for more information about how the program works*

```

data=[2000 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1900 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1800 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1700 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1600 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0.003972 ,6.999e-06;
1500 ,0 ,0 ,4.35 ,2.217 ,0.06422 ,0 ,6.538 ,0.0003937,2.989e-07;
1400 ,0 ,0 ,17.33 ,0.7092 ,0.01819 ,0 ,0.9042 ,2.727e-05,7.354e-09;
1300 ,0 ,0 ,5.898 ,0.1872 ,0.004118,0 ,0.06176 ,1.213e-06,9.572e-11;
1200 ,0 ,0 ,1.65 ,0.03875 ,0.0006949,16.09 ,0.004809 ,3.085e-08,5.552e-13;
1100 ,0 ,0 ,0.3593 ,0.004955 ,8.035e-05,1.672 ,0.0001637,3.381e-10,1.129e-15;
1000 ,0 ,4417 ,0.05651 ,0.00041 ,4.963e-06,0.1034 ,2.742e-06,1.868e-12,1.129e-15;
900 ,0 ,1288 ,0.005759 ,1.914e-05,1.523e-07,0.003136 ,1.784e-08,2.631e-15,5.690e-19;
800 ,0 ,264.6 ,0.0003228,4.066e-07,1.882e-09,2.707e-05,3.167e-11,6.767e-19,4.231e-23;
700 ,0 ,33.12 ,7.701e-06,2.811e-09,6.364e-12,5.554e-11,8.808e-15,1.546e-23,2.054e-28;
600 ,0 ,1.979 ,5.095e-08,3.609e-12,3.087e-15,1.344e-11,1.52e-19 ,9.455e-30,1.674e-35;
500 ,0 ,0.03648 ,4.323e-11,3.14e-16 ,6.734e-20,1.073e-16,3.079e-26,1.792e-38,1.984e-45;
400 ,0 ,8.682e-05,1.008e-15,2.462e-22,6.506e-27,2.217e-24,2.61e-36 ,1.409e-51,2.560e-60;
300 ,0 ,2.729e-09,1.143e-23,8.795e-33,6.421e-39,1.486e-37,1.488e-53,5.609e-74,8.436e-86];
Temperature K1 K2 K3 ...

```

	Cation1	Cation2	Cation3	Cation1	Cation2	Cation3	Cation1	Cation2	Cation3
	Anion1			Anion2			Anion3		

**Figure III.1: input matrix for the algointerpolation program**

The program was very useful to see which cations and anions were the most relevant because it gave a comparison between every combination of anions and cations I found in the literature (see [Figure III.1]).

Here is the code of the *Algointerpolation* program, it gives an overview of the functions included and the commentaries provide information how to use it.

Code of *Algointerpolation*

```

% This program interpolates the temperature corresponding to a particular
% value of the coefficient of stability K

% Example of data : (taken from the litterature)
data=[2000 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1900 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1800 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1700 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
1600 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0.003972 ,6.999e-06;
1500 ,0 ,0 ,4.35 ,2.217 ,0.06422 ,0 ,6.538 ,0.0003937,2.989e-07;
1400 ,0 ,0 ,17.33 ,0.7092 ,0.01819 ,0 ,0.9042 ,2.727e-05,7.354e-09;
1300 ,0 ,0 ,5.898 ,0.1872 ,0.004118,0 ,0.06176 ,1.213e-06,9.572e-11;
1200 ,0 ,0 ,1.65 ,0.03875 ,0.0006949,16.09 ,0.004809 ,3.085e-08,5.552e-13;
1100 ,0 ,0 ,0.3593 ,0.004955 ,8.035e-05,1.672 ,0.0001637,3.381e-10,1.129e-15;
1000 ,0 ,4417 ,0.05651 ,0.00041 ,4.963e-06,0.1034 ,2.742e-06,1.868e-12,1.129e-15;
900 ,0 ,1288 ,0.005759 ,1.914e-05,1.523e-07,0.003136 ,1.784e-08,2.631e-15,5.690e-19;
800 ,0 ,264.6 ,0.0003228,4.066e-07,1.882e-09,2.707e-05,3.167e-11,6.767e-19,4.231e-23;
700 ,0 ,33.12 ,7.701e-06,2.811e-09,6.364e-12,5.554e-11,8.808e-15,1.546e-23,2.054e-28;
600 ,0 ,1.979 ,5.095e-08,3.609e-12,3.087e-15,1.344e-11,1.52e-19 ,9.455e-30,1.674e-35;
500 ,0 ,0.03648 ,4.323e-11,3.14e-16 ,6.734e-20,1.073e-16,3.079e-26,1.792e-38,1.984e-45;
400 ,0 ,8.682e-05,1.008e-15,2.462e-22,6.506e-27,2.217e-24,2.61e-36 ,1.409e-51,2.560e-60;
300 ,0 ,2.729e-09,1.143e-23,8.795e-33,6.421e-39,1.486e-37,1.488e-53,5.609e-74,8.436e-86];

%Temperature K1 K2 K3 K4 . . .

```

```

% I recommend that, when the program takes too much time to calculate on a
% column :
% 1) Cut this column from the original matrix and re-run.
% 2) Make an other program run with this column only and reduce precision
% because it usually takes too much time when the interpolation is not
% accurate (linked to a lack of data therefore precision can be lower).

clc
% data=Tabelle1;

% Desired value of the K coefficient
Kch=10^-1;

% Higher value for better results /\ increases loading time
precision=10;

Size=size(data);
format short

% Interpolated temperatures can be found in the row vector tempres
tempres=zeros(1,Size(2)-1);

for colonne=2:Size(2)

    % Compte les valeurs non nulles dans la colonne

    compteur=0;
    for ligne=Size(1):-1:1
        if data(ligne,colonne)~=0
            compteur=compteur+1;
        else
            0;
        end
    end
    dichoto=0;
    while data(Size(1)-dichoto,colonne)<=Kch && dichoto<Size(1)-1
        dichoto=dichoto+1;
    end
    if compteur==0
        tempres(1,colonne-1)=0;
    else
        Spline=spline((data(Size(1):-1:Size(1)-compteur+1,1)),data(Size(1):-1:Size(1)-
compteur+1,colonne));
        temp=0;
        T=300+dichoto*100/precision;
        while ppval(T,Spline)<=Kch
            temp=temp+1;
            T=T+temp/precision;
        end
        tempres(1,colonne-1)=T;
        disp 'colonne'
        disp(colonne+1)
    end
end
disp(tempres)

```

## 2. Lowliquitern program

After the having studied the behavior of the salts with higher temperatures by getting an idea of their behavior with the decomposition coefficient, the next objective was to create a program that would give the overall behavior of a mixture of salt with the concentration in anions and cations.

There were many steps in the creation of this program because I also incorporated a lot of features to it during its development. At first, I wanted to be able to obtain the lowest interpolated temperature for any given composition of salt. But as the development advanced, I realized there were problems with the missing values for example or even with impossible ratios (50% Li + 50% Na + 50% K). That's why the last version of my program can now ignore missing values, impossible ratios and other unseen errors and give a 3d plot of the result as well as the interpolated lowest temperature for the whole range of values.

*Lowliquitern* is a script taking a matrix of ratios and temperatures as an input and gives the lowest interpolated temperature for a ternary system as well as the 3D plot of both actual and interpolated data.

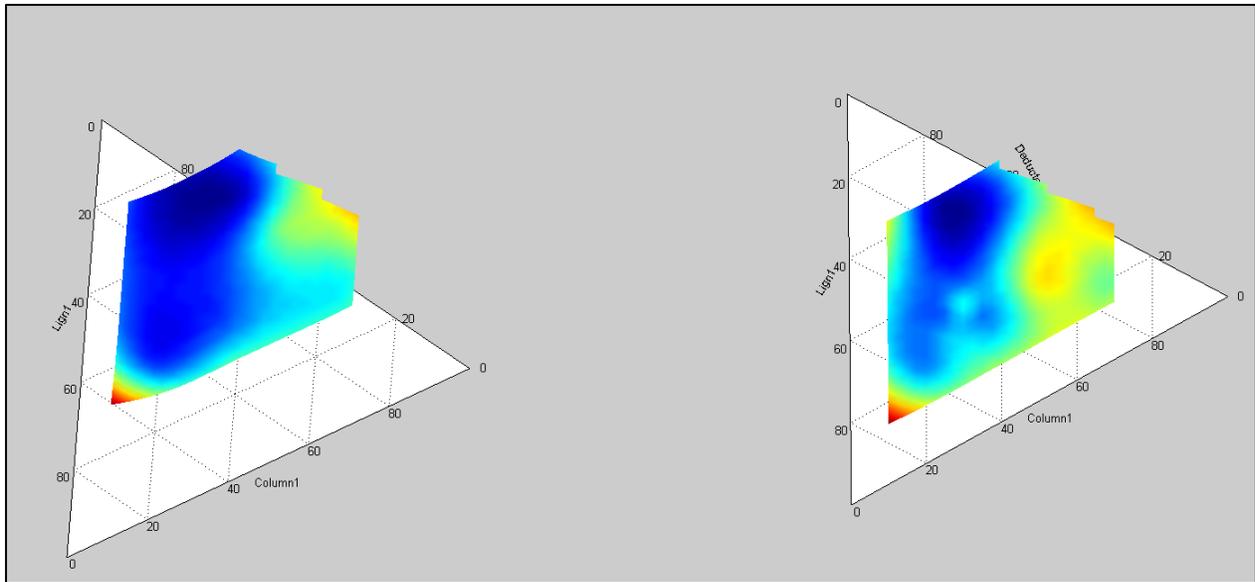
Its main goal is to give a better idea of the eutectic location of a ternary salt after a few experiments.

That's why this program is useful for my experiments as it provides further data in a field where no experiment had been made.

*See the Appendix for more information about how the program works*

```
% data=[0 ,0 ,20 ,20.2 ,20.4,20.6,40 ,40.1,40.2,51 ,59.4,80,80.2;
% 0 ,0 ,0 ,209 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
% 0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,211;
% 9.8 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,145,0 ,0 ,0 ;
% 10.1,0 ,0 ,0 ,0 ,0 ,165,0 ,0 ,0 ,0 ,0 ,0 ;
% 19.7,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,168 ,0 ,0 ;
% 20 ,238 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
% 20 ,0 ,203 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
% 20 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,158 ,0 ,0 ,0 ,0 ;
% 20 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,250,0 ;
% 39.4,0 ,0 ,0 ,0 ,0 ,0 ,163 ,0 ,0 ,0 ,0 ,0 ;
% 39.7,0 ,0 ,0 ,197 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;
% 59.5,0 ,0 ,0 ,0 ,178 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ;];
```

**Figure III.2: input matrix for the lowliquitern program**



**Figure III.3: 3D output of the lowliquitem program**

On this picture, the graphical output of this program is represented. On the left are the interpolated values of the fusion temperatures with respect to the salt ratios (location on the ternary plot) and the temperature (color and height). On the right, the data that actually are given to the program are simply represented on a ternary plot. Some differences appear between the two plots of the “real” and “interpolated” but it is only designed to get a trend of the temperature behavior of a salt.

Once an area including many low temperature points has been found, it is possible to go further with the analysis in this region to have better chances finding the eutectic point.

Code of Lowliquitem

```

% This programs plots a 3D ternary diagram of the lowest interpolated
% liquidus.

%% Parameters initialisation

% Make sure to add the ternplot folder to path

% Examples :
% 1) Results from Charline Jenny (too few data per line/column to interpolate, however the
% program returns the lowest temperature and the correct ratios);

data=[0 ,10 ,15 ,20 ,25 ,30 ,35 ,40 ,50 ,60 ;%K
      10 ,0 ,0 ,0 ,0 ,454 ,0 ,0 ,0 ,495.2 ;
      20 ,0 ,0 ,438.1,0 ,433.4,0 ,432.8,0 ,418.4 ;
      25 ,0 ,0 ,0 ,446.4,432.5,0 ,0 ,0 ,0 ;
      30 ,0 ,0 ,456.3,0 ,460.7,434.9,0 ,0 ,0 ;
      35 ,0 ,0 ,0 ,436.9,0 ,0 ,0 ,0 ,0 ;
      40 ,481.9,0 ,0 ,0 ,0 ,0 ,0 ,425.4,0 ;
      50 ,0 ,0 ,0 ,500 ,0 ,490 ,0 ,0 ,0 ;
      70 ,0 ,475 ,0 ,0 ,0 ,0 ,0 ,0 ,0 ];
%Li

% 2) Test matrix (more result per line/column), the program returns the
% lowest interpolated temperature
% data=[10000 15 25 37 53 49 58 67 100
% 17 885 442 14 1 -22 700 13 0
% 29 66 42 39 12 1 44 0 0
% 52 27 369 181 0 0 0 0 0

```

```

%      68   45  257  0   0   0   0   0   0
%      99   0   0   0   0   0   0   0   0 ];

% Test matrix for columns and lines

% data=[0  5 10 15 20 25 30 35 40 45 50 60 65 70 75 80 85 90 95 100;
%      10 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      20 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      30 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      40 1  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      50 5  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      60 5  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      70 5  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      80 5  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;
%      90 5  2  3  4  5  6  7  8  9 10 11 12 13 14 15 16 17 18 19 ;]
%

% Insert the data sheet here

% data=(0);

% precision : Higher value for better results
precision=100;
% parametre de la DSC (maximum reached temperature)
param=600;

vecnul=0;
clc
format short
hold off

%% Ternary plotting of the interpolated data

skip=1;% Set to 0 to draw the interpolated liquidus for each Ca ratio (useful for debugging)

for etape=1:2
    if etape==1
        A=1;
        B=2;
        Size=size(data);
        allres=zeros(4,Size(1)+Size(2)-2);
        plage=(1:Size(1)-1);
        temp=0;
        for i=2:Size(1)
            for j=2:Size(2)
                if data(i,j)~=0
                    temp=temp+1;
                end
            end
        end
        realval=zeros(temp,1:3);
        clear temp
    elseif etape==2
        data=(data)';
        A=2;
        B=1;
        plage=(Size(1):Size(1)+Size(2)-2);
    end
    %Resultats is the vector of all the lowest interpolated liquidus
    Resultats=zeros(4,Size(A)-1);
    %Valeurs is the vector of all the interpolated liquidus
    Valeurs=zeros(Size(A)-1,(precision)*(Size(A)-1)+1);
    p=0;
    for ligne=2:Size(A)
        % Empty row vectors will be ignored
        if data(ligne,2:end)==zeros(1,Size(B)-1)
            vecnul=vecnul+1;
        else
            indice=(0);
            Val=(0);
            % The matrix data is read vertically
            % Missing values will be ignored during the interpolation

```

```

compteur=2;
while data(ligne,1)+data(1,compteur)<=100 && compteur<=Size(B)-1
    compteur=compteur+1;
end
T=data(ligne,2:compteur);
for i=1:compteur-1
    if T(1,i) ~= 0
        indice=[indice data(1,i+1)]; %#ok<AGROW>
        Val=[Val T(1,i)]; %#ok<AGROW>
        p=p+1;
        if etape==1
            realval(p,1)=data(ligne,1);
            realval(p,2)=data(1,i+1);
            realval(p,3)=T(1,i);
        else
            0;
        end
    else
        0;
    end
end
if length(Val)==2
    Resultats(A,Size(A)-ligne+1)=data(ligne,1);
    Resultats(B,Size(A)-ligne+1)=indice(end);
    Resultats(3,Size(A)-ligne+1)=100-Resultats(A,Size(A)-ligne+1)-
Resultats(B,Size(A)-ligne+1);
    Resultats(4,Size(A)-ligne+1)=Val(end);
elseif length(Val)~=2
    % Temperature interpolation
    Spline=spline(indice(1,2:end),Val(1,2:end));
    % Values of the interpolated temperatures
    Valeurs(ligne-1,1:(indice(end)-indice(2))*(precision)+1)...
        =ppval(indice(2):1/precision:indice(end),Spline);
    [D,I]=min(Valeurs(ligne-1,1:(indice(end)-indice(2))*(precision)+1));
    Resultats(A,Size(A)-ligne+1)=data(ligne,1);
    Resultats(B,Size(A)-ligne+1)=indice(2)+(I/length(1:(indice(end)-
indice(2))*(precision)+1))*(indice(end)-indice(2)+1);
    Resultats(3,Size(A)-ligne+1)=100-Resultats(B,Size(A)-ligne+1)-
Resultats(A,Size(A)-ligne+1);
    Resultats(4,Size(A)-ligne+1)=D(1);
end
if skip == 0 && ligne <= length(data)-1
    % Plots the curve of the interpolated temperatures
    plot(indice(2):1/precision:indice(end),...
        Valeurs(ligne-1,1:(indice(end)-indice(2))*(precision)+1))
    hold on
    % Experimental results
    scatter(indice(2:end),Val(2:end),'r','+')
    legend('Green curve : spline','Red crosses : real data')
    pause
    hold off
end
end
clear indice Val
allres(:,plage)=Resultats(:,:);
end

% values of allres are being sorted
[pasbesoin,idx] = sort(allres(1,:));
allres = allres(:,idx);

Element3=100-allres(1,:)-allres(2,:);
%Element3=Element3(end:-1:1);
Reall=100-realval(:,1)-realval(:,2)
%Reall=Reall(end:-1:1);
subplot(1,2,1)
ternsurf(allres(1,:),allres(2,:),Element3,allres(4,:)/max(abs(allres(4,:))));
ternlabel('Column1', 'Deducted', 'Lign1')
shading interp
subplot(1,2,2)
ternsurf(realval(:,1),realval(:,2),Reall,realval(:,3)/(10*max(abs(realval(3,:))))))

```

```

ternlabel('Column1', 'Deducted', 'Lign1')
shading interp
hold off
realval=realval';
% Prints the result of the lowest interpolated temperature and the
% corresponding ratios
[D,I]=min(allres(4,1+vecnul:end));
disp ' % 1st cation (1st column)'
disp(allres(1,I+vecnul))
disp ' % 2nd cation (1st lign)'
disp(allres(2,I+vecnul))
disp ' % 3rd cation'
disp(allres(3,I+vecnul))
disp 'lowest temperature'
disp(allres(4,I+vecnul))
% Clear not interesting values
clear Reall Element3 compteur etape vecnul skip precision plage pasbesoin p ligne colonne idx i j
T Spline I A B D Size
hold off

```

## C. Laboratory experiments

### 1. Oven experiments

Accurate weighing is important to make sure the ions have the correct ratios. When working with temperatures below 1000°C, porcelain crucibles are used but with higher temperatures, aluminum-oxide crucibles are to be chosen.

This is followed by the setting of a heating program: Two times and two temperatures can be set so that both a ramp and an incubation time can be set too. With such a program, we want that the salt stays long enough at a specific temperature to obtain a homogeneous temperature.

After all those operations have been completed, the oven has still to cool down before to be opened and then the crucibles can be taken out of the oven.

A control panel is here to set the temperature inside the oven over time.



**Figure III.4: control panel of the oven**

A few parameters can be set:

Time 0 can be set in order not to heat the oven for a given duration

Time 1 represents the time taken to reach Temperature 1

Time 2 is the time during which the oven is heated at Temperature 2

### Observing the result

The very last step is to take a look at the inside of the crucible to see if the salt was molten or not and to observe if there was some creeping. The salt is molten as soon as it looks smooth on the surface. Special care for the creeping must be taken because it could destroy a sensor during other experiments (DSC for example).

However, there are some bad aspects to the use of the oven that shouldn't be ignored.

At first, the oven temperature is not perfectly accurate; a rough estimation is to say that the control panel indicates a temperature 50°C higher than the real oven temperature.

Then, since it is impossible to see the inside of the oven during the heating, it reduces the precision on the conclusions. For example, if a salt that melted at 300°C would be put in the oven at 500°C, the only information available is that the salt melts in the range of 300°C-500°C.

That's why the oven experiments are a starting point because they allow obtaining a rough idea about the fusion temperature and the behavior of the salt. With such experiments, one is able to say if a salt can be studied with other devices and up to which temperature (as well as the starting temperature).



**Figure s III.5 & III.6: Salts before (left) and after (right) the introduction into the oven**

Because the oven can reach really high temperature, those experiments have to be done under safe conditions such as wearing glasses and gloves.

To summarize, the oven experiments have been performed for the following reasons:

- once molten, salts have become homogenous.
- the behavior of the salts is known and therefore we can prevent damaging the DSC with a salt that would creep out of the crucible.
- we get a rough idea concerning the melting temperature of a salt in comparison to the other. It allows to know which salts melt first, and around which temperature. Thus, we prevent damaging the DSC once again.

It is necessary to proceed with the gathering of the salts. To do so, two different operations are possible.

The first one is to scratch the salt when it sticks to the crucible. Then we obtain a small amount of powder, which is enough for the DSC.

The second one is when the salt leaves the crucible in one part. With a mortar, it is then possible to crush the hard pieces of molten salt that came off and turn them into a relatively big amount of powder.



**Figure III.7: mortar to turn the solid salts into powder**



**Figure III.8: Polluted crucibles after the melting of the salts**

Usually, I used to make salt samples of three grams and was able to gather at least 50 milligrams of the molten sample. It was sufficient for the DSC as it only required between five and seven milligrams of salts. The salts were then put into aluminum containers and stored before their first use in the DSC. On the following picture, we can see that some salts were more difficult to gather.

For example, quantity of the salt on the bottom left corner is much less than the one on the top right corner. The goal at this step is to make sure to get a sufficient quantity for the further experiments.



**Figure III.9: Aluminum container where the molten salts powder is gathered**

After the gathering of the salts, it is necessary to wash the polluted crucibles in order to use them in further operations. To do so, it is possible to use acetic acid, associated with heating. Thus, concentrated acetic acid will be poured in the polluted crucible and then placed on a heating plate. On an average temperature of 100°C, the process is faster but it is necessary to repeat as all the salts don't come off with the washing. This process can take up to a few days depending on the difficulty to take the salts off the crucible.

After the acetic acid was put into the crucible and everything is heated, the solid salt begins to turn liquid and becomes easier to wash. But however, with such a technique, it is impossible to reuse the salts as they are polluted with acetic acid and it is necessary to wash the crucibles carefully to make sure that no acid stayed into the crucible.

## 2. DSC experiments

The salts must be dried before to be put into the crucibles too.

Once those two crucibles are put into the device, the user must select a heating program with a heat ramp and an incubation time. The output of such an experiment is given on the following figure [Figure II.7].

With the DSC, the user is able to determine the phase change temperature of a salt, when a peak appears; it means that the temperature of phase change has been reached.

The picture [Figure II.peaks] shows the output of DSC experiment on one sample. The black curve represents the first cycle, a peak around 100°C can be interpreted as a loss of water in the sample. The blue curve is the second cycle, with a peak given a 493.3°C which is the phase change of the salt that we are looking for.

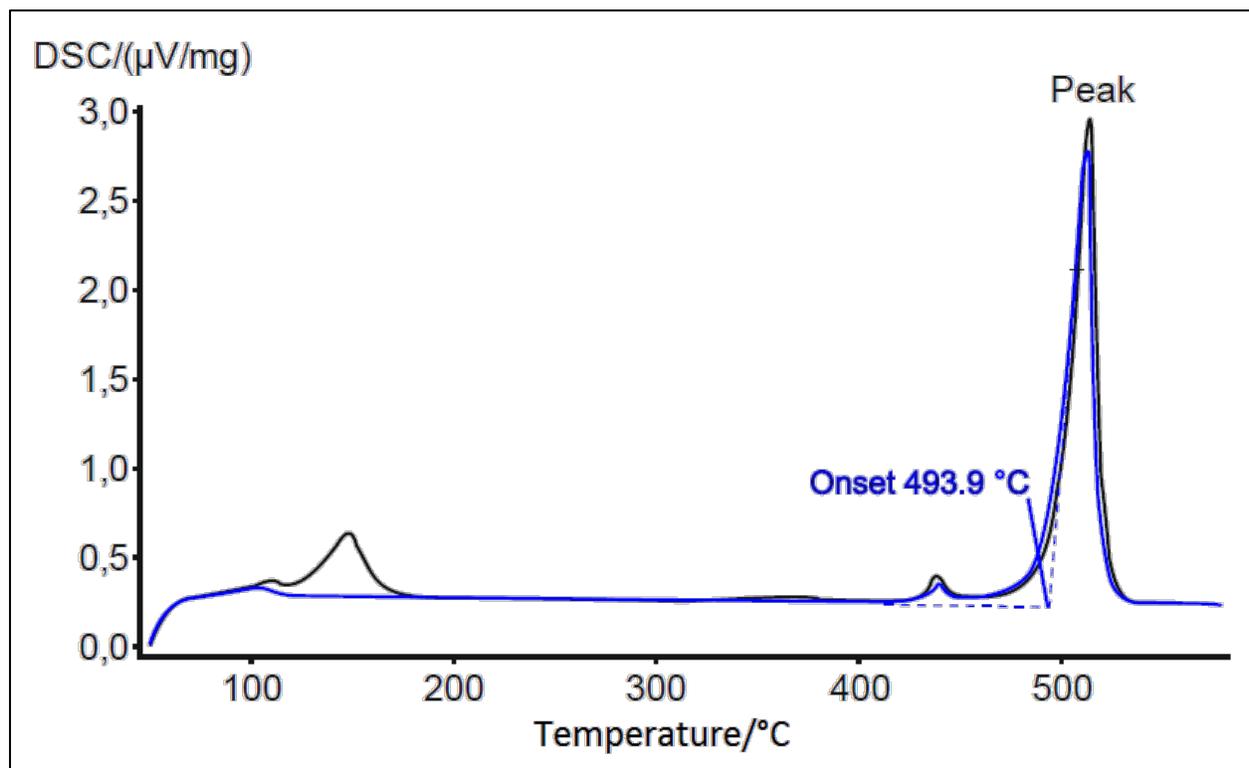


Figure III.10: Output of a DSC measurement

On the table below, the different salts that have been tested are given with their respective proportions in anions and cations. The first salts (marked with an A) were the first to be made. There were even more salts (10 at a total) but not all of them could be used for the DSC. I had more hope for the samples 6 and 7 as the oven experiments had been more successful with them but it appeared that the salt 1A obtained the lowest fusion temperature with the DSC. Therefore I made more samples in “an area around this salt” to study the behavior of some mixtures and find a lower fusion temperature.

The second range of samples (marked with a B) was made in this area. After oven experiments and DSC experiments, the output of the DSC showed that it was possible to find a salt with an even lower fusion temperature.

Final output of the DSC measurements

Sample number	%Carbonate (molaire)	%Sulfate	%Lithium	%Potassium	%Sodium	T <sub>fusion</sub> (°C)
1A	50	50	30	35	35	440
7A	50	50	70	15	15	475
6A	50	50	50	15	35	490
4A	50	50	50	25	25	500
1B	50	50	30	35	35	434,9
2B	50	50	20	40	40	432.8
3B	50	50	20	20	60	438.1
4B	50	50	20	60	20	418.4
5B	50	50	10	60	30	495.2
6B	50	50	10	30	60	454
7B	50	50	40	10	50	481.9
8B	50	50	40	50	10	425.4
9B	50	50	30	20	50	456.3
10B	50	50	25	25	50	446.4
11B	50	50	20	30	50	433.4
12B	50	50	35	25	40	436.9
13B	50	50	30	30	40	460.7
14B	50	50	25	30	45	432.5

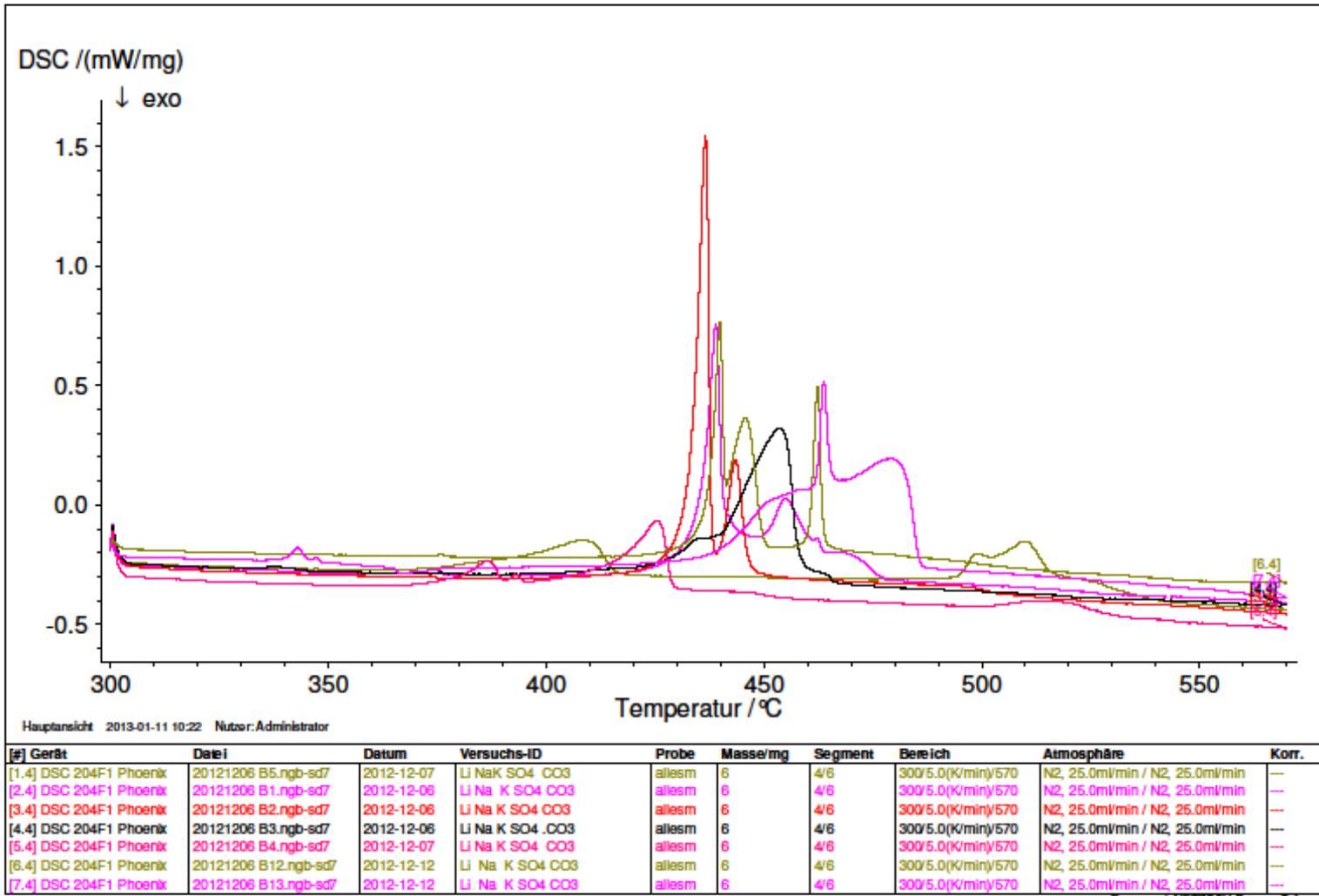
**Table 3: Fusion temperatures of salt samples depending on their composition**

The samples with an A are the very first samples that were done. They were made so that a large range of the quaternary system was covered. Some of them seemed more promising and were put into the DSC. Once we knew the fusion temperatures of this sample, I made several additional samples with similar compositions to the one with the lowest fusion temperature. And this is how I obtained the results of the B samples.

I also tried several samples around the 1A but with a different anions ratio. Unfortunately, the oven experiments were not promising and we stopped studying them.

### 3. Extracting the liquidus peaks

For all of the samples studied in [Table 3], the fusion temperature was read on the curve given by the program controlling the DSC. I had to distinguish many peaks for each sample (see Appendix) and determine which one was corresponding to the fusion temperature.



**Figure III.11: Analyse of the output of DSC measurements**  
(Made by the Author)

Some peaks were clearly under or above the fusion temperature area studied before with the literature and the oven. That's why I had to "skip" some peaks and focus on the remaining ones.

The objective was then to select the best corresponding peak.

Sometimes, many peaks are in the same area and make it harder to read. On the picture above, the different color of the curves represent different samples and cycles. During the analyze of a curve, some peaks can be on each other and made difficult to see, that's why we tried to separate the liquidus peak from the other ones.

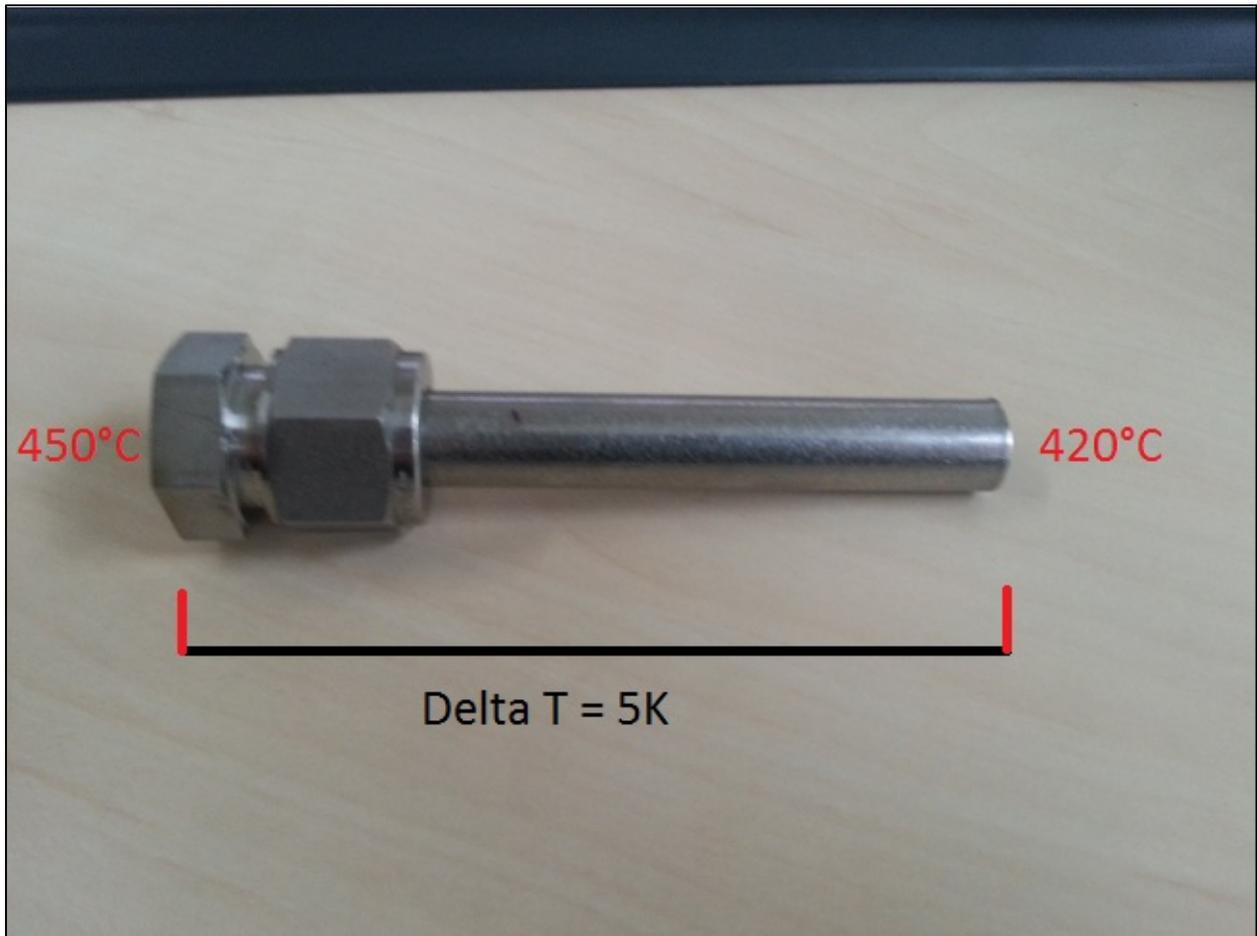
The next experiment we planned to make was to use the tool of [Figure IV.2].

The small container is filled with the sample to analyze, heated then cooled down slowly (100K/24H). Then, it is again heated but with two different temperatures on each end. As the tool is in stainless steel, it is possible to obtain a temperature difference around 5 Kelvins between the two ends of the tool.

This way it is possible to concentrate the liquid part of the sample on a side and that is how we expect to get better eutectic curves. It is also expect that with the gravity, the heaviest parts of the sample would fall to the bottom of the container during the heating making it easier to separate the liquidus curve from the other.

This step was the last one we wanted to achieve and it represents an outlook of what the next experiments should be:

- Find ways to obtain a better idea of the eutectic point location
- End up the measurements concerning the lowest part of the temperatures and do the same with the highest part.



**Figure III.12.a: Tool used to extract the liquidus peak.**



**Figure III.12.b: Tool used to extract the liquidus peak.**

## 4. Thermogravimetry experiments

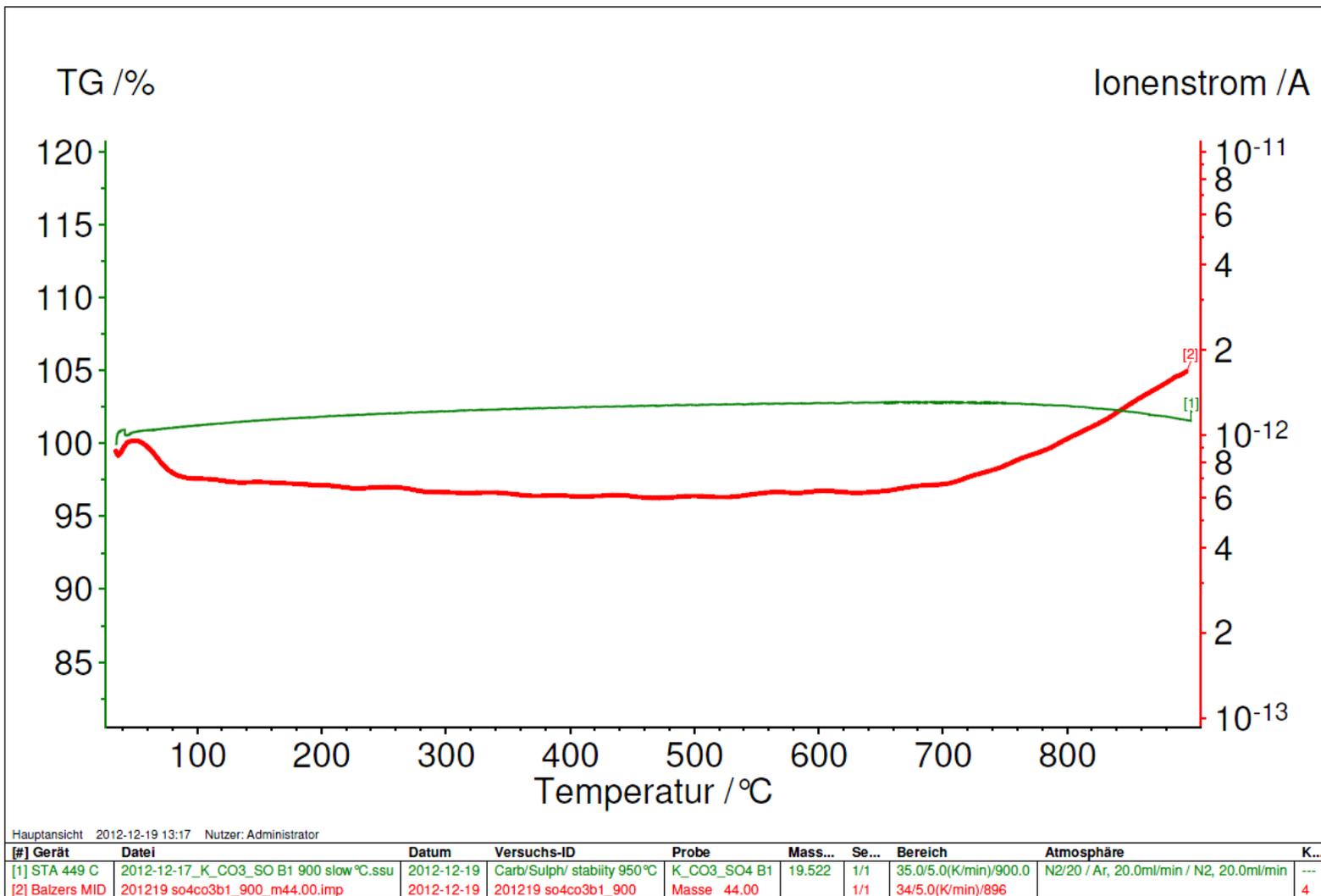
The principle of the thermogravimetry is to measure the loss of mass of a sample during its heating. Therefore, this technique is used to study the higher temperatures of a salt.

While the temperature rises, the device is able to see a loss of mass in the sample. Thus this device is able to determine starting which temperature does a sample start to decompose itself. So, with the thermogravimetry technique, it is easy to see which sample is the most stable.

To obtain the best results possible, the experiments are lead under Argon or Nitrogen atmosphere.

Results of the thermogravimetry are not included (except for [Figure III.11]) because even with temperatures around 900°C, samples were still stable and we didn't want to go above yet.

Everything that goes inside the device is carefully weighed before to be put into the thermogravimetry oven. Salt is put inside a little crucible which is put into a bigger one and. Then the whole system is put into the thermogravimetry device. Too, a tare is made on the balance of the machine to make sure that the mass of the sample inside is stable before starting experiments. The output of this kind of experiment is represented on the [Figure III.A.10] where it is possible to see both the thermogravimetry curve (in green)



and the flow of a carbon dioxide (red curve). CO<sub>2</sub> is represented on this graph because out of the entire

spectrum that has been analyzed, this was the one that appeared the most during the decomposition. And this means that the problem of decomposition in the samples are at first linked with the carbonates which decompose into carbon dioxide.

## IV. Conclusion

With the analysis of the oven and the DSC, we were able to determine an « area » where the ratio of the eutectic should be.

Indeed, with all the experiments we made, we could find out that with a ratio of 50% carbonates and sulfates and % Lithium %Sodium %Potassium, a salt with a melting temperature of 420°C could be found.

The few thermogravimetry experiments that I was able to make showed that the samples I studied had a decomposition temperature around 1000°C which gives a big  $\Delta T$  then a big enthalpy and this is a satisfying result.

The study of a salt with 50% carbonate and 50% sulfate is now better known and opens new fields of research and use as it is a salt with high decomposition temperature (high enthalpy).

The experiments currently made on such a system revealed a fusion temperature around 420°C and paves the way for the decomposition temperature side of experiments.

This salt should fill the criteria of a CSP plant as it is less toxic but most of all because it offers a relatively low fusion temperature and a high decomposition temperature. Therefore it should be a perspective of use as a next generation solar salt.

All this scientific approach and those experiments got me to obtain a better view of the work as an engineer. In order to study in a scientific way, it is compulsory to have a good overview of the state of the art. It is also required to establish a protocol and to think about what comes next: What will be the experiments? Which devices are going to be used? How long will it take? ...

And as these steps are done, it is possible to get on rails for the laboratory experiments and start gathering results for analysis.

That's why this internship gave me the opportunity to get in touch with many field of the engineering work: working as a team, acquiring knowledge, thinking about the solutions, experimenting and analyzing.

**Figure III.13: Output of a thermogravimetry measurement**  
(Made by the author)

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# Appendix



104928 Carbonate de potassium  
pour analyses EMSURE® ACS,ISO,Reag. Ph Eur

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Germany  
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11 décembre 2012

Numéro d'article	Conditionnement	Qté	Prix
1049280500	Flacon plastique	500 g	77,20 €
1049281000	Flacon plastique	1 kg	119,00 €
1049289050	Carton ondulé	50 kg	prix sur demande

Les prix peuvent être modifiés sans préavis.

Informations produit	
Grade	ACS,ISO,Reag. Ph Eur
Synonyms	potash
Formule brute (selon Hill)	$\text{CK}_2\text{O}_3$
Formule chimique	$\text{K}_2\text{CO}_3$
Numéro SH	2836 40 00
Numéro CE	209-529-3
Masse molaire	138.21 g/mol
Numéro CAS	584-08-7

Données physiques et chimiques	
Solubilité dans l'eau	1120 g/l (20 °C)
Point de fusion	891 °C
Masse molaire	138.21 g/mol
Densité	2.43 g/cm <sup>3</sup> (20 °C)
Bulk density	750 kg/m <sup>3</sup>



106392 Carbonate de sodium  
anhydre pour analyse EMSURE® ISO

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Numéro d'article	Conditionnement	Qté	Prix
1063920500	Flacon plastique	500 g	47,00 €
1063921000	Flacon plastique	1 kg	71,90 €
1063925000	Flacon plastique	5 kg	202,00 €
1063929025	Carton ondulé	25 kg	prix sur demande
1063929050	Carton ondulé	50 kg	prix sur demande

Les prix peuvent être modifiés sans préavis.

Informations produit	
Grade	ISO
Synonyms	anhydrous soda
Formule brute (selon Hill)	$\text{CNa}_2\text{O}_3$
Formule chimique	$\text{Na}_2\text{CO}_3$
Numéro SH	2836 20 00
Numéro CE	207-838-8
Masse molaire	105.99 g/mol
Numéro de l'index CE	011-005-00-2
Numéro CAS	497-19-8

Données physiques et chimiques	
Solubilité dans l'eau	220 g/l (20 °C)
Point de fusion	854 °C



## 105676 Lithium carbonate

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Numéro d'article	Conditionnement	Qté	Prix
1056760250	Flacon plastique	250 g	1.030,00 €

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Accessoires	
101514	Acide chlorhydrique 30% Ultrapur
101518	Acide nitrique 60% Ultrapur
100441	Acide nitrique 65% Suprapur®
100318	Acide chlorhydrique 30% Suprapur®

Informations produit	
Formule brute (selon Hill)	$CLi_2O_3$
Formule chimique	$Li_2CO_3$
Numéro SH	2836 91 00
Numéro CE	209-062-5
Masse molaire	73.89 g/mol
Numéro CAS	554-13-2

Données physiques et chimiques	
Solubilité dans l'eau	13 g/l (20 °C)
Point de fusion	720 °C
Masse molaire	73.89 g/mol
Densité	2.1 g/cm <sup>3</sup> (20 °C)



## 105697 Lithium sulfate monohydraté

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11 décembre 2012

Numéro d'article	Conditionnement	Qté	Prix
1056970050	Flacon plastique	50 g	330,00 €

Les prix peuvent être modifiés sans préavis.

Accessoires	
100318	Acide chlorhydrique 30% Suprapur®
101514	Acide chlorhydrique 30% Ultrapur
101518	Acide nitrique 60% Ultrapur
100441	Acide nitrique 65% Suprapur®

Informations produit	
Formule brute (selon Hill)	$\text{Li}_2\text{O}_4\text{S} \cdot \text{H}_2\text{O}$
Formule chimique	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
Numéro SH	2833 29 80
Numéro CE	233-820-4
Masse molaire	127.96 g/mol
Numéro CAS	10102-25-7

Données physiques et chimiques	
Solubilité dans l'eau	340 g/l (20 °C)
Point de fusion	120 °C
Masse molaire	127.96 g/mol
Densité	2.05 g/cm <sup>3</sup> (20 °C)



## 105152 Potassium sulfate

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11 December 2012

Product number	Packaging	Qty/Pk	Price
1051520100	Plastic bottle	100 g	price on request
1051520500	Plastic bottle	500 g	price on request

Prices are subject to change without notice.

Accessories	
101514	Hydrochloric acid 30% Ultrapur
100441	Nitric acid 65% Suprapur®
100318	Hydrochloric acid 30% Suprapur®
101518	Nitric acid 60% Ultrapur

Product information	
Synonyms	Potassium pyrosulfate
Hill Formula	$K_2O_4S$
Chemical formula	$K_2SO_4$
HS Code	3105 10 00
EC number	231-915-5
Molar mass	174.26 g/mol
CAS number	7778-80-5

Chemical and physical data	
Solubility	111 g/l (20 °C)
Melting point	1069 °C



## 106643 Sodium sulfate

anhydrous suitable for use as excipient EMPROVE® exp Ph Eur,BP,USP,E 514

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11 December 2012

Product number	Packaging	Qty/Pk	Price
1066432500	Plastic bottle	2.5 kg	price on request
1066439025	Fibre carton	25 kg	price on request

Prices are subject to change without notice.

Product information	
Grade	Ph Eur,BP,USP,E 514
Hill Formula	Na <sub>2</sub> O <sub>4</sub> S
Chemical formula	Na <sub>2</sub> SO <sub>4</sub>
HS Code	2833 11 00
EC number	231-820-9
Molar mass	142.04 g/mol
CAS number	7757-82-6

Chemical and physical data	
Solubility	44.55 g/l (20 °C)
Melting point	888 °C
Molar mass	142.04 g/mol
Density	2.70 g/cm <sup>3</sup> (20 °C)
Bulk density	1400 - 1600 kg/m <sup>3</sup>
pH value	4 - 7 (200 g/l, H <sub>2</sub> O, 20 °C)

Result analysis of the output of the DSC measurements

Sample	Cycle (H/C)	Peak one (start)	Peak one (end)	Peak two (start)	Peak two (end)	Peak three (start)	Peak three (end)	Peak four (start)	Peak four (end)
1B	H	430	444	450	460	461	464	0	0
1B	C	412	428	428	436	437	444	445	458
2B	H	432	439	440	448	0	0	0	0
2B	C	405	412	412	418	418	424	424	435
3B	H	420	440	440	460	460	468	0	0
3B	C	419	423	425	428	498	505	0	0
4B	H	380	390	390	396	414	435	502	528
4B	C	372	390	391	411	425	440	503	520
5B	H	395	420	495	502	505	515	0	0
5B	C	374	390	401	411	450	480	502	518
6B	H	430	443	451	461	506	523	0	0
6B	C	411	425	441	452	485	509	0	0
7B	H	472	500	0	0	0	0	0	0
7B	C	460	477	504	521	0	0	0	0
8B	H	423	439	528	551	0	0	0	0
8B	C	413	428	494	504	509	523	523	542
9B	H	456	465	465	470	470	479	0	0
9B	C	437	443	443	449	449	458	0	0
10B	H	432	442	444	468	0	0	0	0
10B	C	425	431	432	434	434	440	0	0
11B	H	427	440	440	456	460	470	0	0
11B	C	421	426	426	428	428	435	450	460
12B	H	431	441	441	452	457	470	0	0
12B	C	411	417	419	423	423	425	425	434
13B	H	340	348	440	460	460	468	469	490
13B	C	440	450	454	457	457	464	0	0
14B	H	337	352	426	440	440	456	459	477
14B	C	408	425	428	434	436	447	450	465

The numbers are the temperatures of the peak.

H means heating cycle.

C means cooling cycle.

## Masseversmol and Molarconverter programs

In order to gain time on every measurement made, I designed two smaller programs to help me calculate the ratios I wanted to measure.

On the one hand and in the process of weighing various salts (around 10), the program *Molarconverter* gives me the mass of every salts.

This program has for input the ratios of the cations and anions (carbonates and sulfates will be 50%) and returns the mass of every salt that I have to put into a crucible.

On the other hand, *Masseversmol* is a program that requires the weighed masses of the salts as an input and returns the ratios of the cations.

This second program is useful to make corrections or adjustments to the analysis knowing that the pouring into the crucible may be too few or too much.

With these two programs, I am able to obtain the quantity of each salt very quickly in order to make more samples in a shorter time. And I am also able to correct the ratios of the salts if I poured too much or not enough.

<pre>% Carbonates voulu C=.5; % Sulfates voulu S=.5;  % Li molaire voulu Li=20; % K molaire voulu K=60; % Na molaire voulu Na=20; % masse voulue (g) m=3;</pre>	<pre>mK2SO4 =       1.1454  mK2CO3 =       0.9084  mNa2SO4 =       0.3112  mNa2CO3 =       0.2322  ans =        3</pre>
---	---

Figure III.14: Example of input of the Molarconverter program (on the left) and output (on the right)

No image from the *Masseversmol* program is given because it makes the opposite of the first program.

# Documentation for the programs

## Lowliquitern Program

**Inputs :** datasheet of the temperature corresponding to various ratio of cations.  
**Output :** Interpolated lowest temperature and the corresponding cations ratios.

---

**The datasheets :** First column is the ratio of the "studied" cation.  
 First row is the ratio of the other cation.  
 First value is not read.  
 All other values are the temperatures corresponding to the ratio. **B**

<del>c= [0.0000]</del>		8.500	10.000	14.5000	55.297	95.000	96.000	Ratio of Ca for example
Ratio of K <b>A</b>	13.000	0.000	-0.5921	-4.7596	-2.1024	-0.0616	0.0004;	In green : There is no need to go from 0% to 100% ans there is no need to set a frequency of measures either.
	15.000	-0.1301	1.8559	-0.7239	-0.2729	0.4996	0.0130;	
	67.510	-1.3327	-1.5523	0.0000	2.9369	1.4122	0.0331;	
	95.000	-0.4808	0.2289	3.6886	2.4338	0.5805	0.0125;	
	98.000	0.0797	2.0967	5.8591	2.2099	0.1328	0.0013;	
	100	0.0053	0.1099	0.2995	0.1107	0.0057	0.0000];	

Zeros aren't read by the program, they represent missing values.

---

**Parameters :** precision=100; %Higher value for better results A higher value of precision gives more accurate results.

**Before to run :** Don't forget to add the scripts contained in the ternplot folder to path.

Run :) 

## algoterpolation Program

**Inputs :** Datasheet of the variations of the coefficient K with the temperature, for various cations. + desired K.  
**Output :** Temperature corresponding to the desired K for every given cations in the datasheet.

---

**Input :** Make sure to set Kch to the desired value of K.

The matrix should look like this

1000	K11	K21	...	
900	K12	K22	...	% Desired value of the K coefficient
800	K13	K23	...	Kch=10^-1;
700	K14	K24	...	
600	K15	K25	...	% Higher value for better result !\ increases loading time
500	K16	K26	...	precision=1;
400	K17	K27	...	
Temperature	Coefficients			

---

**Output :** In vector tempres, all the temperatures corresponding to the desired K can be found.

Run :) 

Carbonates decomposition coefficients [14]

T(K)	XCO <sub>3</sub> =XO+CO <sub>2</sub> (g)					
	Be	Mg	Ca	Sr	Ba	
2000		0	0	0	0	0
1900		0	0	0	0	0
1800		0	0	0	0	0
1700		0	0	0	0	0
1600		0	0	0	0	0
1500		0	0	4,35	2,217	6,42E-02
1400		0	0	1,73E+01	7,09E-01	1,82E-02
1300		0	0	5,898	1,87E-01	4,12E-03
1200		0	0	1,65	3,88E-02	6,95E-04
1100		0	0	3,59E-01	4,96E-03	8,04E-05
1000		0	4,42E+03	5,65E-02	4,10E-04	4,96E-06
900		0	1,29E+03	5,76E-03	1,91E-05	1,52E-07
800		0	2,65E+02	3,23E-04	4,07E-07	1,88E-09
700		0	3,31E+01	7,70E-06	2,81E-09	6,36E-12
600		0	1,98E+00	5,10E-08	3,61E-12	3,09E-15
500		0	3,65E-02	4,32E-11	3,14E-16	6,73E-20
400		0	8,68E-05	1,01E-15	2,46E-22	6,51E-27
300		0	2,73E-09	1,14E-23	8,80E-33	6,42E-39
T(K)	Li	Na	K	Rb	Cs	
2000		0	0	0	0	0
1900		0	0	0	0	0
1800		0	0	0	0	0
1700		0	0	0	0	0
1600		0	0	0	0	0
1500	1,06E-01	6,76E-05	1,17E-06	4,26E-07	1,32E-07	
1400	4,63E-02	1,09E-05	1,48E-07	5,14E-08	1,53E-08	
1300	1,75E-02	1,75E-06	1,32E-08	4,36E-09	1,24E-09	
1200	5,45E-03	2,11E-07	7,62E-10	2,38E-10	6,40E-11	
1100	1,33E-03	1,66E-08	2,08E-11	1,53E-11	1,87E-12	
1000	2,32E-04	5,94E-12	2,57E-13	1,70E-13	2,58E-14	
900	1,48E-05	9,89E-12	1,55E-15	6,61E-16	1,33E-16	
800	4,20E-07	5,72E-14	2,46E-18	6,08E-19	1,74E-19	
700	4,08E-09	7,36E-17	5,79E-22	1,03E-22	3,25E-23	
600	7,67E-12	9,19E-21	7,86E-27	1,04E-27	3,25E-28	
500	1,06E-15	2,79E-26	1,13E-33	1,09E-34	2,99E-35	
400	1,58E-21	1,35E-34	5,67E-44	3,46E-45	7,55E-46	
300	1,67E-31	7,87E-49	1,36E-61	3,59E-63	5,14E-64	

Sulfates decomposition coefficients [14]

XSO <sub>4</sub> =XO+SO <sub>2</sub> (g)+1/2*O <sub>2</sub>					
Be	Mg	Ca	Sr	Ba	
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	3,97E-03	7,00E-06		0
0	6,538	3,94E-04	2,99E-07		0
0	9,04E-01	2,73E-05	7,35E-09		0
0	6,18E-02	1,21E-06	9,57E-11		0
1,61E+01	4,81E-03	3,09E-08	5,55E-13		4,39E-13
1,672	1,64E-04	3,38E-10	1,13E-15		1,63E-15
1,03E-01	2,74E-06	1,87E-12	1,13E-15		1,96E-18
3,14E-03	1,78E-08	2,63E-15	5,69E-19		5,23E-22
2,71E-05	3,17E-11	6,77E-19	4,23E-23		1,75E-26
5,55E-11	8,81E-15	1,55E-23	2,05E-28		3,02E-32
1,34E-11	1,52E-19	9,46E-30	1,67E-35		6,03E-40
1,07E-16	3,08E-26	1,79E-38	1,98E-45		9,49E-51
2,22E-24	2,61E-36	1,41E-51	2,56E-60		5,50E-67
1,49E-37	1,49E-53	5,61E-74	8,44E-86		9,17E-95
Li	Na	K	Rb	Cs	
0	9,64E-08	0	0		0
0	1,59E-08	0	0		0
0	2,13E-09	0	0		0
0	2,25E-10	0	0		0
0	1,79E-11	0	0		2,16E-13
3,05E-07	1,00E-12	3,82E-14	1,88E-13		5,76E-15
2,17E+08	3,77E-14	5,72E-16	2,41E-15		9,09E-17
1,01E+09	1,14E-15	4,01E-18	1,37E-17		7,47E-19
2,71E-11	1,97E-17	1,03E-20	2,72E-20		2,16E-21
3,55E-13	1,49E-19	8,70E-24	1,68E-23		1,94E-24
1,74E-15	3,70E-22	1,81E-27	2,26E-27		4,13E-28
2,41E-18	2,37E-25	7,57E-32	3,92E-32		1,26E-32
4,60E-22	2,32E-29	2,21E-37	4,01E-38		2,51E-38
5,10E-27	1,54E-34	1,41E-44	1,12E-45		1,06E-45
1,14E-33	1,80E-41	3,25E-54	1,07E-55		1,40E-55
5,02E-43	3,01E-51	9,76E-68	1,17E-69		1,85E-69
4,17E-75	3,37E-66	4,68E-88	1,39E-90		2,53E-90
		8,13E-			
3,25E-81	8,63E-92	123	2,74E-126		5,22E-126

Sulfites decomposition coefficients [14]

XSO <sub>4</sub> =XO+SO <sub>3</sub> (g)					
Be	Mg	Ca	Sr	Ba	
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	9,06E-05	0	0	0
0	2,41E-01	1,45E-05	2,57E-07	0	0
0	5,76E-02	1,74E-06	1,90E-08	0	0
0	9,83E-03	1,46E-07	8,84E-10	0	0
4,077	1,22E-03	7,82E-09	2,43E-11	1,11E-13	
1,027	1,01E-04	2,35E-10	3,41E-13	1,00E-15	
1,85E-01	4,89E-06	3,33E-12	2,02E-15	3,50E-18	
2,07E-02	1,18E-07	1,74E-14	3,76E-18	3,46E-21	
9,26E-04	1,08E-09	2,32E-17	1,45E-21	6,00E-25	
1,58E-05	2,51E-10	4,41E-21	5,86E-26	8,62E-30	
6,52E-08	7,38E-16	4,59E-26	8,13E-32	2,93E-36	
2,78E-11	7,80E-21	4,64E-33	5,14E-40	2,46E-45	
2,24E-16	2,64E-28	1,43E-43	2,59E-52	5,56E-59	
3,96E-25	3,97E-41	1,50E-61	2,52E-73	2,44E-82	
Li	Na	K	Rb	Cs	
0	1,75E-05	0	0	0	
0	2,14E-06	0	0	0	
0	2,06E-07	0	0	0	
0	1,50E-08	0	0	0	
0	7,83E-10	0	0	4,94E-15	
1,12E-08	2,73E-11	1,40E-15	6,90E-15	2,12E-16	
1,38E-09	5,93E-13	3,64E-17	1,53E-16	5,79E-18	
1,21E-10	9,48E-15	4,82E-19	1,65E-18	8,98E-20	
5,88E-12	7,78E-17	2,61E-21	6,90E-21	5,48E-22	
2,18E-13	2,43E-19	5,34E-24	1,03E-23	1,19E-24	
3,10E-15	2,08E-22	3,23E-27	4,04E-27	7,37E-28	
1,59E-17	3,59E-26	5,00E-31	2,59E-31	8,34E-32	
1,54E-20	6,78E-31	7,55E-36	1,37E-36	8,59E-37	
1,45E-24	5,40E-37	4,00E-42	3,20E-43	3,02E-43	
5,53E-30	3,70E-45	1,58E-50	5,20E-52	6,78E-52	
1,30E-37	1,15E-56	2,53E-62	3,02E-64	4,79E-64	
4,22E-49	3,33E-74	4,73E-80	1,40E-82	2,56E-82	
8,67E-69	3,24E-104	2,17E-110	7,26E-114	1,39E-113	

*Nitrates and nitrites based system decomposition coefficients are not given since they were not relevant.*