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Barocaloric Effects on Plastic Crystals

REPORT

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APPENDIX A: Tables of values

APPENDIX B: Baselines

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Abstract

The operation of most refrigeration systems is currently based on gas compression refrigeration cycles. The gases used are toxic substances or contribute to the greenhouse effect in the event of leaks or poor waste management. This situation has led to the search for new techniques or materials to improve the current panorama. In recent decades, an important step has been taken in the study of materials that provide caloric effects while remaining in the solid phase, although the results cannot yet be compared to current gas compression refrigerants. In the solid state, giant caloric effects are expected due to the application of an external field around first-order phase transitions with a large latent heat associated.

This project studies the caloric effects induced by the application of hydrostatic pressure (barocaloric effects or BCEs). The research has focused on materials called plastic crystals because they present a very high-energy transition due to their transformation from a plastic solid high-temperature phase (with directional disorder) to a completely ordered low-temperature phase. Specifically, *tris(hydroxymethyl)aminomethane* (Tris) and *2,2-Dimethyl-1-propanol-99%* (NPA) have been analyzed. For this experimental study, differential scanning calorimetry (DSC) at atmospheric pressure and differential thermal analysis (DTA) at high pressure were used, allowing quasi-direct measurements of the barocaloric effect to be obtained, specifically of the entropy variation in an isothermal process of pressure change.

The results show atmospheric pressure transition temperatures of 405 K for Tris and 246 K for NPA (heating) and conventional barocaloric effects of $\Delta s = 673 \text{ J/(K}\cdot\text{kg)}$ at a pressure of 2.1 kbar for Tris and $200 \text{ J/(K}\cdot\text{kg)}$ at 2.2 kbar for NPA, which far exceed (by a factor of almost 11 and 3, respectively) the largest giant BCEs analyzed so far in the solid state. Conversely, the values obtained for the cooling capacity for the same pressures are 4420 J/kg for Tris and 9030 J/kg for NPA. However, the BCE in Tris is irreversible in the pressure range studied due to the presence of a large hysteresis of approximately 60 degrees. In the case of NPA, although it also presents a notable hysteresis (30-35 degrees), the temperature displacement with pressure is large enough ($dT/dp = 22 \text{ K/kbar}$) to begin to give reversible barocaloric effects from 1.7 kbar. These results show that NPA has better properties for the operation of a cycle compression refrigeration machine than Tris.



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1 Glossary

CFC	Chlorofluorocarbon
Tris	Tris(hydroxymethyl)aminomethane
NPA	2,2-Dimethyl-1-propanol (neopentyl alcohol)
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
T	Temperature
p	Hydrostatic pressure
V	Volume
H	Enthalpy (h specific enthalpy)
S	Entropy (s specific entropy)
m	Mass
C	Heat capacity
C_p	Heat capacity at constant pressure
Q	Heat
G	Gibbs free energy
RC	Refrigerant capacity
BCC	Body-centered cubic
FCC	Face-centered cubic
OP	Order parameter

FWHM *Full width half-maximum*

BCS *Barocaloric strength*



2 Introduction

Currently, the vast majority of refrigeration systems operate thanks to the caloric effect of a gas when it is compressed and decompressed. The materials used for refrigeration are generally very polluting for the environment and contribute to the greenhouse effect. Additionally, waste management is complicated due to their gaseous or liquefied state; therefore they are pollutants as it is not fully possible to control the discharge of such substances into the environment.

The objective of this project is to find an alternative to current refrigerants, specifically materials that remain in a solid state throughout the refrigeration cycle. Working with solid-state refrigerants will make environmental controls easier throughout the life cycle of these materials since their solid state is easier to confine, preventing contamination.

Countless studies over the last half century have shown that some materials have more than one different solid phase (polymorphism) and it is possible to take advantage of the caloric effect of the transition between the phases by applying external fields of different natures, depending on the degrees of freedom that the transition undergoes. For example, good results have been obtained in magnetization changes between solid phases. Materials that exhibit these changes in the solid phase are called magnetocaloric and the transition can be achieved by applying a magnetic field (magnetocaloric effect). Magnetocaloric effects generally require the application of large magnetic fields which are difficult to achieve by permanent magnets or they have a high cost. Conversely, the caloric effects of the application of electric fields (electrocaloric effects) have also been studied. These require high magnitudes of electric fields that can only be applied uninterruptedly in thin samples. These disadvantages contrast with the results obtained by the application of hydrostatic pressures (barocaloric effects) since caloric effects equal to or even greater than the magnetocaloric and electrocaloric effects have been obtained at pressure magnitudes that are relatively easy to achieve. Therefore, it is interesting to investigate barocaloric effects further.

Accordingly, the study of barocaloric effects on materials called plastic crystals, which have already proven to be useful as a heat reservoir due to their great latent heat, is proposed. The aim of this paper is to prove whether plastic crystals are appropriate candidates to replace current refrigerants or not, thus contributing to the development of more environmentally friendly refrigeration technologies. In order to do, the experimental study of the barocaloric effects of two different materials will be performed: *tris(hydroxymethyl)aminomethane* (Tris) and *2,2-Dimethyl-1-propanol-99%* (NPA).

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In order to carry out the study, general research into caloric effects and studies on different caloric effects in solids have been carried out. The operation of the instruments necessary to carry out the experiments has also been briefly summarized. Finally, an analysis of the data obtained will be carried out and conclusions drawn.

2.1 Caloric effects

This chapter provides a brief review of the caloric effects of refrigeration systems. First, the current methods based on gas compression are explained and then the different caloric effects on solids are discussed.

2.1.1 Gas compression refrigeration cycle

Refrigeration is the transfer of heat from one system to a temperature lower than the temperature of another source where heat is released. The process is carried out through cycles called refrigeration cycles. The most common cycle today is vapor compression, which consists of taking advantage of the thermodynamic properties of compressing vapor condensation. Furthermore, there are also cycles where the vapor condenses before being compressed (absorption refrigeration) and some that use different cycles at the same time (cascade refrigeration).

A refrigeration cycle is based on a reverse Carnot cycle as in Figure 2.1. The entire cycle occurs within the liquid-vapor equilibrium zone (zone represented by the curve). It consists of compressing adiabatically by means of a turbine from state 1 to 2, saturated vapor. Consequently, the temperature increases and then the heat (Q_H) can be transferred to a source at a lower temperature in an isothermal process to state 3, saturated liquid. An expansion is then made adiabatically in order to reduce the temperature to the initial temperature of the cycle, state 4. Finally, it returns to state 1 by absorbing heat from what is to be cooled (Q_L), which is at a temperature higher than the temperature of the refrigerant at states 1 and 4.

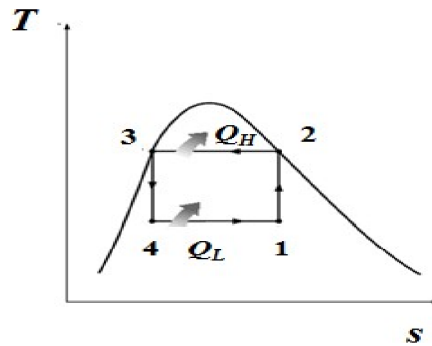


Figure 2.1. T - s diagram of the reverse Carnot cycle [1].

Unfortunately Carnot's reverse cycle is ideal but cannot be put into practice, so some small changes are applied that lead to the ideal cycle for vapor compression: instead of using a turbine, the substance is expanded with a valve and state 2 is brought to the edge of the dome, saturated vapor, implying that it compresses beyond the dome and state 3 is unsaturated vapor. The final T - s diagram is given in Figure 2.2. State 4' corresponds to the ideal point for adiabatic expansion from state 3, but this is not possible in practice and ends in state 4.

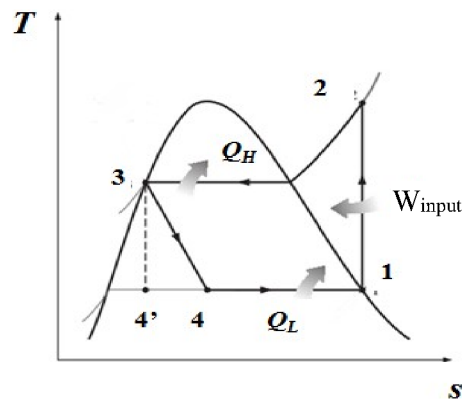


Figure 2.2. Ideal vapor compression refrigeration cycle in a T - s diagram [1].

A refrigeration cycle is given below in Figure 2.3. by reversing the axes. This represents the rest of the paper and shows how the adiabatic processes follow the isentropic curves better. The parameter Y is used to refer to the applicable conjugate field, which in this case is equivalent to the hydrostatic pressure field.

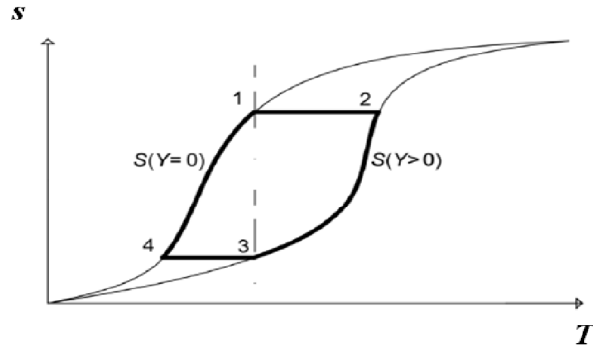


Figure 2.3. Refrigeration cycle in an s - T diagram [2].

The equations for the refrigeration cycle can be calculated as below from the TdS equation of a pVT system [eq. (2.1)] [1] and Maxwell relations [eq. (2.2)] .

$$TdS = T \left(\frac{\partial S(T, p)}{\partial T} \right)_p dT + T \left(\frac{\partial S(T, p)}{\partial p} \right)_T dp \quad (2.1)$$

$$\left(\frac{\partial S(T, p)}{\partial p} \right)_T = - \left(\frac{\partial V(T, p)}{\partial T} \right)_p, \quad \left(\frac{\partial S(T, p)}{\partial T} \right)_p = \frac{C_p}{T} \quad (2.2)$$

According to the isothermal process ($dT = 0$), applying a pressure field causes a change in entropy following the equation:

$$\Delta S_{isotherm}(T, \Delta p) = \int_{p_I}^{p_F} dS_{isotherm}(T, p) = - \int_{p_I}^{p_F} \left(\frac{\partial V(T, p)}{\partial T} \right)_p dp \quad (2.3)$$

According to the process where the outer field is removed adiabatically ($ds = 0$), a change in temperature is forced as in the following equation:

$$\Delta T_{ad}(T, \Delta p) = \int_{p_1}^{p_2} dT_{ad}(T, p) = \int_{p_1}^{p_2} \left(\frac{T}{C(T, p)} \right) \left(\frac{\partial V(T, p)}{\partial T} \right)_p dp \quad (2.4)$$

From the equations of the two types of processes, it can be deduced that the greater the variation in volume, the greater the caloric effect. This can occur in two cases: in gases due to their high coefficient of expansion and in first-order phase transitions (as explained in section 2.2.1).

2.1.2 Gas compression refrigerants

The main factors for choosing a refrigerant are that it is cheap, has a high enthalpy variation, is not corrosive or flammable and the temperature and working pressure ranges are as required. Other properties are considered depending on each particular case.

The liquid or vapor state of the refrigerant has many disadvantages, such as the fact that waste management is more difficult to control than a solid one, implying that there is a high probability of leaking into the environment. In addition, most of today's refrigerants are toxic or pollutants that contribute to the greenhouse effect. It should also be taken into account that vapor has large expansion coefficients, which means there must be sufficient space.

The best known are ammonia (highly toxic), hydrocarbons such as propane and ethane, carbon dioxide and chlorofluorocarbons (CFCs) [1].

The group of CFCs, apart from being used for refrigeration, are also found in aerosols, cleaning solvents, sterilization solutions, etc. However, they are substances derived from saturated hydrocarbons in which the hydrogens have been totally or partially replaced by fluorine and chlorine atoms. The presence of halogens makes them candidates for serious ecological problems. In fact, in the 1980s it was discovered that they actively participated in the destruction of the ozone layer [3]. It should be remembered that the ozone layer is the layer of the atmosphere of planet Earth that is responsible for filtering small-wavelength solar radiation that is harmful to living beings; its destruction is therefore a serious issue. Therefore, its manufacture and use was prohibited by the 1987 Montreal Protocol of the United Nations. Among the best known are R-11, R-12 and R-114. R-123 and R-134a, which are not halogenated and are currently among the most common refrigerants, were subsequently used as an alternative.

In addition, all of them (old and current refrigerants) also contribute to the greenhouse effect. The greenhouse effect consists of water vapor and carbon dioxide (among others) present in the atmosphere helping to maintain the Earth's warmth by absorbing infrared radiation even if there is no sun. If it were not for this effect, much of the heat radiation from the sun would be lost by reflection. However, this effect becomes problematic if gaseous masses contributing thereto accumulate, increasing the average temperature of the Earth.

2.2 Caloric effects on solids

In order to understand where the caloric effect on solids comes from, a series of concepts must be explained.

First, as demonstrated in the previous section, the application of an external field causes changes in isothermal entropy or adiabatic temperature depending on the nature of the process. These are called caloric effects and named in a particular manner according to the external field applied, as can be seen in Table 2.1. The associated coordinate is the magnitude that can change when applying the conjugate field.

Conjugate field (Y)	Associated coordinate (X)	Type of system	Caloric effect
Magnetic (H)	Magnetization (M)	HMT	Magnetocaloric
Electric (E)	Polarization (P)	EPT	Electrocaloric
Hydrostatic pressure (p)	Volume (V)	pVT	Barocaloric
Stress (σ)	Strain (ε)	$\sigma\varepsilon T$	Elastocaloric

Table 2.1. Summary of types of systems and caloric effects as a function of field applied.

It is important to understand the difference between the effect and the type of material. In other words, a change in magnetization can be achieved in a magnetocaloric material by applying a magnetic field (magnetocaloric effect) but the transition may be caused when pressure is applied (barocaloric effect) if it also has an associated change in volume depending on the type of material.

Now that these concepts have been explained, the caloric effect on solids shall be explained.

2.2.1 First-order transitions

A first-order transition occurs when an order parameter (OP) is equal to zero for temperatures above the transition temperature (T_t) and becomes nonzero for temperatures below the transition as seen in Figure 2.4. It should be explained that in first-order transitions the OP changes discontinuously, just as enthalpy and entropy are discontinuous. However, in second or higher order transitions, the OP changes are continuous.

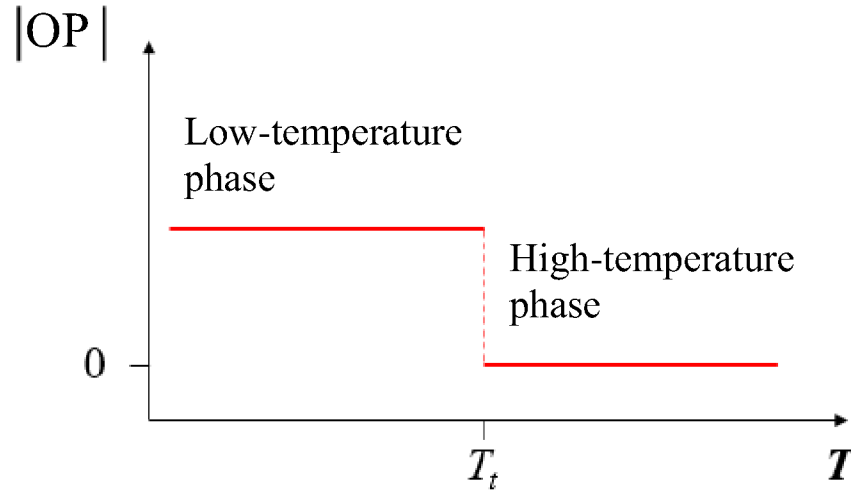


Figure 2.4. Order parameter (OP) as a function of temperature.

The order parameter is defined as:

$$OP = X(\text{high } T \text{ phase}) - X(T)$$

where X is related to the generalized coordinate according to the type of field. The barocaloric effect is studied in this paper, which means that its generalized coordinate is the volume, (pVT system) when hydrostatic pressures are applied. Thus the order parameter is the volume at the high temperature phase minus the volume at the given temperature.

When there is a change in volume, a caloric effect occurs (demonstrated by equations [2.3] and [2.4]).

In conclusion, there can be giant caloric effects near first-order phase transitions since the volume changes can be significant, but in general solids and any system change volume according to the temperature, therefore there will always be a barocaloric effect although this will be small for solids far from the transitions.

2.2.2 Gibbs energy and hysteresis

Gibbs free energy (G) is defined as [eq. (2.5)]:

$$G = H - TS \quad (2.5)$$

Taking the differential form and taking into account the first and second principles of thermodynamics (diagram not included), the equation (2.6) is as follows:

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$$dG = -SdT + Vdp \quad (2.6)$$

$$V = \left(\frac{\partial G}{\partial p} \right)_T \quad (2.7)$$

Knowing that T and p remain constant in a transition, the conclusion is that the dG phase transition = 0. According to the Maxwell relation of the equation (2.7), it follows that if the volumes of each phase are different, so are the slopes in the G - p diagram. Furthermore, $dG = 0$ can mean that the system is in the situation of thermodynamic equilibrium.

On the other hand, it is known that the second law of thermodynamics can be expressed in many ways. One of them is that entropy in the universe tends to increase. However, another way of stating the second law is through Gibbs free energy: a system tends to have the lowest possible Gibbs energy; this never increases spontaneously, but the action of an external system providing energy is necessary.

According to the above postulation, if a substance is heated and experiences a phase change at a certain temperature, when cooled it will have to return to the initial phase at the same temperature of the transition to heating. This is not exactly the case in reality. The transition to cooling is usually at a lower temperature than to heating. This phenomenon is known as hysteresis.

Figure 2.5 illustrates that there can be two Gibbs curves (a) for a certain temperature range, one for each phase, corresponding to two minima in the isothermal Gibbs curves as a function of volume (c), one local and the other corresponding to thermodynamic equilibrium. The transition does not take place if there is not enough energy to overcome the energy barrier between minima. The jump may be due to thermal fluctuations inherent to the system due to its temperature or energy input from external systems.

The transition to equilibrium (a) is the situation that should ideally occur when cooling, since the system would have to go at all times along the curve of the lowest Gibbs energy (corresponding to thermodynamic equilibrium). As for the metastable transition (b), it can be seen that it does not follow the lowest energy curve during a temperature range lower than the transition, meaning that it is at a local minimum but not at the thermodynamic equilibrium minimum. In the latter case, it is said that the cooling process presents hysteresis.



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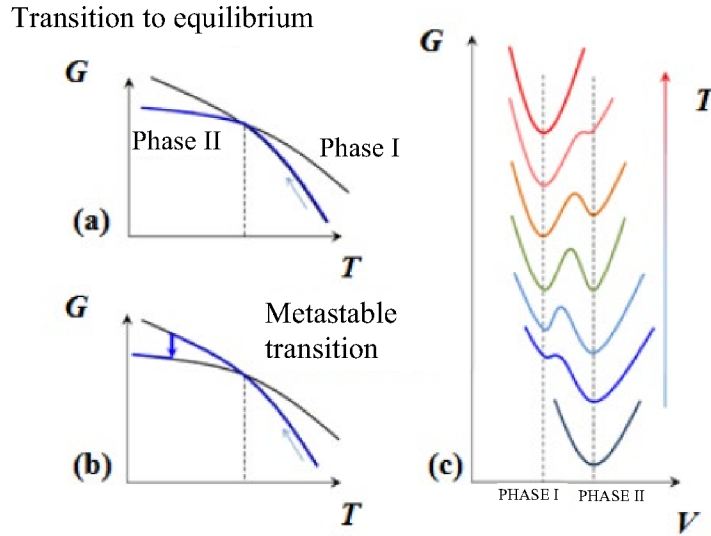


Figure 2.5. Gibbs free energy for phase transitions [2].

The minimum energy to pass from one minimum to the other can be exceeded by thermal fluctuations. However, it must be taken into account when the substance is in a controlled environment or in the case of materials that have a lot of hysteresis. The different transition temperatures in heating and cooling can be several tens of degrees for some substances. It can even sometimes vitrify, meaning that it never transitions when cooled, the hysteresis thereby becoming infinite.

Finally, based on the definition of Gibbs free energy (2.6) and knowing that for the phase transition $dG = 0$, the Gibbs energy of one phase (phase 1) can be equalized with the G of the other phase (phase 2). If there is equality, an equation known as the Clausius–Clapeyron equilibrium is performed [eq. (2.8)]. This equation connects the two changes that occur in a phase transition. The validity of the measurements can be verified from this equation and with different types of experiments and/or it is possible to access magnitudes that may eventually be outside the experimental scope from the inverse relationship.

$$-S_1 dT_t + V_1 dp_t = -S_2 dT_t + V_2 dp_t \rightarrow \frac{dT_t}{dp_t} = \frac{\Delta v_t}{\Delta s_t} \quad (2.8)$$

2.2.3 Reversibility

Once the concept of hysteresis has been explained, the effect of the hysteresis of a material used as a refrigerant in a refrigerator with compression and decompression cycles must be analyzed. Figure 2.6 shows an example of the isobaric entropy curves when undergoing the transition, representing the heating and cooling processes of two different pressures ($p_1 < p_2$). Hysteresis is evident as the transition of cooling occurs at a lower temperature than in heating due to both pressures.

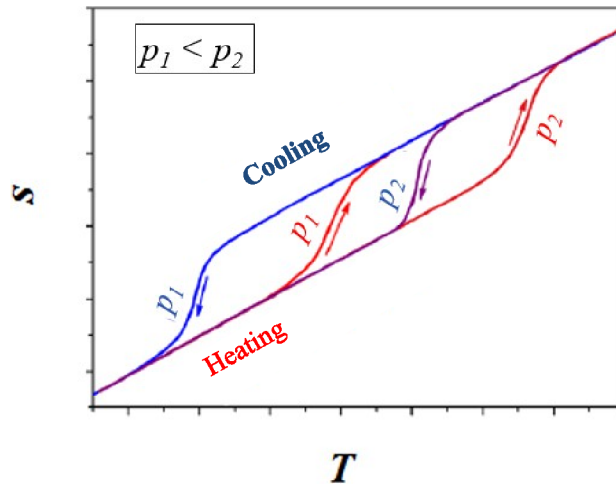


Figure 2.6. Example of isobaric entropy curves at the transition for low (p_1) and high pressure (p_2) [2].

The previous example is used to explain the refrigeration cycle with a solid (Figure 2.7). The cycle begins at point 1, which is low pressure (p_1) and in the high temperature phase. It is adiabatically compressed to the high-pressure curve (p_2), corresponding to point 2 of the figure, causing the transition to the low-temperature phase and causing an increase in temperature. From process 2 to 3, the system is brought into contact with a thermal bath at the initial temperature for the heat to be released at constant pressure to return to the initial temperature (point 1). It should cool from 2 to 3 by the same curve as point 2 (isobaric curve) with no hysteresis. Instead, it first experiences an entropy decrease adiabatically to the cooling curve at the same pressure (point 2b) and then the entropy decreases isobarically. Based on this fact, part of the refrigeration capacity is lost since the jump achieved from 2b to 3 is absorbed. The same problem arises in the remaining part of the cycle: an adiabatic expansion of 3 to 4 is performed to reduce the temperature at the same initial state T . This process causes a transition to the high temperature phase. When the heat absorbed from the system to be cooled increases the entropy, the phenomenon of hysteresis presents again, first as 4b state (adiabatic process); finally the entropy increases isobarically from 3b to 4.



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Consequently, the cycle is reduced considerably and forms 1-2b-3-4b-1. In conclusion, the presence of hysteresis decreases the caloric effect of refrigeration cycles.

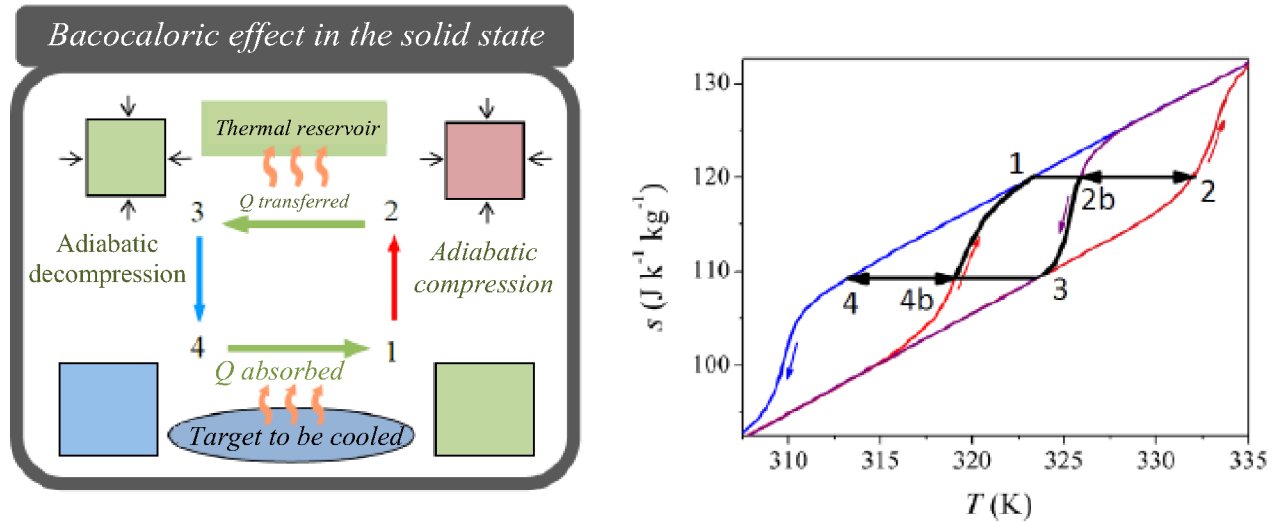


Figure 2.7. Refrigeration cycle of a machine, hysteresis present [2].

Reduction in efficiency has been demonstrated by several studies. An article by B. Emre et al. [4], sets out the following results: a 20-30% reduction in the entropy variation when cycling the material compared to the first time the field is applied in an alloy with magnetic shape memory based on Ni-Co-Mn-Ga-In. In another study, E. Stern-Taulats et al. [5] calculate a 40% reduction in the adiabatic variation of caloric effects due to hysteresis.

3 Experimental methods

As mentioned above, the objective of the project is to search for new refrigerants that undergo large heat exchanges in their change of state. Measurements of a caloric effect can be made in three ways: direct, quasi-direct or indirect.

Firstly, direct measurements, as their name suggests, allow us to determine the variation of isothermal entropy and/or the variation of adiabatic temperature directly. To carry out these measurements, measuring equipment not available in the laboratory is required. For example, a calorimeter that isolates the sample and at the same time increases the pressure.

Then, quasi-direct measurements are made. The quasi-direct method consists of calorimetry measurements at constant pressures, varying the temperature to obtain constant pressure entropy curves as a function of the temperature. It is possible to extract the isothermal entropy variation curves between two different pressures (equation [3.1]) thanks to these curves, and subsequently the adiabatic temperature variation (equation [3.2]) with the knowledge of the calorific capacity.

$$\Delta S_{isotherm}(T, p_1 \rightarrow p_2) = \Delta S(T, p_2) - \Delta S(T, p_1) \quad (3.1)$$

$$\Delta T_{adiabatic} \approx \left(\frac{T}{C}\right) \cdot \Delta S_{isotherm} \quad (3.2)$$

A third option is indirect measurements, which in this case consists of calculating the change in volume at transition. The variation in volume can be measured by two techniques: by observing the X-ray diffraction that passes through the material or dilatometry. The heat capacity obtained by a technique called calorimetry is needed to calculate the adiabatic temperature change from the isothermal change of entropy, which is explained below. With the variation in volume and heat capacity, the equations of Chapter 2 (2.3) and (2.4) can be applied to calculate the caloric effect. This option is not chosen since there is no dilatometry equipment for different pressures. In addition, the quasi-direct method is more precise.

In order to make quasi-direct measurements, isobaric heat variation curves as a function of temperature for different pressure values are needed, and they are then analyzed to obtain enthalpy and entropy curves. These curves are achieved by a method that is known by the name of calorimetry. Calorimetry consists of calculating the changes in heat produced in chemical reactions or by physical changes.

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The instruments used for these tests are calorimeters; there are different types of calorimeters available in the department's laboratory. The differential scanning calorimeter (DSC) and the differential thermal analysis (DTA) one shall be used for this project.

3.1 DSC

DSC has been used to perform experiments at atmospheric pressure. The laboratory has a commercial DSC, model: Q100, brand: *TA Instruments* [6].

The DSC consists of a cell about 9.5 cm in diameter and 10.5 cm in height, formed by a thermostatic block of silver with high mass and conductivity that is heated and cooled continuously when measurements are taken. A schematic representation of the cell can be seen in Figure 3.1. Inside there is a disc of a material called constantan with high thermal conduction, which is an alloy of copper and nickel. The disc has two raised areas of about 5 mm in diameter that act as a platform for two samples. There are welded discs of an alloy based on chromium and nickel known as chromel underneath the platforms; simultaneously the chromel discs are also welded to a cable of the same material. This set of chromel pieces and the constantan disc form the thermocouples.

Thermocouples are the thermoelectric sensors of calorimeters and they work thanks to a weld joining two different metals. A potential passes through the weld when the metals are at different temperatures. A reference sample is measured simultaneously with another thermocouple; thus the voltage differential between the two wires of the thermocouples is measured. The voltage differential values are calibrated for each type of thermocouple. Thus tables of heat differential values are created and entered into the internal calorimeter programs. The thermocouple is used to measure temperatures, taking advantage of the previous chromel wires plus alumel ones (an alloy of nickel, magnesium, aluminum and silicon), which are also welded to the chromel discs.

As can be seen in the diagram, the samples are indirectly connected to the thermostatic block (these samples are the reference sample), with no phase change in the entire range of study and the sample to be studied. When using the DSC, the temperature must be kept the same in both samples.

When the sample to be studied performs a phase transition in the case of a heating experiment, it is maintained at a constant temperature until the transition is completed. Therefore the DSC increases the heat flow in the sample to be studied in order to equalize the temperature of the reference sample that has not stopped rising. Having different flows implies difference change in potential between the chromel thermocouples that returns to zero at the end of the transition.



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Additionally, temperature is controlled by means of liquid nitrogen and a thermal resistance located inside the thermostatic block, allowing a fairly high temperature range compared to other types of DSC, from 120 to 870 K. Both temperature control systems are controlled by *Thermal Solutions* software.

Finally, a purge gas is also introduced in order to thermally homogenize the interior of the cell.

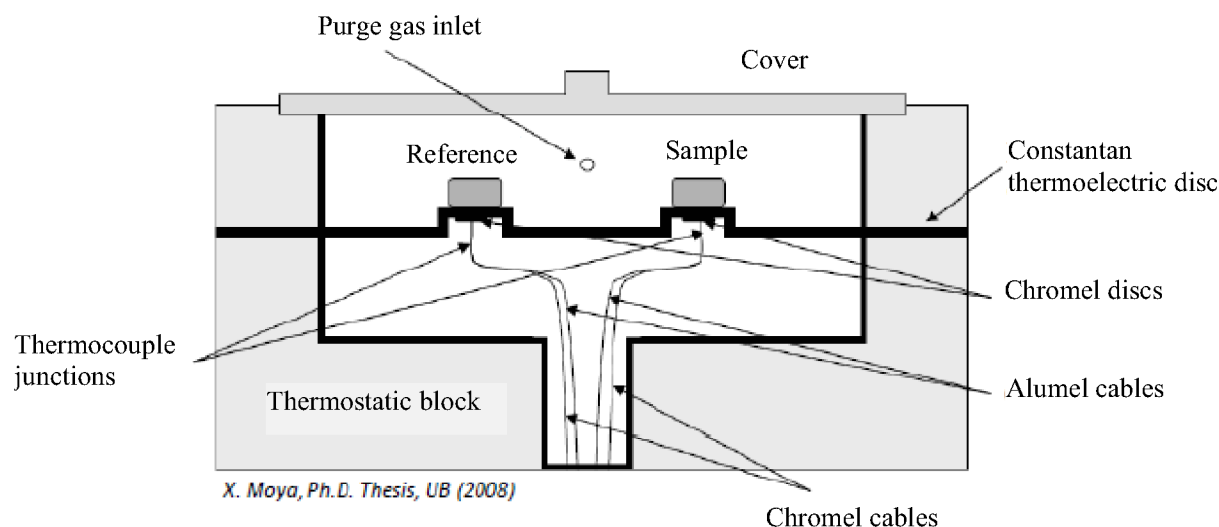


Figure 3.1. Schematic representation of DSC model 2920 (TA Instruments) [6].

The disadvantage of this DSC is that experiments can only be carried out at atmospheric pressure. This makes it necessary to apply another technique, which is explained in the next section. The photograph below (Figure 3.2) shows the DSC in use and in the background you can see the nitrogen cylinders used for refrigeration, which are connected to the DSC by the black tubing.

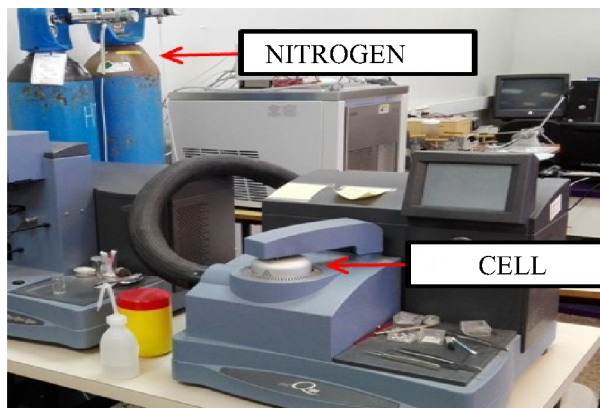


Figure 3.2. DSC model Q100 (TA Instruments).

The samples are placed in the cell in hermetic aluminum capsules 6 mm in diameter (Figure 3.3.a, a key has been included for visual comparison). The capsules are enclosed in special presses (Figure 3.3.b) and the material is weighed on high-precision scales since the DSC needs the value to perform internal calculations. It should be noted that the amount of material introduced is a few milligrams.

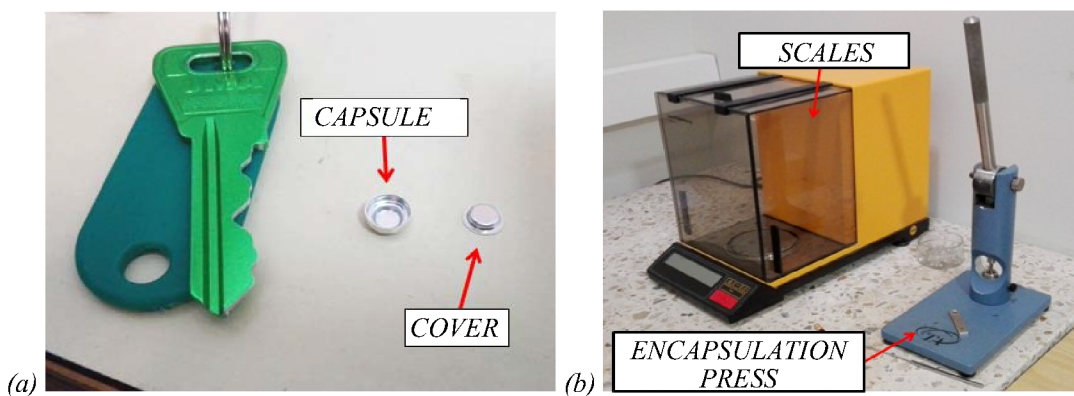


Figure 3.3. Capsule and capsule cap to insert into the DSC (a). Encapsulation press and scales (b).

3.2 DTA

The DTA calorimeter works opposite to the DSC: instead of controlling the temperature and measuring changes in heat flows, the constant flow is monitored and the temperature variation is measured.

There are two types of DTA in the laboratory, one that allows experiments to be carried out up to 6 kbar and another that only reaches 3 kbar. Both have been used since each has a different operating temperature range and, for example, it is not possible to perform NPA experiments in the 3 kbar DTA. This shall be explained in more detail below.

3.2.1 3 kbar DTA

The 3 kbar DTA is non-commercial; it was designed and assembled as part of a degree final project [7].

Figure 3.4 is a diagram of its components and connections.

It is based on a manual pump that sucks compression fluid from a container, closes the valve through the container (adjustable valve) and injects the liquid through capillaries (1.6 mm diameter, green in the figure) to the cell where the sample to be pressurized is located. Before reaching the cell it must go through a non-return valve and an on/off valve that help to keep the pressure constant in the system; between the two valves a bypass has been placed to connect the manganin gauge. Manganin pressure gauges consist of an extensiometric gauge that sends the signal directly to the computer.

The compression fluid is introduced into the two pressure chambers inside the cell (thermal block) with the help of two Bridgman seals (Figure 3.5), one for each chamber. There is a thermocouple at each end of the seals. The sample to be studied is placed in one thermocouple and the reference sample (which is usually left empty) in the other. The thermocouple assembly and the sample are entered into the chambers and the seal is screwed into the cell.

The thermal block consists of a copper cylinder with high thermal conduction, allowing the temperature to be considered uniform throughout the block. The block is heated with a heating element that can heat up to 723.15 K and a power of 400 W and is connected to a controller where the heating ramps are programmed. A Pt-100 probe is also connected to the controller to measure the temperature of the thermal block. Conversely, it is cooled by leaving it at room temperature in the laboratory and with the help of a ventilator.

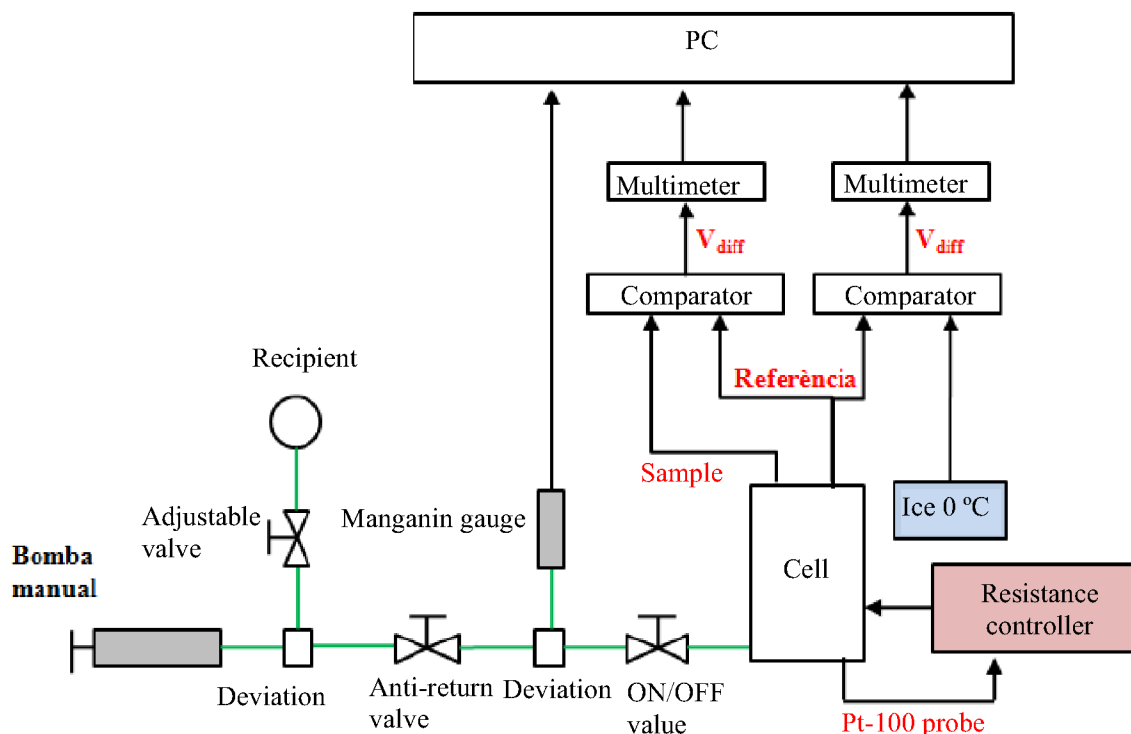


Figure 3.4. DTA diagram (up to 3 kbar).

The thermocouples of the Bridgman seals, which are also made of chromel and alumel as in the DSC, send the signal to comparators. One comparator measures the difference of the signals between the study sample and the reference sample, while another comparator measures the difference between the reference sample and a thermos with water and ice. The thermos with water and ice ensures a reference temperature of 273.15 K (0° C). The result of each comparator is sent to a multimeter to obtain a compatible signal for the computer.

The samples are placed in tin capsules (Figure 3.5.b, the key for visual comparison has also been included) with a liquid (*Galden* perfluorinated fluid from *Bioblock Scientist*) to eliminate air bubbles that could lead to excessive deformation of the capsule due to its high compressibility. In addition, the dilation of the liquid may be underestimated.

Tin capsules are used because this material has high thermal conductivity: it is a metal and is malleable to be able to close the capsule but at the same time it restricts the maximum temperature of the experiments since its melting temperature is 505.05 K.

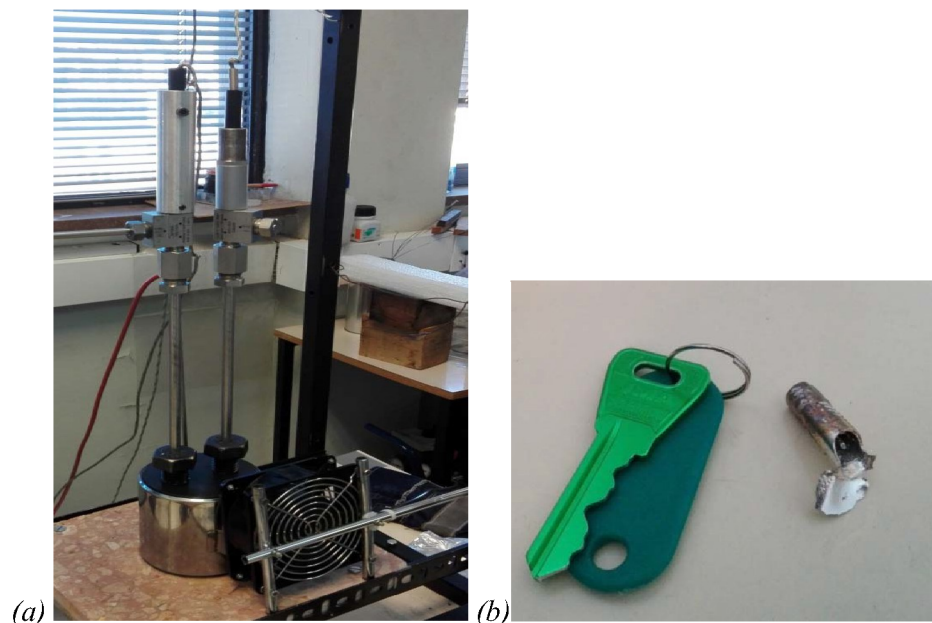


Figure 3.5. Cell and Bridgman seals (a). Tin capsule (b).

The choice of a liquid as a compressor element is due to the fact that liquids allow isotropic (hydrostatic) pressure, unlike solids. A gas also allows it, but as it has high compressibility coefficients, in order to reach the same pressure as with a liquid, a much more concentrated mass is needed, implying three disadvantages: compressor devices are more expensive than those used to compress a liquid, there is a danger of shock wave due to leakage and they have high diffusivity coefficients that can contaminate the study sample. Therefore, liquids are used to compress. The chosen liquids must maintain their state over wide temperature ranges and be able to be used at the working temperature so that they do not experience changes in state during the course of the experiments. After a study of substances and their properties, a silicone (AS100) was chosen, which is in a liquid state from 193.15 to 543.15 K.

It should be noted, however, that the silicone used has a pressure-dependent sensitivity. Sensitivity refers to all those factors in the environment that may affect the calorimetry measurement of the sample. Therefore, this must be taken into account when processing the data obtained. The sensitivity of the calorimeter to be applied to the data can be obtained experimentally with a sensitivity analysis for a sample that does not experience volume changes (Cu-Zn-Al or Cu-Al-Ni type compounds). Knowing that $\Delta V = 0$ and by the Clausius–Clapeyron equation [eq. (2.8)] we obtain that $dT/dp = 0$ and therefore it is deduced that Δs does not depend on the pressure for the calibration samples.

It was concluded that sensitivity could be approximated by a regression line of temperature-dependent parameters [eq. (3.3)].

$$Sens = A(T) + B(T)p \rightarrow \begin{cases} A(T) = A_0 + A_1T \\ B(T) = B_0 + B_1T \end{cases} \rightarrow Sens = A_0 + A_1T + (B_0 + B_1T)p \quad (3.3)$$

Let A_0 , A_1 , B_0 and B_1 be constants with the following values (Table 3.1), S is the factor by which the data obtained with the DTA at pressure p and temperature T must be divided:

A_0	A_1 [K ⁻¹]	B_0 [bar ⁻¹]	B_1 [bar ⁻¹ ·K ⁻¹]
0.994	$-1.580 \cdot 10^{-3}$	$-1.096 \cdot 10^{-4}$	$1.663 \cdot 10^{-7}$

Table 3.1. Coefficients of the sensitivity adjustment extracted experimentally [2].

3.2.2 6 kbar DTA

The operation of the 6 kbar DTA (Figure 3.6) is based on the same pressure injection system as the 3 kbar DTA but with a commercial high-pressure cell model *MV1-30* from *Polish Academy of Sciences* instead of the thermal block with Bridgman seals. The cell head has 5 T-type thermocouples of copper and constantan and 5 electrical signal inputs/outputs. However, two thermopiles are included to have an amplified signal with more sensitivity, since thermocouples break easily. Thermopiles work the same as thermocouples (two different joined metals) but instead of a single pair of metals, several are connected in series or in parallel for greater precision.

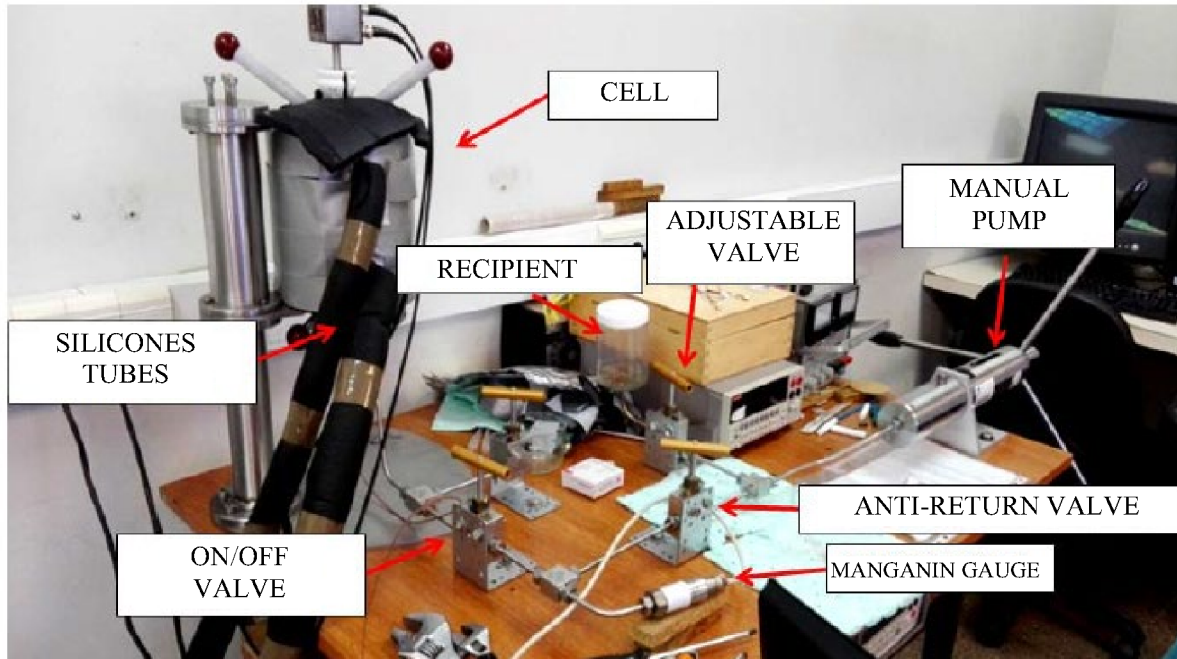


Figure 3.6. Part of the 6 kbar DTA system: cell and pressure system.

The cell is heated and cooled by a LAUDA Proline RP 1290 thermal bath [8] connected to the cell through two silicone tubes insulated from the outside that transport the liquid. A Pt-100 probe is also included to send the temperature signal to the thermal bath in order to minimize errors, allowing an accuracy of ± 0.02 K. The thermal bath is also connected to the computer with software that acts as a controller of the desired temperature ramps.

The working temperature range is from 183.15 to 393.15 K, which limits the ability to carry out experiments on the Tris substance to be studied. The refrigerant is responsible for this drawback: Kryo-51 with an evaporation temperature of 393.15 K.

Conversely, the compression fluid chosen is the DW-Therm M90.200.02 thermo-fluid (brand: Huber). In this case, its calorimetric sensitivity is independent of pressure, so it will not be necessary to calculate the sensitivity factor to correct the data obtained at the end of the experiment.

The rest of the setup is similar to that of the 3 kbar DTA.

4 Plastic crystals

This chapter aims to review the discoveries about caloric effects and the reasons that have motivated the study of the barocaloric effects of plastic crystals.

4.1 History of caloric effects on solids

The first to observe the caloric effect on a solid was Warburg in 1881. He observed a change in temperature in iron due to a change in the external magnetic field (magnetocaloric effect) but the first to propose a practical use as refrigeration techniques were Debye and Giaque in 1926 and 1927, respectively [9]. Since then, numerous investigations have been carried out and better results have been found year after year.

Historically, therefore, magnetocaloric effects have been studied more, but during the last decade it has been shown that many of the materials studied in magnetocaloric effects also present BCEs due to the fact that magnetic transitions have an associated volume change.

The magnitude of the field required by the caloric effects must be taken into account as the former gives a measure of the work that must be carried out in the refrigeration cycle and, therefore, of its efficiency. For example, for the Ni-Mn-In-based shape memory alloy, a pressure of 2.6 kbar is required to acquire a refrigerant power (RC) of 120 J/kg. A magnetic field of 3.5 T is required to achieve the same value due to a magnetocaloric effect. It should be noted that, in practice, only 1 T fields are created with permanent magnets, higher fields are too expensive in terms of energy. Conversely, machines that apply pressures of 2.6 kbar can be easily acquired. However, the effects achieved at such pressures are 20 times greater than the elastocaloric effects [10]. In view of the results, more experiments were carried in 2015 using different compositions of the same alloy, reaching the best result of BCE to date: 2.5 kbar 35 J/(kg K) and 23 J/(kg K) at 6 T [11].

It was again demonstrated in 2011 that one of the most promising materials with giant magnetocaloric effects, the compound La-Fe-Si-Co, gives more caloric effects at a pressure that is more affordable to apply than the required magnetic field: 9.2 J/(kg K) at 5 T and 8.7 J/(kg K) at 2 kbar [12].

Recently, the first BCE study has been carried out on ferroelectric plants, in particular ammonium sulphate, with a BCE value of 60 J/(kg K) [13]. Ferroelectric systems promise great potential in this change, due to their large volume changes in transition.

Thanks to the results of this research, it is concluded that it is necessary to continue studying the caloric effects of applying pressure.

This paper proposes to study BCEs in plastic crystal materials since it has not yet been carried out but it is known that they have a high latent heat value in the plastic transition (explained in the next section).

4.2 Definition

To understand the type of material studied in this paper (plastic crystals), it is necessary to make a brief introduction of what a crystal is.

A crystalline solid or crystal is one that is periodic in its molecular structure, that is, the arrangement of the molecules in the solid is completely homogeneous. Therefore, they form crystal lattices with translational symmetry and the unit cell is defined as the smallest portion of the lattice that can generate the entire crystal lattice by repetition. The intermolecular bonds of crystals are generally thanks to electrons, so the main force that maintains a crystal is the electric force.

There are four types of crystals according to the type of bond between particles: ionic, covalent, metallic and molecular. Ionic crystals are made up of positive and negative ions joined by electrostatic forces; covalents are joined by covalent bonds that occur when atoms share electrons to complete the last shell. Metallic electrons are those that at each lattice point of the crystal are occupied by an atom of the same metal and their electrons are free throughout the lattice, the reason why they are highly conductive. Finally, molecular crystals are formed by non-polar molecules and are joined by Van der Waals forces, very weak forces, and have zero conductivity. They also have low melting points.

That said, we can move on to define plastic crystals.

Plastic crystals are substances that form molecular crystals and are often polymorphic. The solid phases found when the temperature decreases from the liquid phase are called I, II, III, etc. Thus, I is the stable phase between the temperature of transition II to I and the melting point and the one that forms plastic crystals [14]. Phase I is actually a mesophase, but behaves mechanically like solids, an important property for this paper.



Phase I, also called the plastic phase, is made up of globular-shaped molecules, that is, they are practically spherical. This feature is the reason why phase I has more freedom of movement than phase II. The molecules rotate on their axis but without freedom of translation in a phase that is dynamic. The barrier between two positions of minimum potential is small enough and therefore different orientations appear.

In addition, phase I molecules are symmetrical in structure, building a crystal lattice with a body-centered or face-centered cubic (BCC, FCC) structure. The formation of crystal lattices is a property of solids only, which is why phase I is considered another phase of the solid state.

On the other hand, in phase II, the molecules all have the same orientation and do not have freedom of movement. The crystal lattice is usually of tetragonal-unit-cell type but can be orthorhombic or monoclinic, etc.

Figure 4.1 shows the orientation of the molecules through the different phases of plastic crystals. It can be observed that phases I and II retain the crystalline structure (property only of solids) and, on the other hand, the liquid phase does not present any type of structure or orientational order.

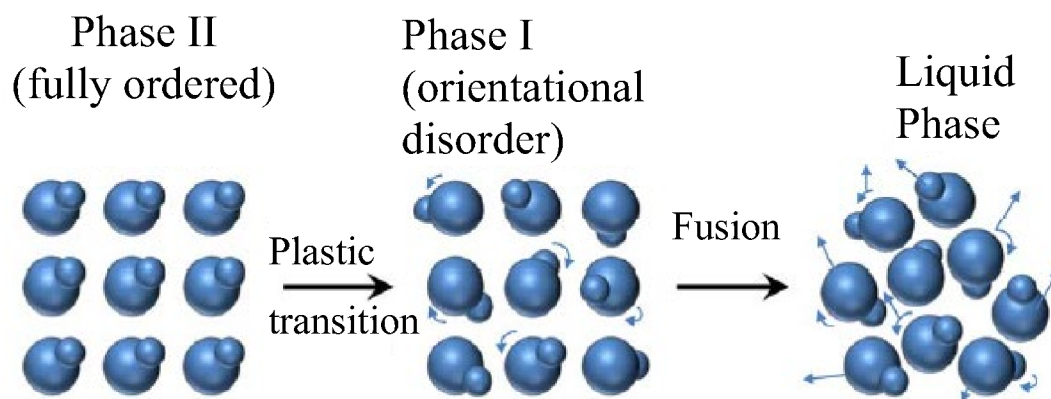


Figure 4.1. Representation of the orientational order according to plastic crystal phases.

The different characteristics of the phases are demonstrated in the fact that from phase II to I there is a considerable increase in entropy. It has also been observed that there is a considerable change in volume between the two phases and that it is practically independent of pressure [15], unlike fusion where the change in volume decreases with increasing pressure. In any case, the finite change in volume indicates that the transition is of the first order (explained in section 2.2.1). These are the properties to take advantage of to achieve giant caloric effects.

It has been experimentally discovered in plastic crystals that the variations in transition entropies between solid phases are greater than those of fusion. This property is very interesting in the present case study, where a refrigerant that works in a solid state is desired.

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It is interesting to know that some plastic crystals have an intermediate phase between I and II with practically no orientation order, which sometimes only appears at high temperatures.

As seen in Figure 4.2, there is a point where the solid and fusion transition curves intersect. At higher pressures, only the liquid and ordered phases are found.

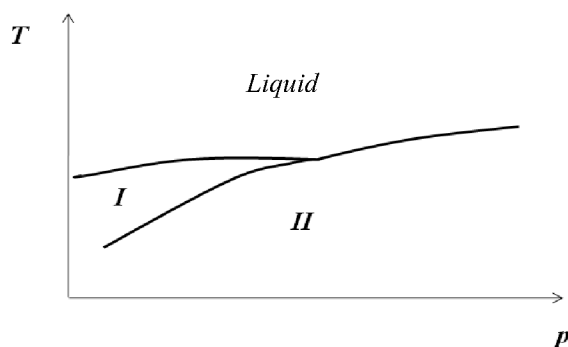


Figure 4.2. Diagram of the plastic crystal phases in a T - p diagram.

4.3 Materials under study

This paper deals with experiments carried out with two different materials: both plastic crystals. The first is *tris(hydroxymethyl)aminomethane* and the second is *2,2-Dimethyl-1-propanol-99%*. For brevity, they are cited as Tris and NPA, respectively, and Table 4.1 summarizes their properties.

Properties	Tris	NPA
Molecular formula	$\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3$	$(\text{CH}_3)_3\text{CCH}_2\text{OH}$
Structural formula		
Molecular mass (g/mol)	121.14	88.15

Plastic transition temperature (K)	406.8	236.5
Fusion temperature (K)	442.7	331.4
$\Delta H_{\text{plastic transition}}$ (J/g)	280.67	45.38
ΔH_{fusion} (J/g)	26.0	44.24
$\Delta S_{\text{plastic transition}}$ (J/K·kg)	690.94	0.19
ΔS_{fusion} (J/kg)	58.77	0.13
$[dT/dp \text{ (K/kbar)}]_{\text{plastic transition}}$	6.06	23.70
High T phase crystalline structure	BCC	FCC
Low T phase crystalline structure	Orthorhombic	Tetragonal

Table 4.1. Main properties of both materials used [16], [17].

5 Data analysis

The following chapter explains, step by step, the experiments carried out for each of the materials that are intended to be studied. First, the curves are extracted at atmospheric pressure in the DSC as are the curves for different pressures in the DTA. Finally, the curves are processed with the *Origin* computer program to calculate the caloric effects.

5.1 DSC experiments

For both cases, the material has been introduced into aluminum capsules to make a calorimetry measurement at atmospheric pressure with the DSC. It is necessary to know the mass in each capsule since the DSC software program will be able to perform a series of calculations, such as obtaining the C_p (heat capacity at constant pressure) and the variation of enthalpy and entropy in the transitions. The DSC results are used to calibrate the data obtained by nonzero pressures with the other techniques (DTA). The calibration is due to the fact that differential voltages supplied by thermocouples are actually obtained from high-pressure calorimeters.

As for the DSC, experiments are designed knowing the phase change temperatures of the literature (Table 4.1) so that the sample experiences plastic transition and fusion. Different experiments are carried out at different heat flow rates. It is important to take into account the temperature of the fusion because if it is brought to a temperature that is too much higher than the fusion temperature, it is likely that the vapor pressure will be too high and the sample will leak out of the capsule, causing the sample to lose too much. If this happens, the calculations made with subsequent transitions are wrong. Therefore, a new sample must be re-encapsulated, weighed and the experiment repeated. In conclusion, the ramps must be programmed in such a way that it begins to cool down as soon as the transition from phase I to liquid has finished.

The most relevant curves obtained with the DSC are given below. Figure 5.1 shows a sample of Tris of 7.28 mg in phase II at room temperature, heated to 5 K/min and going through plastic and fusion transition (endothermic processes). Subsequently, it is followed by cooling at the same rate until the two reverse transitions (exothermic processes) are achieved. Then, the result is a cycle between 280 and 465 K, approximately; arrows have been drawn to indicate the direction followed in the process.

It should be noted that it can be seen, with the naked eye, that the plastic transition absorbs much more heat than fusion, a common property in plastic crystals as mentioned above. Conversely, when cooling, the transition from liquid to plastic phase (I) occurs only a few degrees lower than the transition from plastic to liquid phase when heating. On the other hand, the transition from plastic phase to ordered phase (II), in cooling, is about 60 degrees less than the transition temperature for heating. This phenomenon has been explained in chapter 2.1; it is the hysteresis of the material. It should be remembered that it is not advisable to use materials with a great deal of hysteresis as it reduces or eliminates the reversible caloric effects that can be implemented in a cyclic operation refrigeration machine.

As can be seen in the case of NPA, hysteresis is much lower (Figure 5.3), only around 20 degrees. The high hysteresis of Tris means that the transition peaks from phase I to II in cooling are very elongated (even going beyond the graph); this is because they undergo a very abrupt phase transition.

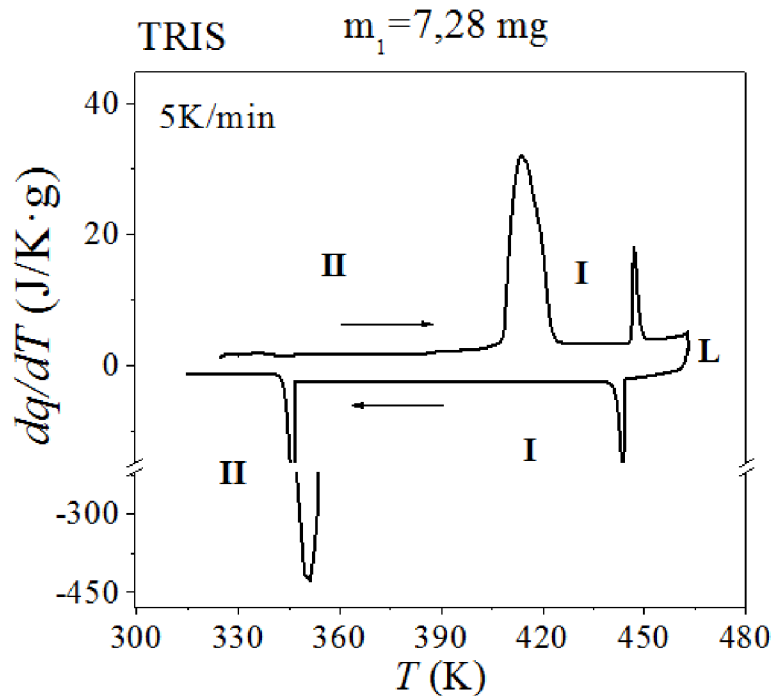


Figure 5.1. DSC curve with plastic transition and fusion at 5 K/min for the first Tris sample of 7.28 mg.

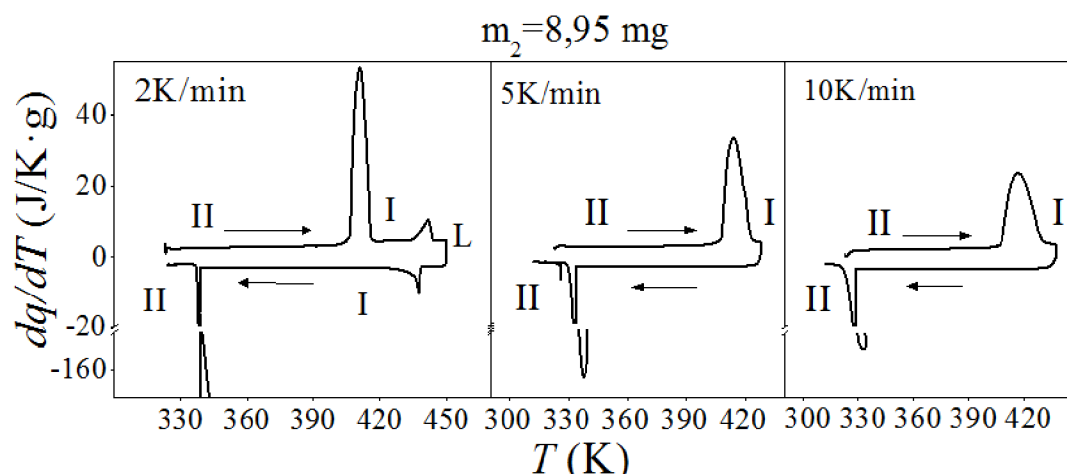


Figure 5.2. DSC curves at 5, 10 and 2 K/min for the second Tris sample of 8.95 mg.

Figure 5.2 shows three more curves for the second sample of Tris of 8.95 mg at different rates: 2, 5 and 10 K/min; fusion is only present in the first, the others only undergo plastic transition. It should be noted that the lower the heat flow rates, the narrower and higher the curves in the transitions. The reason for this is that there needs to be an equal enthalpy variation, meaning that it must have an equal area. Therefore, if the transition is made more slowly, the temperature range in which the transition lasts is smaller, implying a higher peak. This situation also causes the temperatures of the calorimetric peaks to vary according to the rate of heating. Consequently, the transition temperature is generally determined as the peak start temperature. More specifically, the temperature at which the maximum slope of the calorimetric peak crosses the baseline.

On the other hand, Figure 5.3, corresponding to the NPA, shows that the two transitions are of similar magnitudes to each other.

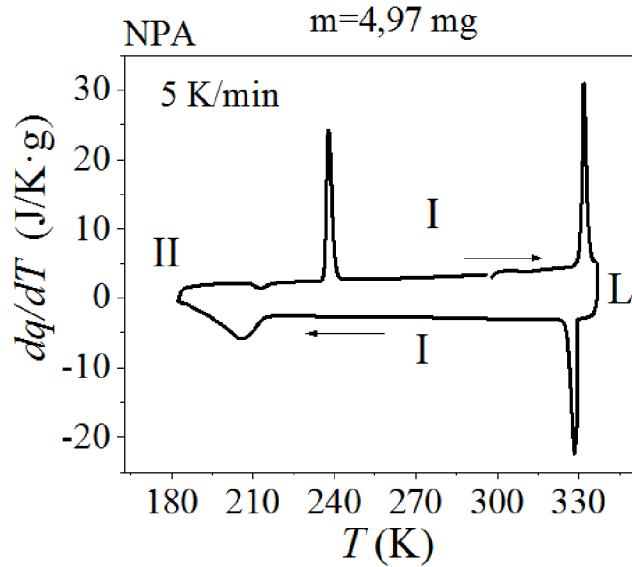


Figure 5.3. DSC curve with plastic transition and fusion at 5K/min rate for the NPA sample of 4.97mg.

Once the curves have been obtained, they are integrated into the transitions as a function of the temperature to obtain the enthalpy. In reality, DSC performs curves in watts, therefore, a unit change must be made. The changes in enthalpy and transition entropy are calculated with equations (5.1) and (5.2). Tables 5.1 and 5.2 show the most relevant results extracted from the DSC of the two materials and the average that is then needed to calibrate the results obtained with the other experimentation techniques (DTA). To calculate the averages, the results that differ most from the majority or the values of the literature have been discarded.

$$\Delta h_t = \frac{1}{m} \int_{T_i}^{T_F} \left(\frac{dQ}{dt} \frac{1}{\dot{T}} \right) dT \quad (5.1)$$

$$\Delta s_t = \frac{1}{m} \int_{T_i}^{T_F} \left(\frac{\left(\frac{dQ}{dt} \right) \frac{1}{T}}{\dot{T}} \right) dT \quad (5.2)$$

Mass (mg)	$\frac{dT}{dt}$ (K/min)	Heating or cooling	$ \Delta h_t $ (J/g)	$ \Delta s_t $ (J/kg·K)
7.28	5	Heating	280.1	681.8
7.28	5	Cooling	203.7	585.4
7.28	2	Heating	270.6	663.5

8.95	5	Heating	284.8	685.7
8.95	10	Heating	290.2	698.4
8.95	10	Cooling	202.9	605.5
Average		Heating	281.4	682.4
		Cooling	203.1	599.3

Table 5.1. Results of the Tris DSC.

Mass (mg)	$\frac{dT}{dt}$ (K/min)	Heating or cooling	Δh_t (J/g)	Δs_t (J/kg·K)
4.97	5	Heating	239.7	203.9
4.97	5	Cooling	200.5	197.3

Table 5.2. Results of the NPA DSC.

In principle, the absolute value in heating and cooling a transition must be equal. Once again, the difference in the values in heating and cooling is explained by hysteresis (Section 2.2.2). It can be seen that the values of NPA are less disparate because it has less hysteresis than Tris.

5.2 DTA experiments

As explained in section 3.2, the laboratory has two differential thermal analysis (DTA) systems. One works up to 6 kbar and the other up to 3kbar. The high-pressure chamber works at a temperature range of 183.15 to 393.15 K. This is why it is used for NPA experiments since its range can handle the transition. On the other hand, the 3 kbar system works at a higher temperature range, up to the fusion temperature of the tin capsule: 505.05 K. That is why the Tris experiments are carried out in this equipment. Because of these restrictions, curves of up to 3 kbar are obtained for Tris and, on the other hand, curves of up to 6 kbar are obtained for NPA.

In addition, due to the cooling of NPA and due to hysteresis, it has not been possible to reach the sufficiently low transition temperatures due to the pressures from zero to 0.5 kbar. Therefore, the tests have not been carried out for such pressures.

It is important to note that the experiments have taken into account the expansion of the compression liquid as the temperature rises, causing an increase in pressure. In other words, when one wants to look at the transition at a certain pressure, the pressure before starting the trial must be less than the one one wants to study. An approximation of the initial pressure of the test can be calculated by calculating the pressure slope as a function of the temperature (dp/dT) of the experimental data, in a first test curve. For the 6 kbar cell the variation of pressure with temperature is approximately 10 bar/K, while for the 3 kbar cell it is 1 bar/K. In the case of the 3 kbar cell (where experiments have been carried out on Tris) it has been decided to underestimate variation when designing the experiments.

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Each cycle of heating and cooling to a certain pressure is stored in a file with the temperature, pressure and voltage differential data for each second, which is the period chosen before starting the experiment. These files are treated and analyzed in the *Origin* program minus the integral to calculate the enthalpy, entropy and transition start temperature, which is done in the *CALATO* 9.BAS program. This program is designed exclusively for the integration of calorimetric signals in BASIC version 6.0, January 2001. The integral is not performed directly in *Origin* because its method is not as accurate since it uses a more imprecise derivative.

Figures

Figure 5.4 and Figure 5.5 show the curves that are entered into the *CALATO* program to make integrals.

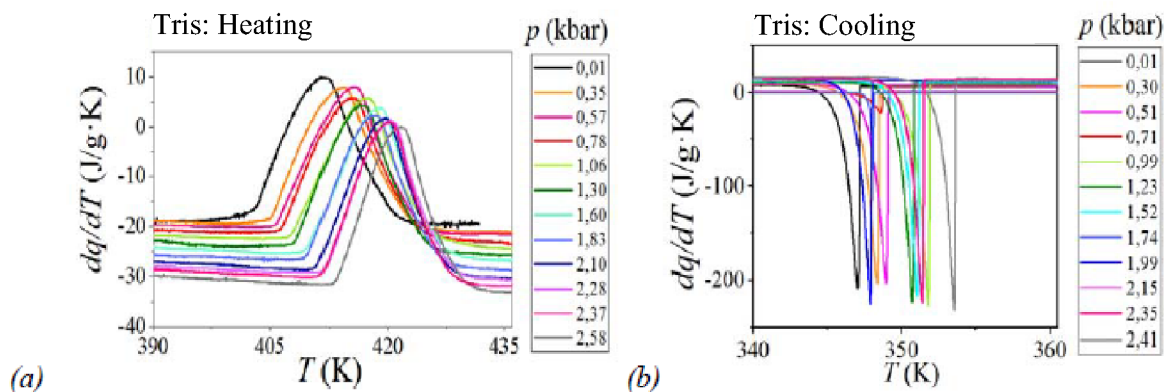


Figure 5.4. Calorimetric signal as a function of temperature for the Tris heating (a) and cooling (b) process.

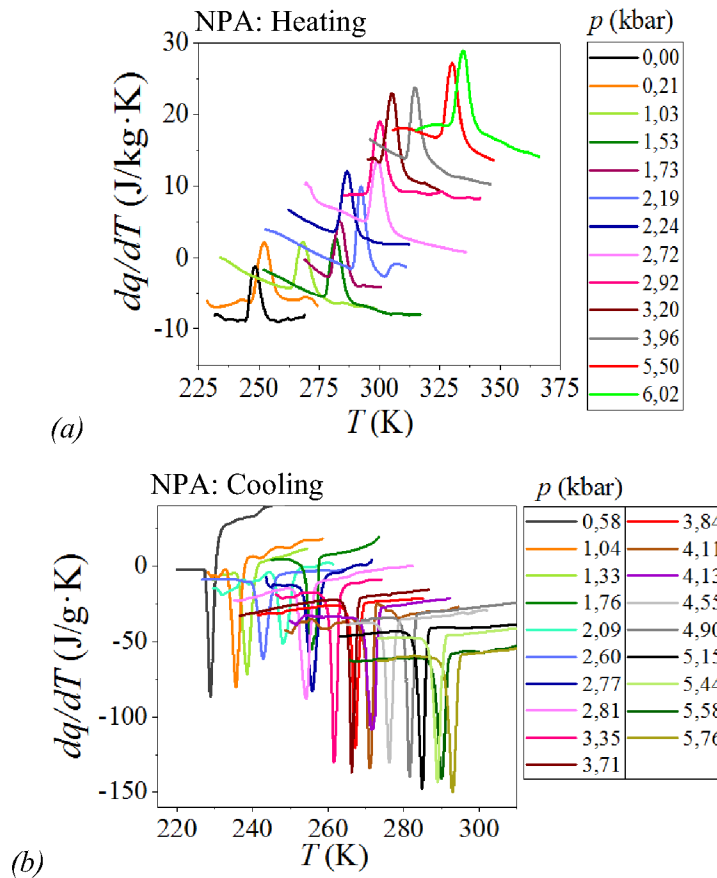


Figure 5.5. Calorimetric signal as a function of temperature for the NPA heating (a) and cooling (b) process.

Once the transition start temperatures have been obtained, a regression is made with the pressure and temperature data collected with the DTA to find out exactly at what pressure it occurs. The results obtained are shown in Figure 5.6, where the great hysteresis of Tris is once again evident, with almost 60 degrees of difference between the transition temperatures in heating and cooling. This characteristic of Tris makes the material unsuitable for use in cyclical machines. On the contrary, the NPA shows a behavior with much less hysteresis and is, therefore, completely reversible by a cyclic machine from a minimum of approximately 1.7 kbar: the temperature is observed in the heating to zero bars and for this temperature, the corresponding pressure is sought (minimum pressure at which there is reversibility) in cooling. That is, simulating the high-temperature to low-temperature isothermal process of the hysteresis refrigeration cycle (Figure 2.7).

The experimental dT/dp slope of the adjustment line of the transition temperatures as a function of the pressure of Tris (Figure 5.6.a) is almost half of the value provided by the literature. Perhaps this may have to do with the experimental methods in which they were obtained. With respect to NPA, it begins with a fairly similar slope (22.1 K/kbar compared to 23.7 K/bar in the literature) but is not constant and decreases with pressure. (Figure 5.6.b). On the other hand, the conventional behavior of the barocaloric effect can be observed: the temperature increases as the pressure increases.

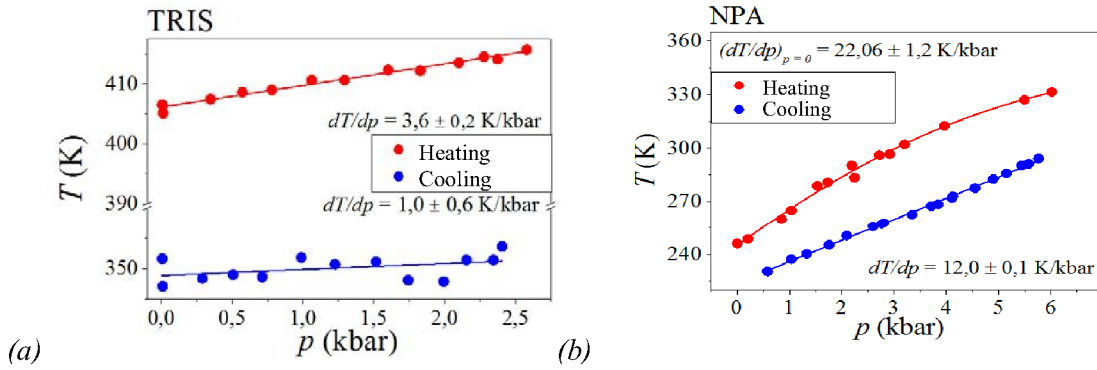


Figure 5.6. Transition temperatures as a function of pressure for Tris (a) and NPA (b).

Next, the values of enthalpies and entropies obtained with *CALATO* are calibrated with the value obtained in DSC, since in reality what we obtain with DTA are voltage differences and the magnitudes must be calibrated.

Parameter Y refers to uncalibrated enthalpies resulting from *CALATO* analysis and parameter Z refers to uncalibrated entropies. A linear regression of Y with respect to pressure is performed. Next, it must be supposed that the ordinate of origin of the regression line is the enthalpy at zero bars achieved with DSC. Therefore, dividing the entropy at atmospheric pressure by the intersection of the regression line gives the corrective factor to be applied to all virtual entropies.

For a resulting regression line such as (5.3):

$$Y(p) = a + bp \quad (5.3)$$

The correction factor (CF) is (5.4):

$$CF = \frac{\Delta h_t(p = 0 \text{ bar})}{a} \quad (5.4)$$

The appendix contains the tables of values of the transitions for the pressures studied.

Figure 5.7 shows the entropy (a) and entropy (b) values of transition after calibration of Tris and Figure 5.8 the same for NPA. The red dots correspond to the transitions due to heating and the blue dots to cooling.

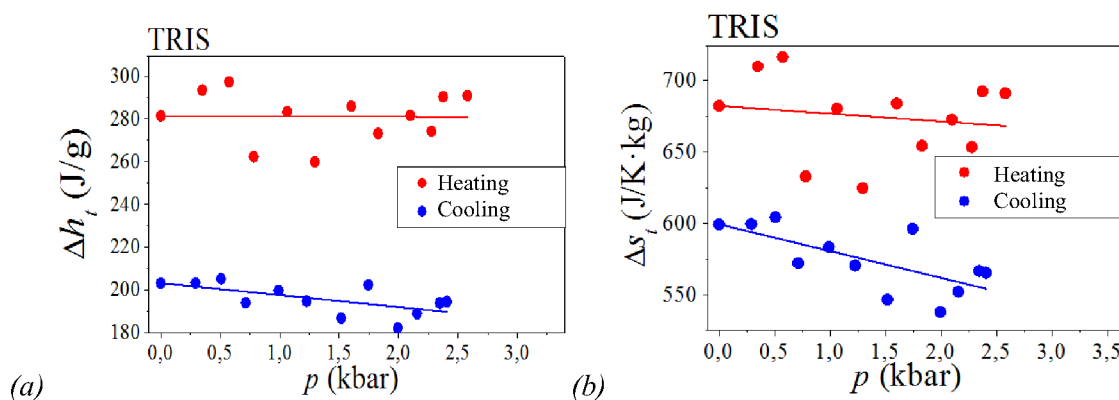


Figure 5.7. Enthalpies (a) and entropies (b) of Tris transition as a function of pressure. Heating is marked in red and cooling is marked in blue.

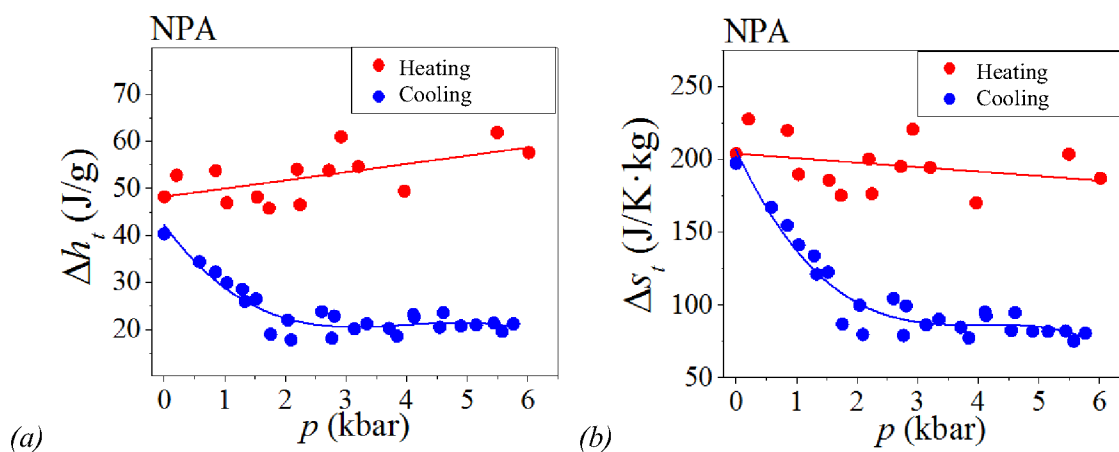


Figure 5.8. Enthalpies (a) and entropies (b) of NPA transition as a function of pressure. Heating is marked in red and cooling is marked in blue.

Of note is that in almost all cases, a linear adjustment can be made, except in the case of NPA cooling, which require third-degree regressions.

The following graphs (Figure 5.9 and Figure 5.10) that correspond to the entropy variation have been extracted from the cumulative integral and the value of the transition entropy following equation (5.5). Knowing that the cumulative integral obtained with *CALATO* is:

$$x(T) = 1 - \frac{\int_{T_I}^T \frac{\dot{Q}}{\dot{T}} dT}{\int_{T_I}^{T_F} \frac{\dot{Q}}{\dot{T}} dT} \rightarrow \int_{T_I}^T \frac{\dot{Q}}{\dot{T}} dT = \Delta s(T) = (1 - x(T)) \int_{T_I}^{T_F} \frac{\dot{Q}}{\dot{T}} dT \quad (5.5)$$

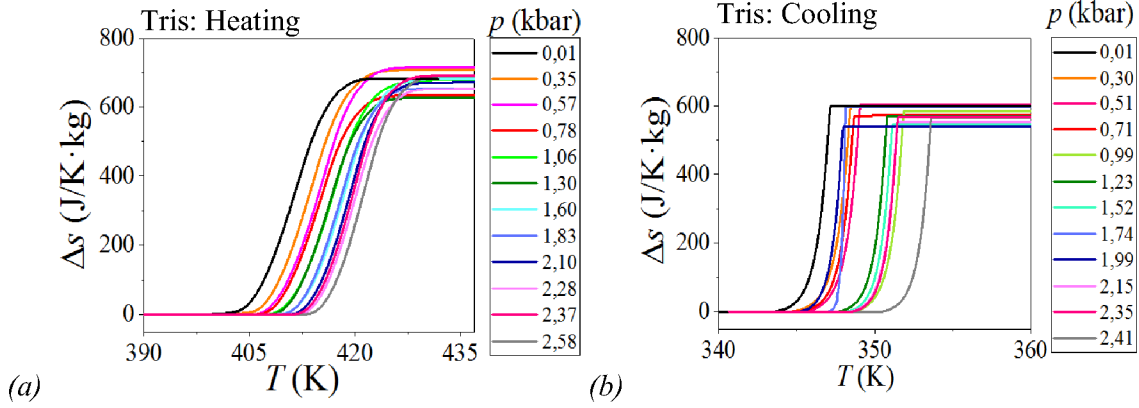


Figure 5.9. Variation of heating entropy (a) and cooling entropy (b) in the Tris transition as a function of temperature at different pressures.

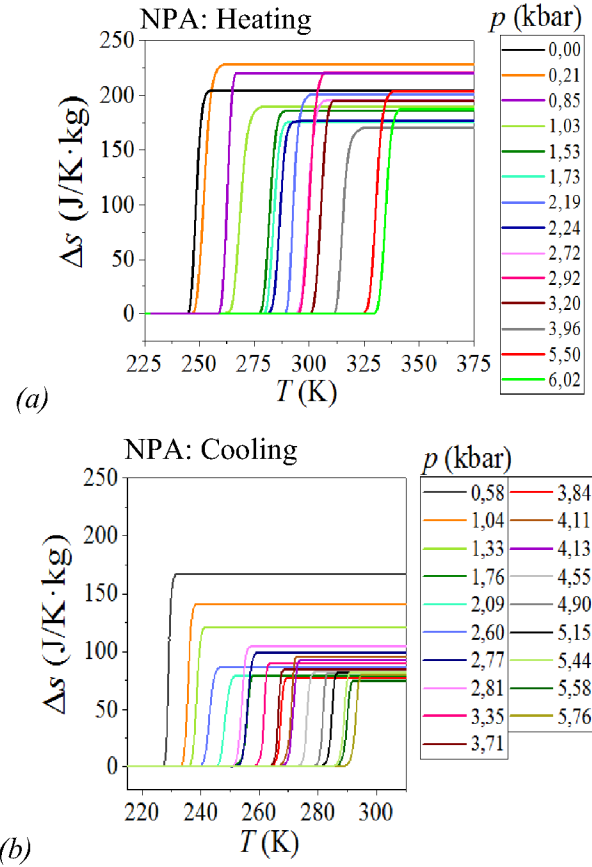


Figure 5.10. Variation of heating entropy (a) and cooling entropy (b) in the NPA transition as a function of temperature at different pressures.

With regard to the cooling curves of NPA (Figure 5.10.b), it should be noted how it reduces considerably with the increase in pressure. Applying this condition to the Clausius–Clapeyron equation [eq. (2.8)] and knowing that dT/dp is constant (Figure 5.6.b), it is deduced that there is a change in volume in the transition. By the same reasoning and looking at the heating of NPA, the entropy variation remains constant as the pressure increases, while dT/dp decreases, so it is again concluded that as the pressure rises, the volume variation decreases. This fact explains the need for adjustment with a second-degree equation for the transition temperatures in the heating of NPA.

At this point, the barocaloric effect can be calculated by doing the rest of the entropy variations at a given pressure minus the lowest pressure, which is zero pressure, except in the case of NPA cooling, which is 0.58 kbar.

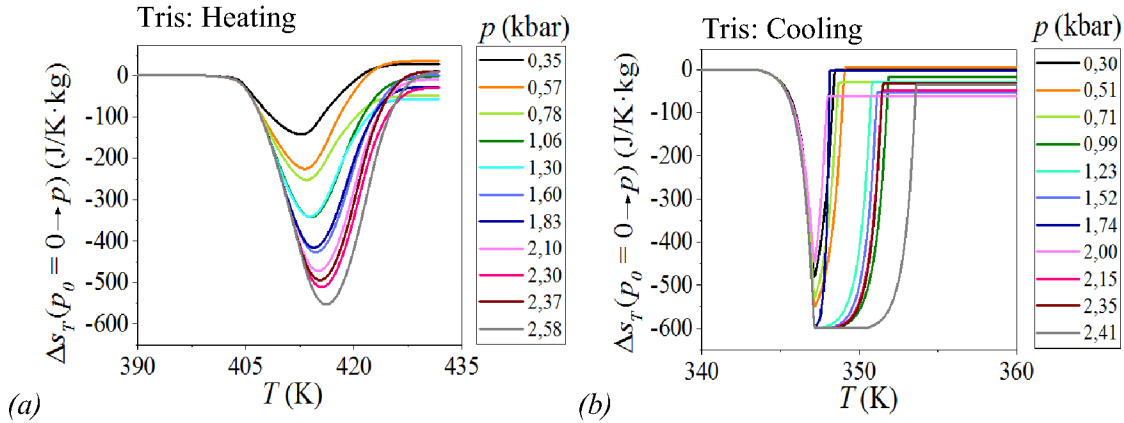


Figure 5.11. Entropy variation in an isothermal compression process from atmospheric pressure to the pressure indicated by each curve. The heating (a) and cooling (b) curves correspond to Tris.

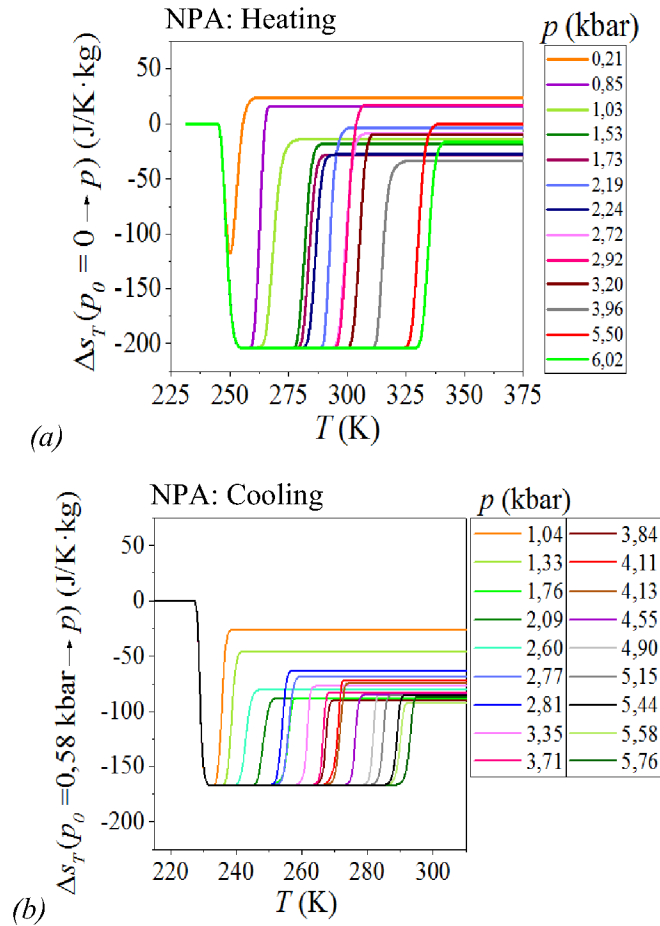


Figure 5.12. Entropy variation in an isothermal compression process from atmospheric pressure for heating (a) and from 0.58 bar for cooling (b) to the pressure indicated by each curve. The curves correspond to NPA.

As mentioned, we have reversibility only in the case of NPA from 0.58 kbar. The entropy variation curves in a cycle can be calculated by taking the entropy variation cooling curves of each pressure (Figure 5.10.b) and then subtracting the entropy variation in heating at zero pressure, instead of cooling at zero bars.

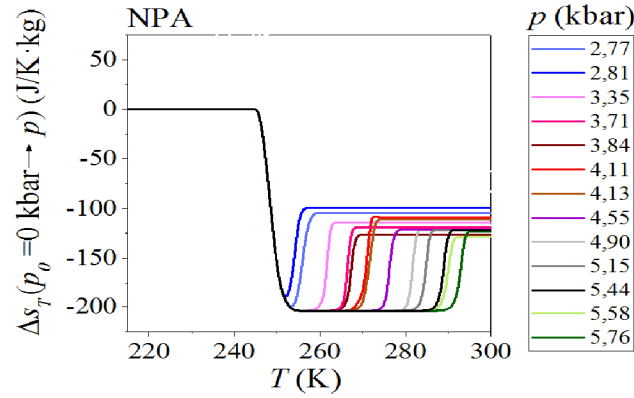


Figure 5.13. Caloric effect of NPA in a reversible cycle.

Finally, the calorific value (RC which stands for relative capacity) can be calculated with the equation:

$$RC = \Delta s_{max} FWHM \quad (5.6)$$

Where Δs_{max} is the maximum caloric effect at a pressure and $FWHM$ is the range of temperatures that have the value of half Δs_{max} . The calorific value of NPA cooling has not been calculated since the curves are not available for half of their maximum and to be able to know the temperature range. Figure 5.14 shows the values of Tris (a) and NPA as a function of pressure.

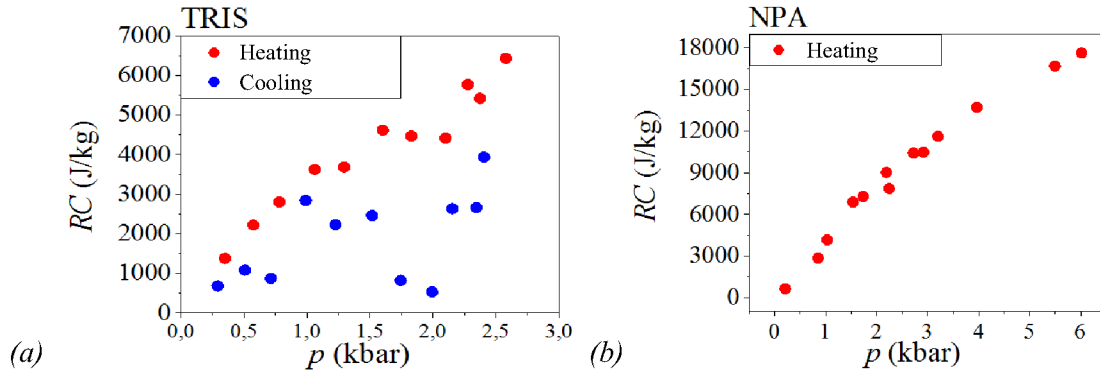


Figure 5.14. Calorific capacity of Tris (a) and NPA (b) as a function of pressure.

Below is a summary of the process carried out for the barocaloric study of Tris and NPA (Figure 5.15). The red boxes represent the technique, method or equation used and the green boxes represent the data obtained.



Figure 5.15. Diagram of the experimentation process to obtain the caloric effect.

Other parameters can be calculated to provide more information once the caloric effects have been obtained. For example, barocaloric strength (BCS), indicating the pressures at which maximum performance is obtained [eq. (5.7)].

$$BCS = \frac{\Delta s_T}{\Delta p} \quad (5.7)$$

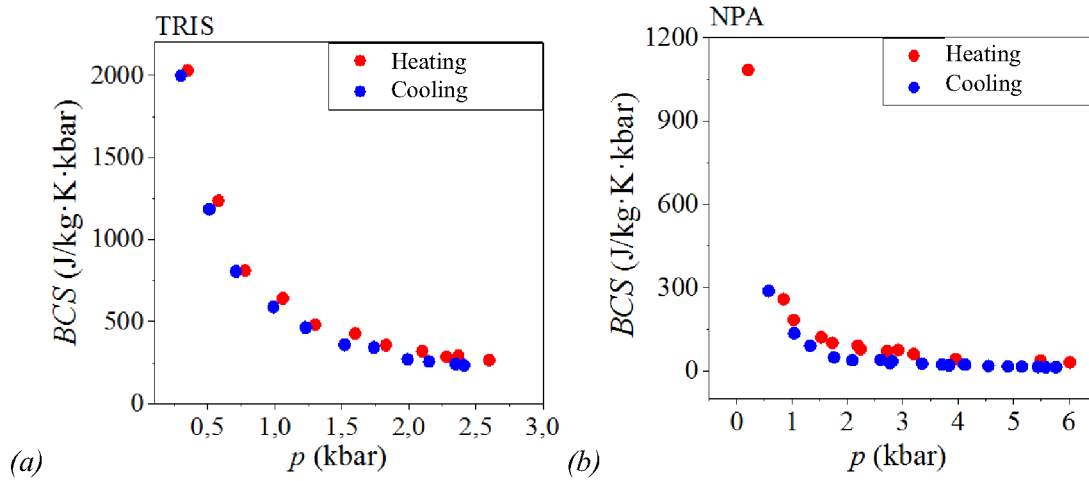


Figure 5.16. Barocaloric strength as a function of the pressure of the Tris (a) and the NPA for heating (in red) and cooling (in blue).

Figure 5.16 shows the decreasing behavior of the barocaloric strength value as the pressure increases, i.e. its maximum value is in the smallest magnitude of the pressure field.

Finally, the volume change at transition can also be calculated using the Clausius–Clapeyron equation (2.8) as can be seen in Figure 5.17. The results of NPA are to be expected for the nonlinear behavior of the transition temperature as a function of the pressure in heating (Figure 5.6.b) and the nonlinear behavior of the entropy variation in the transition of the cooling (Figure 5.8.b.).

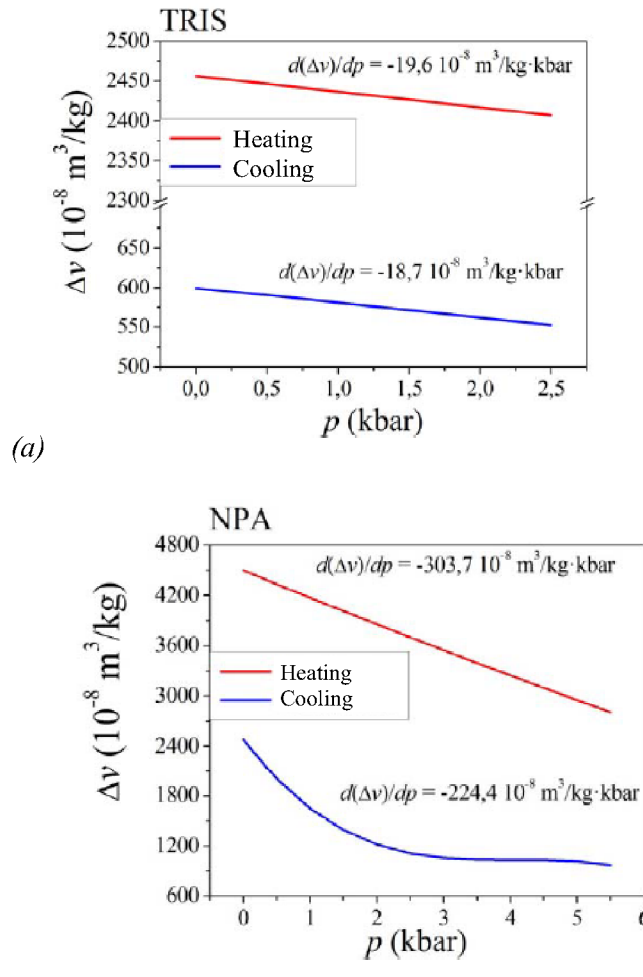


Figure 5.17. Volume variations in the transition of Tris (a) and NPA (b) due to heating and cooling.

5.3 Errors

It has been considered appropriate to introduce a section to estimate the reliability of the results, since there are certain errors that accumulate throughout the experiment at each step.

Firstly, with regard to DSC, the following errors may occur: when measuring the mass of the material inside the capsule (very small due to the great precision of the scale), in the calorimetric signal, calibration and, finally, in differences according to the integration interval which is the greatest source of uncertainty.

Secondly, with regards to DTA there is an error in the calorimetric signal, in the measurement of temperature, in the calibration and in the integration interval. Calibration is carried out with the data obtained in the DSC, which implies that all the accumulated errors in the DSC and separately, the error of calibrating the compressor fluid, must be included. It should be noted that the curves in the DTA are more irregular and this means that the choice of the integration interval usually presents more error.

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For all these reasons, an error of around 10% is estimated in the results obtained by the BCEs and the RCs. It is worth mentioning that no error bars have been placed in the project but that there are enough statistics for the dispersion of the measurements to give us an estimate of the magnitude of the error.

5.4 Comparison of results

The aim of this section is to compare the values obtained from the BCE with other substances previously studied, in order to be able to draw conclusions. The first three substances in Table 5.3 are refrigerants that are currently used for vapor compression systems, so the value of the entropy variation and temperature belong to the evaporation variation. The rest of the table contains the most remarkable results that have been obtained in the research to date. It has been decided to make the comparison with the data obtained at pressures of approximately 2 kbar since the other results are also around these pressures. In addition, it is a relatively easy field to apply in practice.

<i>Material</i>	<i>State</i>	<i>p(kbar)</i>	<i>T (K)</i>	<i> \Delta s_t (J/kg·K)</i>	<i>RC (J/kg)</i>
R-134a [18]	Vapor	1.0	247	1825	-
R-22 [18] ; Error! Reference source not found.	Vapor	1.0	116	1745	-
Ammonia [18]	Vapor	0.0	240	5820	-
Ni_{49.26} Mn_{36.08} In_{14.66} [10]	Solid	2.6	293	24	120
LaFe_{11,33} Co_{0,47} Si_{1,2} [12]	Solid	2.0	237	8.7	180
Fe₄₉Rh₅₁ [4]	Solid	1.1	308	12.5	105
Ammonium sulfate [13]	Solid	1.0	219	60	276
Tris [values obtained in this paper]	Solid	2.1	414	673	4417
NPA [values obtained in this paper]	Solid	2.2	290	200	9029

Table 5.3. Caloric effects of different substances.

Seeing the results, it can be compared with the best value prior to the study, ammonium sulfate. For isothermal entropy variations, we obtained results almost 11 times better for Tris and a factor of 3 for NPA. On the other hand, for RC there is an increase of 16 for Tris and 33 for NPA.

It is important to note that we currently do not yet have the magnitudes of current refrigerants such as R-22

6 Time planning and costs:

The estimate of the time invested in the project can be seen in Table 6.1. Neither the hours for searching for information nor the time invested in writing the paper have been taken into account.

Task	Estimate	Approximate number	Hours
DSC experiments	2 hours/experiment	10 experiments	20
DTA experiments at low pressure	2 hours/experiment	15 experiments	30
DTA experiments at high pressure	2 hours/experiment	30 experiments	60
Data processing	40 hours/material	2 materials	80
		Total	190

Table 6.1. Hours needed to carry out the study.

An approximation of the cost of the project has been drawn up and broken down by costs related to the machines required (Table 6.2, Table 6.3 and Table 6.4) for the drawing up of the paper and the consumable products used (Table 6.5). In terms of machinery, the device to assemble the DSC capsules and the high-precision scale have not been included, due to the short time they are used compared to their useful life, rendering them negligible.

6 kbar DTA		Unit price	Units	Price (€)
Wall support	Polish Academy of Sciences [17]	1256.00	1	1256.00
MVI-30 container	Polish Academy of Sciences	16106.00	1	16106.00
Apparatus for electrical measurements	Polish Academy of Sciences	4000.00	1	4000.00
Proline thermal bath RP 1290	LAUDA [20]	1200.00	1	1000.00
Manual pump	Sitec [7]	3359.66	1	3359.66

Deviation	<i>Sitec</i>	132.22	2	264.44
Adjustable valve	<i>Sitec</i>	356.40	1	356.40
Non-return valve	<i>Sitec</i>	745.26	1	745.26
ON/OFF valve	<i>Sitec</i>	297.50	1	297.50
Capillary (D = 1.6mm)	<i>Sitec</i>	59.35	4	237.40
Pt-100 probe	<i>Sitec</i>	53.20	1	53.20
Multimeter	<i>Hewlett Packard</i>	1250.00	2	2500.00
Manometer	<i>Martin-Marten</i>	811.37	1	811.37
Thermopiles	<i>RS Components [21]</i>	134.34	6	806.04
			Total	31793.27

Table 6.2. Prices of the elements of the 6 kbar DTA.

DTA 3kbar [7]	Brand	Unit price	Units	Price (€)
Manual pump	<i>Sitec</i>	3359.66	1	3359.66
Deviations	<i>Sitec</i>	132.22	2	264.44
Adjustable valve	<i>Sitec</i>	356.40	1	356.40
Non-return valve	<i>Sitec</i>	745.26	1	745.26
ON/OFF valve	<i>Sitec</i>	297.50	1	297.50
Capillary (D = 1.6mm)	<i>Sitec</i>	59.35	4	237.40
Temperature controller	<i>Sitec</i>	2043.45	1	2043.45
Thermal resistance	<i>Schlee and Co.</i>	111.79	1	111.79
Pt-100 probe	<i>Sitec</i>	53.20	1	53.20
Type K thermocouples	<i>Schlee and Co</i>	43.87	3	131.61
Multimeter	<i>Hewlett Packard</i>	1250.00	2	2500.00
Thermos	<i>Sitec</i>	50.00	1	50.00
Ventilator	<i>Sitec</i>	40.00	1	40.00
Thermal block	<i>CLALMSX</i>	169.49	1	169.49
Measuring cell	<i>Taller</i>	182.11	1	182.11
Bridgman seal	<i>Taller</i>	147.17	2	294.34
Machining bolts and tools	<i>Sitec</i>	4350.65	1	4350.65
Manometer	<i>Martin-Marten</i>	811.37	1	811.37
			Total	15998.67

Table 6.3. Prices of the elements of the 3 kbar DTA.



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To calculate the depreciation (Table 6.4), an approximation of the use of the machines has been made, assuming that they operate 25 hours a week with 6 weeks of vacation per year and estimating the service life of the machines at 20 years. With regard to consumable products (Table 6.5), a superficial estimate of the product used has been made. Finally, the total costs of the project have been added, estimating the cost of laboratory materials such as tweezers, capsules, etc.: €30. (Table 6.6).

Machines	Machine price (€)	Approximate service life (years)	Depreciation (€/hour)	Time used (h)	Cost (€)
DSC Instruments TA Q100	60000.00	20	2.61	20	52.17
3kbar DTA	15998.67	20	0.70	30	20.87
6 kbar DTA	31793.27	20	1.38	60	82.94
				Total	155.98

Table 6.4. Machinery costs.

Consumables	Brand	Price (€)	Quantity used	Cost (€)
Liquid nitrogen pump	<i>Air Liquide</i>	832.40	0.03	24.97
Liquid silicone (20 liters)	<i>Walker</i>	588.99	0.03	17.67
Thermofluid DW-Therm M90.200.02 (20 liters)	<i>Huber [20]</i>	1000.00 ¹	0.06	60.00
Kryo-51 20 liters	<i>LAUDA</i>	1000.00 ¹	0.06	60.00
Tris 500 g	<i>Sigma Aldrich [17]</i>	75.10	0.02	1.50
NPA 100 g	<i>Sigma Aldrich</i>	83.60	0.02	1.67
			Total	165.81

Table 6.5. Costs of consumables.

¹The price of DW-Therm thermofluid and Kryo-51 could not been found; a value of €1000 has been estimated by comparing it with similar liquids.

Summary	Total cost (€)
Depreciation of equipment	155.98
Consumables	165.81
Laboratory material	30.00
Total	351.79

Table 6.6. Summary of costs and the total cost of the project.

In conclusion, the final cost of the project is €351.79. Knowing that scientific research, in general, requires large economic investments of thousands of euros, it is considered an affordable budget in order to avoid the conflict surrounding current refrigerants.

7 Environmental impact

As mentioned in the introduction of the work, the most widely used refrigerants today contribute to the greenhouse effect and in the destruction of the ozone if they leak into the environment by accident or negligence. Chlorofluorocarbons are the main culprits for the destruction of the ozone layer and although their production was banned, it cannot be assured that the ban is complied with in all countries. In other words, even if there is legislative control, it does not ensure the eradication of the problem. Finding solids that can provide caloric effects of similar magnitudes to current refrigerants would be a great step forward for the sustainability of the planet since the materials in this solid are easier to confine. In addition, systems that work with solids are more compact as they do not have a gas in high constant expansion, implying a lower visual impact and a greater use of space.

It should be mentioned that the improvement in sustainability can be of enormous magnitude in the case of a field that is so widely used in the daily life of developed countries. For example, refrigeration systems are installed in air conditioning systems in transport and in buildings, freezers and refrigerators, all of which are essential in the day-to-day life of much of the world. In fact, a very significant increase in the demand for refrigeration is expected with the growth of the middle classes in developing countries.

With regard to the impact of carrying out the project, of particular note is the consumption of electricity to carry out heating and cooling, therefore we must look at the electricity mix of Barcelona (the sources of electricity generation). The higher the percentage of renewables in the electricity mix, the more sustainable the study. The effect of the material on the environment can be underestimated due to the small amount used and the neutral properties of the substance, although for a future large-scale application, the impact of what Tris and NPA could mean for the environment has not been studied.

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Conclusions

The first conclusion that can be drawn at first glance is the conventional nature of the barocaloric effect, i.e. that the transition temperature increases with pressure, implying that an adiabatic compression leads to heating of the material and vice versa. In addition, it can also be deduced from the conventional nature that pressure stabilizes phase II (phase II has a smaller volume). However, both materials present a remarkable hysteresis; 60 degrees for Tris and 30-35 degrees for NPA. The danger of the presence of hysteresis causes irreversibility. Tris is totally irreversible for the pressure range studied, however, the temperature displacement with the pressure NPA undergoes ($dT/dp = 22$ K/kbar) provides reversibility from about 0.5 kbar. For these reasons, only NPA could be applied in cycle compression refrigeration machines for working pressures greater than 0.5 kbar.

Secondly, the isothermal entropy variation values of Tris are three times higher than those of NPA (673 and 200 J/K·kg, respectively). In addition, both considerably exceed the best BCE results studied in solids to date by a factor of almost 11 for Tris and 3 for NPA. On the other hand, the RC value of NPA at a pressure of approximately 2 kbar is two times that of Tris at the same pressure (4420 and 9030 J/kg, respectively), achieving results of 16 and 33 times better, respectively, than the most promising results to date in solids.

With regards to the working temperature range, NPA has a temperature range that includes ambient temperature, between 240 and 330 K depending on the pressure applied. The Tris range is much higher with a minimum of 340 K for both heating and cooling.

Therefore, the final conclusion is that the properties of NPA provide more advantages in terms of its application in compression and decompression refrigeration systems than Tris, in addition to providing benefits for sustainable development. NPA currently costs €836.00/kg (retail value), therefore a study of its economic profitability would have to be carried out.

Although it is still far from the values of current gaseous refrigerants, it can be concluded that further research is needed on plastic crystal-type materials as they have been shown to give much better results than, for example, the magnetocaloric materials that have been studied.

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Words of thanks

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Appendices

Appendix A. Tables of values

Tables of results. The zero-pressure data have been obtained by DSC and the others by DTA.

p (kbar)	T (K)	$ \Delta h_t $ (J/g)	$ \Delta s_t $ (J/kg·K)	BCS (J/kg K·kbar)
0.00	405.1	281.4	682.4	-
0.35	407.4	293.5	710.3	2029
0.58	408.6	297.3	717.3	1237
0.78	409.0	262.3	632.9	811.4
1.06	410.6	283.4	680.5	642.0
1.30	410.6	259.8	624.7	480.5
1.60	412.3	285.9	684.1	427.6
1.83	412.2	273.1	654.3	357.5
2.10	413.5	281.6	672.7	320.3
2.28	414.5	274.1	653.5	286.6
2.37	414.1	290.3	692.5	292.2
2.60	415.7	290.9	691.3	265.9

Table 0.1. Values of p , T and changes in enthalpy and entropy at the transition, Tris heating.

p (kbar)	T (K)	$ \Delta h_t $ (J/g)	$ \Delta s_t $ (J/kg·K)	BCS (J/kg K·kbar)
0.00	347.1	203.1	599.3	-
0.30	348.4	203.2	599.6	1999
0.51	349.0	205.1	604.2	1185
0.71	348.6	193.9	572.2	805.9
0.99	351.8	199.7	583.4	589.3

1.23	350.7	194.7	570.5	463.8
1.52	351.1	186.7	546.5	359.5
1.74	348.1	202.3	596.3	342.7
1.99	347.9	182.1	537.8	270.3
2.15	351.4	188.9	552.2	256.8
2.35	351.4	193.8	566.7	241.1
2.41	353.6	194.5	565.4	234.6

Table 0.2. Values of p , T and changes in enthalpy and entropy at the transition, Tris cooling.

p (kbar)	T (K)	$ \Delta h_t $ (J/g)	$ \Delta s_t $ (J/kg·K)	BCS (J/kg K·kbar)
0.00	246.0	48.2	203.9	-
0.21	248.7	52.8	227.7	1084
0.85	260.0	53.8	219.8	258.6
1.03	265.0	46.9	189.7	184.2
1.53	278.9	48.2	185.6	121.3
1.73	280.8	45.8	175.2	101.3
2.19	290.3	54.0	200.3	91.5
2.24	283.4	46.5	176.4	78.8
2.72	296.1	53.8	195.2	71.8
2.92	296.6	61.0	220.7	75.6
3.20	302.1	54.6	194.4	60.8
3.96	312.5	49.4	170.2	43.0
5.49	327.0	61.9	203.7	37.1
6.02	331.4	57.6	187.1	31.1

Table 0.3. Values of p , T and changes in enthalpy and entropy at the transition, NPA heating.

p (kbar)	T (K)	$ \Delta h_t $ (J/g)	Δs_t (J/kg·K)	BCS (J/kg K·kbar)
0.00	221.2	40.3	197.3	-
0.58	230.4	34.4	167.1	288.1

1.04	237.3	29.9	141.2	135.8
1.33	240.3	26.0	121.2	91.1
1.76	245.3	19.0	86.8	49.3
2.09	250.5	17.8	79.7	38.1
2.60	255.7	23.8	104.4	40.2
2.77	257.2	18.1	79.0	28.5
2.81	257.9	22.8	99.4	35.4
3.35	262.7	21.2	90.1	26.9
3.71	267.5	20.3	84.7	22.8
3.84	268.5	18.6	77.4	20.2
4.11	272.0	23.2	95.2	23.2
4.13	273.0	22.6	92.7	22.5
4.55	277.6	20.5	82.5	18.1
4.90	282.7	20.7	81.9	16.7
5.15	285.9	20.9	81.9	15.9
5.44	290.3	21.3	82.2	15.1
5.58	291.2	19.5	75.1	13.5
5.77	294.2	21.2	80.5	14.0

Table 0.4. Values of p , T and changes in enthalpy and entropy at the transition, NPA cooling.

The following tables summarize the cooling capacity values for each pressure studied.

p (kbar)	ΔS_{max} (J/K·kg)	$FWHM$ (K)	RC (J/kg)
0.35	142.4	9.7	1381
0.58	225.6	9.8	2220
0.78	252.4	11.1	2804
1.06	342.8	10.6	3625
1.30	341.1	10.8	3686
1.60	427.1	10.8	4621
1.83	415.7	10.7	4469
2.10	472.0	9.4	4417
2.28	511.7	11.3	5767
2.37	494.3	11.0	5422
2.60	552.9	11.6	6433

Table 0.5. Maximum values of the change in isothermal entropy (BCE), FWHM and RC, Tris heating.

p (kbar)	ΔS_{max} (J/K·kg)	$FWHM$ (K)	RC (J/kg)
0.30	479.7	1.4	684
0.51	549.6	2.0	1081
0.71	528.6	1.7	877
0.99	599.3	4.7	2842
1.23	599.3	3.7	2231
1.52	599.3	4.1	2460
1.74	595.9	1.4	820
1.99	445.7	1.2	533
2.15	599.3	4.4	2632
2.35	599.3	4.4	2660
2.41	599.3	6.6	3937

Table 0.6. Maximum values of the change in isothermal entropy (BCE), FWHM and RC, Tris cooling.

p (kbar)	ΔS_{max} (J/K·kg)	$FWHM$ (K)	RC (J/kg)
0.21	117.1533	5.5	645
0.85	203.9	14.0	2861
1.03	203.9	20.4	4157
1.53	203.9	33.8	6883
1.73	203.9	35.8	7293
2.19	203.9	44.3	9029
2.24	203.9	38.5	7852
2.72	203.9	51.1	10420
2.92	203.9	51.4	10490
3.20	203.9	56.9	11610
3.96	203.9	67.2	13710
5.49	203.9	81.9	16690
6.02	203.9	86.4	17630

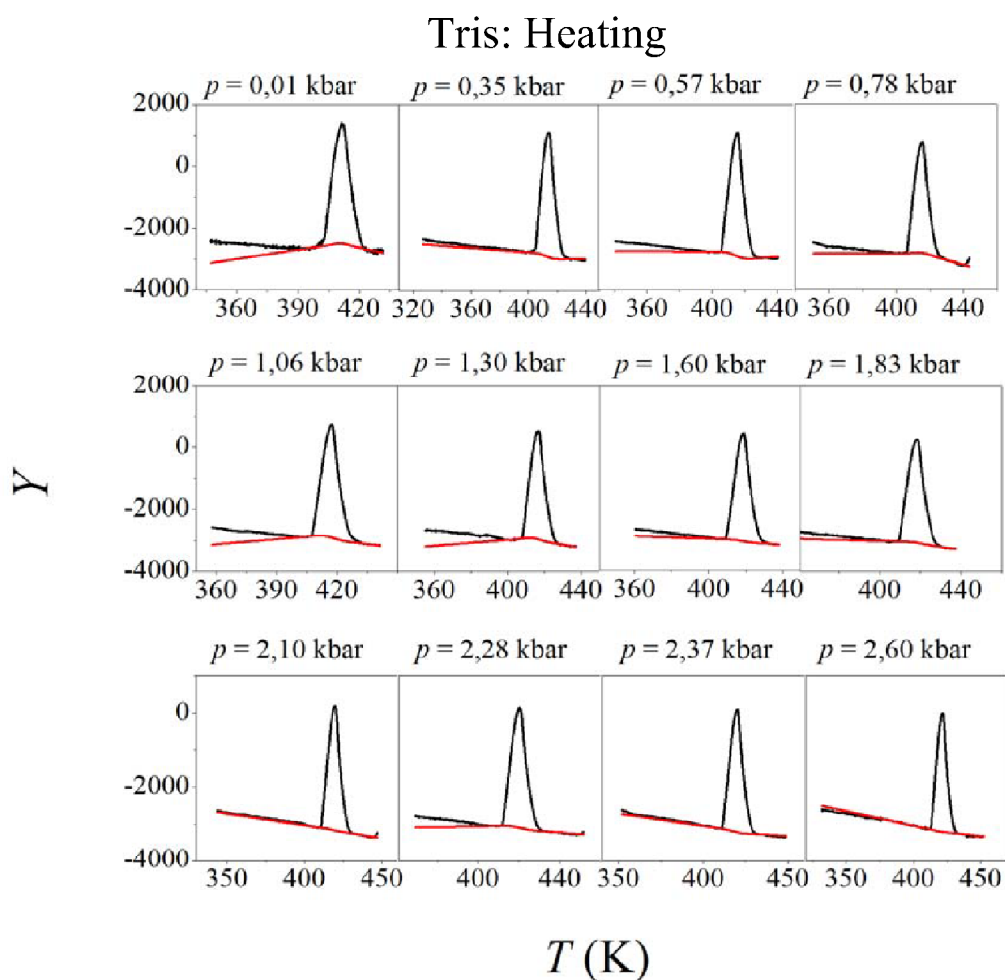
Table 0.7. Maximum values of the change in isothermal entropy (BCE), FWHM and RC, NPA heating.



Núria Pol Català

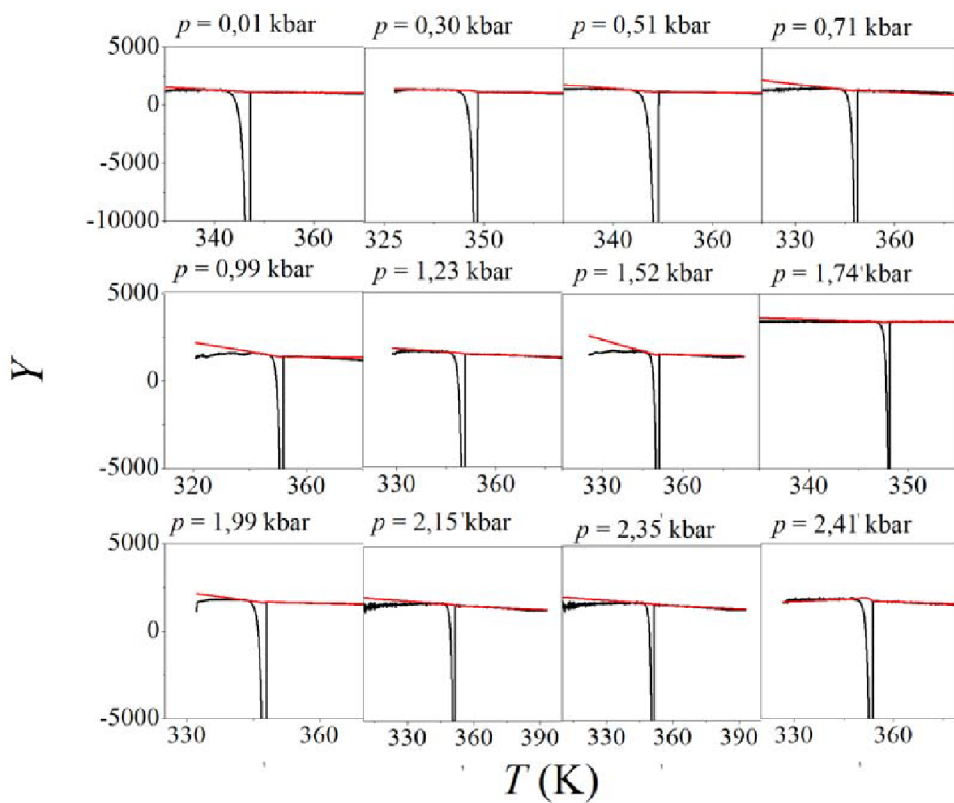
Appendix B. Baselines

The following appendix sets out the baselines for the integration of the curves obtained by DTA without calibration, therefore the ordinate axis with arbitrary units is considered for the figures.

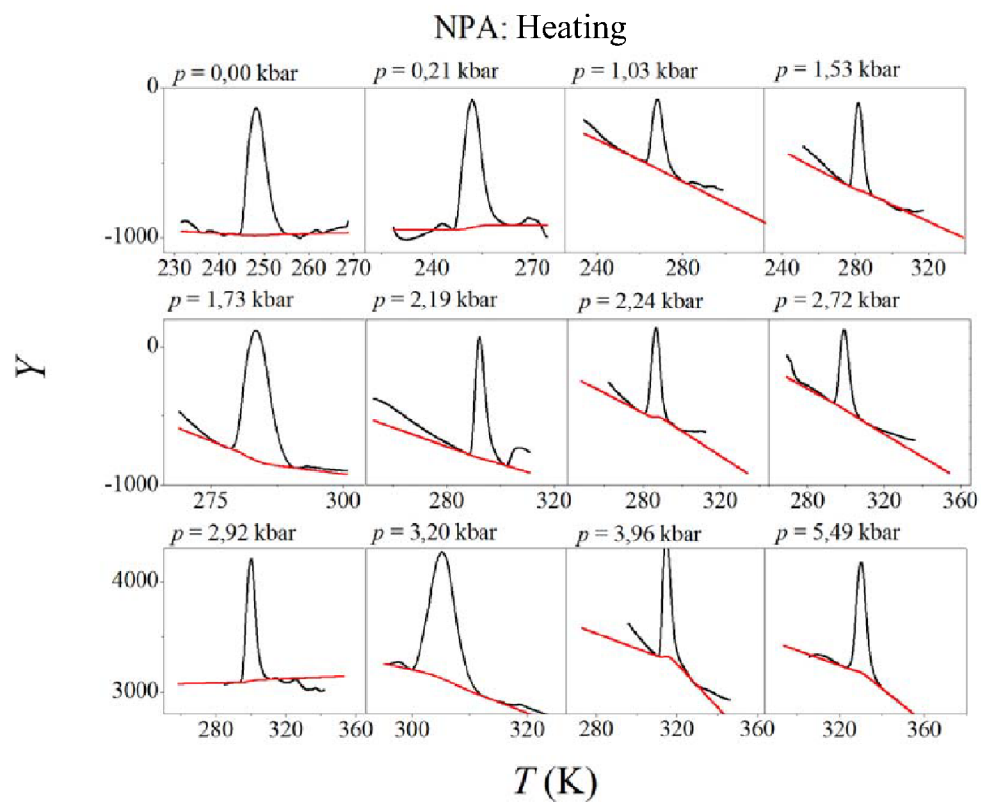


0.8. Baselines of the Tris heating.

Tris: Cooling

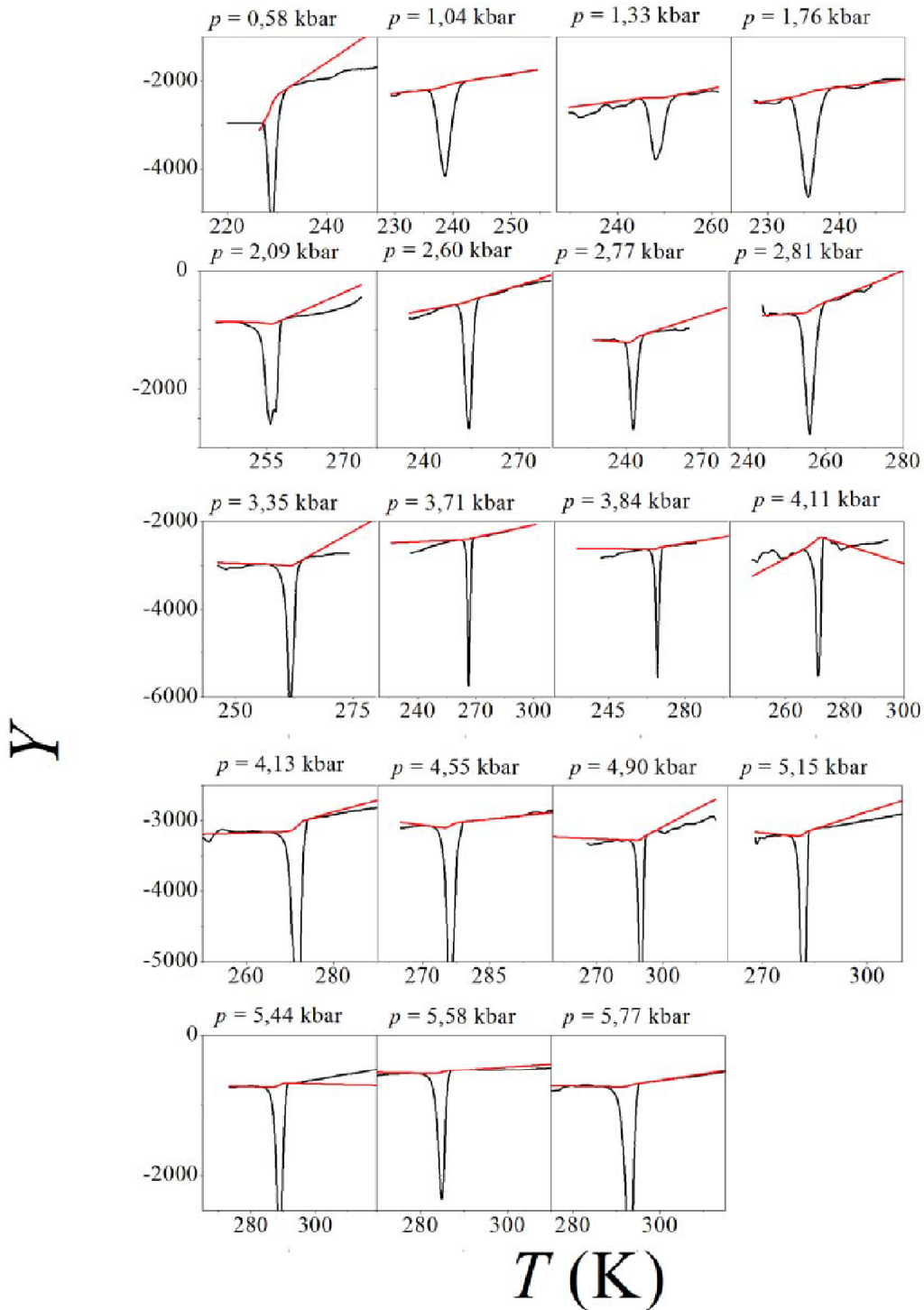


0.9. Baselines of Tris cooling.



0.10. Baseline of NPA heating.

NPA: Cooling



0.11. Baseline of NPA cooling.



July 12, 2024

Certification

Welocalize Translations

TRANSLATOR'S DECLARATION:

I, **Fee Dooms** hereby declare:

That I possess advanced knowledge of the Catalan and English languages. The attached Catalan into English translation has been translated by me and to the best of my knowledge and belief, it is a true and accurate translation of:
Efectes barocalòrics en cristalls plàstics

(Digital or printed signature here above the line)

A handwritten signature in black ink, appearing to be "Fee Dooms", written over a horizontal line.

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