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# Temperature Negative

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# Negative Temperature

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## 1 Introduction

The temperature of a system may conveniently be regarded as a parameter that determines the distribution of energy among the particles of the system. The concept of absolute temperature is based on the second principle of thermodynamics and in general absolute temperature can only assume positive value. We will see that this is based on the implicit assumption that the entropy is always an increasing function of energy however there are specific systems for which this is not valid and they can be described with negative absolute temperature. Of course the conditions for the existence of one of these systems are so restrictive that they are rarely met in practice. However, the thermodynamics and statistical mechanics of negative temperatures are more general than their application to a single type of system so we will first study the general theory for negative temperature systems and only later will specific applications be made to spin systems.

## 2 Definition of temperature

Before we start our study on negative temperatures we need a clear definition of ”temperature”. First definitions were based on the linear expansion of liquids but because the expansion has not been perfectly linear scientists developed new definitions based on the powerful principles of statistical mechanics.
Our intuitive notion is that two systems in thermal contact should exchange no energy (in form of heat) if and only if they are at the same temperature, so what we are doing is searching for a parameter that becomes the same for the two systems in contact when they reach equilibrium.

Let’s suppose we have two systems: system $A$ with internal energy $E_1$ and system $B$ with internal energy $E_2$.
With $\Omega_A(E_1)$ we indicate the number of microstates accessible to the system $A$ given his value of energy and with $\Omega_B(E_2)$ we indicate the same thing for the system $B$. When we put them in thermal contact they start to exchange energy until they reach equilibrium. We know from statistical mechanics that

the state of the system at equilibrium is the one that maximizes entropy (always respecting the other physical constrains). The entropy is:

$$S = kln(\Omega)$$

Where $k$ is the Boltzmann constant and $\Omega$ is the number of microstates accessible to the system.
In our case the system is $C = A \cup B$ and, given a distribution of energy between $A$ and $B$, we have that

$$\Omega = \Omega_A(E_1)\Omega_B(E_2)$$

If $S$ reaches its maximum we obviously have that $\frac{\partial S}{\partial E_1} = 0$; developing the calculations we have:

$$\frac{\partial ln(\Omega_A(E_1)\Omega_B(E_2))}{\partial E_1} = 0$$

$$\frac{\partial ln(\Omega_A(E_1))}{\partial E_1} + \frac{\partial ln(\Omega_B(E_2))}{\partial E_1} = 0$$

now using conservation of energy we note that: $\partial E_1 = -\partial E_2$; so we can write:

$$\frac{\partial ln(\Omega_A(E_1))}{\partial E_1} - \frac{\partial ln(\Omega_B(E_2))}{\partial E_2} = 0$$

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_1}$$

We have finally found a physical quantity for the two systems that becomes the same at equilibrium. We decide to name it $\frac{1}{T}$ (where $T$ is the temperature) to be consistent with previous definitions.

# 3 Negative temperature

Given this definition of temperature it is easy to note that the only condition that must be satisfied in order to have a system capable of negative temperatures is that its entropy should be a decreasing function over a certain range of energy. This is not an easy condition to satisfy, the easiest way to do it is to have a system whose energy levels are limited as we can see with the following simple example:
Let's suppose we have a system of $N$ particles and that each of these particles has only two possible states: a ground state (with a lower energy value) and

an excited state (with an higher energy value). The lowest energy state for this system is obviously the state in which all the particles are in the ground state, this is an highly ordered state with an entropy value $S = 0$ (the entropy is maximized when the occupation of every state is the same; it is important to note that this situation is not always possible for a given system because of its other physical constrains). If we give energy to the system the occupation of the excited level starts to increase and so does the entropy until we reach the state where half of the particles are in the ground state and half are in the excited state. As noticed above this is the state that has the maximum value of entropy for the system so, if we continue to add energy, we have an inversion of population between the two levels and the entropy decreases because we are returning in an ordered situation where the particles tend to be in the same state.

With this explanation we have shown that it is possible to have negative temperature in this theorized system because $S$ starts to decrease if we increase $E$. These type of systems are difficult to build and are not found in nature mainly because there is almost always the kinetic energy that has no upper bound.

If we draw the graphs of the entropy and temperature as a functions of energy we obtain:

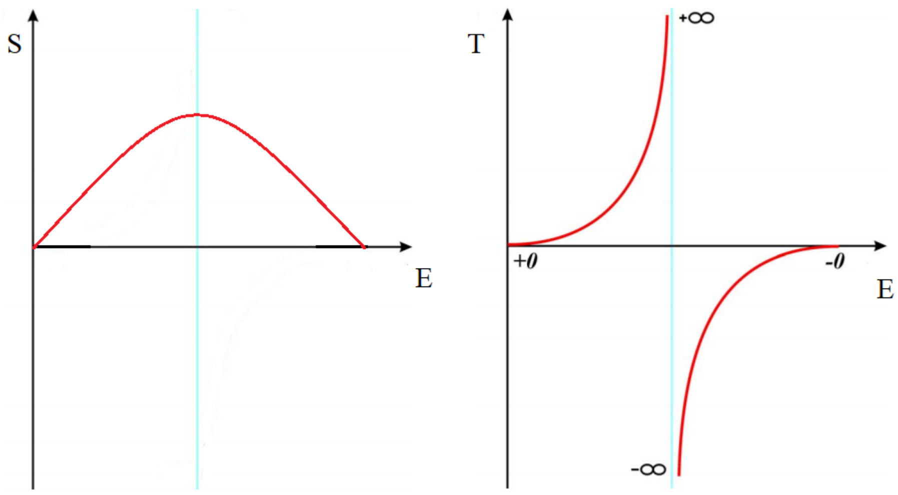

Figure 1: Entropy and temperature as functions of internal energy; note that the temperature is the inverse of the derivative of entropy

We notice that negative temperatures corresponds to states that are more excited than positive temperature ones.

# 4 Two levels system

We want to use statistical mechanics to derive the graphs of the previous paragraph. The essential requirements for a physical system to be capable of negative temperature in the way described before are:

- The elements of the system must be in thermodynamic equilibrium (in order for the system to be described with a temperature at all);
- There must be an upper limit to the possible energies accessible to the elements of the system;
- It is necessary that the system is isolated from all the systems that don't respect the first two conditions.

Given these rules we are going to study a system of $N$ indistinguishable particles. These particles have only two possible states: the first state is the ground state and we assign to it the energy value of 0, the other state is excited and we assign to it the energy $h$.
If our system has a value of total energy $E$ then we know exactly how many particles are in the excited state ($N_1$ = number of particles in the excited state, $N_0$ = number of particles in the ground state):

$$N_1 = \frac{E}{h}$$

Now given the fact that the particles are indistinguishable the number of the microstates accessible to the system is (in how many ways can we choose $N_1$ excited particles from a total of $N$ particles?)

$$\Omega(N_1) = \frac{N!}{N_1!(N - N_1)!}$$

Now we can use the Boltzmann formula to derive the entropy

$$S(N_1) = kln(\frac{N!}{N_1!(N - N_1)!})$$

$$\frac{S(N_1)}{k} = lnN! - lnN_1! - ln(N - N_1)!$$

Using the logarithmic form of the Stirling approximation that is

$$ln(N!) \approx NlnN - N$$

we have

$$\frac{S(N_1)}{k} = NlnN - N - N_1lnN_1 + N_1 - (N - N_1)ln(N - N_1) + (N - N_1)$$

$$\frac{S(N_1)}{k} = NlnN - N_1lnN_1 - (N - N_1)ln(N - N_1)$$

returning in the variable $E$ using the following relation $N_1 = \frac{E}{h}$

$$\frac{S(E)}{k} = NlnN - \frac{E}{h} ln\frac{E}{h} - (N - \frac{E}{h})ln(N - \frac{E}{h})$$

If we draw the graph we obtain:

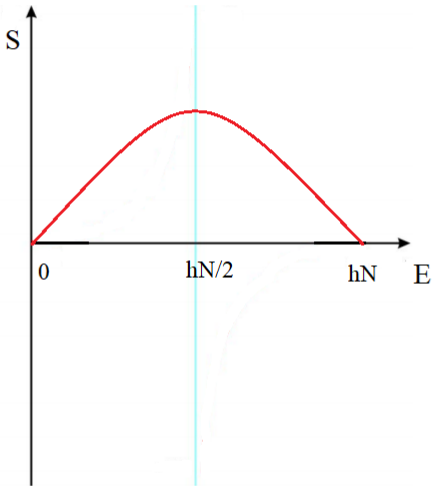

Figure 2: Entropy as a function of internal energy

We can also obtain the temperature of the system:

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

$$\frac{1}{kT} = \frac{1}{h} ln(N - \frac{E}{h}) - \frac{1}{h} ln(\frac{E}{h})$$

$$\frac{1}{kT} = \frac{1}{h} ln(\frac{N_0}{N_1})$$

$$kT = \frac{h}{ln(\frac{N_0}{N_1})}$$

We note that if the excited state is more populated than the ground state we have a negative temperature, exactly what we expected.
We can also draw the graph of the temperature as a function of $E$ and we obtain:

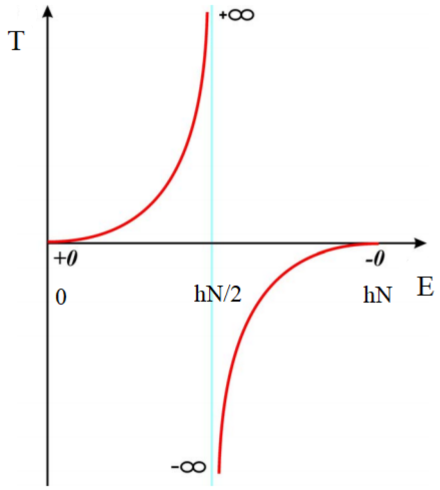

Figure 3: Temperature as a function of internal energy

All the results are consistent with the qualitative analysis made before.

## 5 Are negative temperatures ”hotter” than positive ones?

To answer this question we must first agree a condition that allows us to say when a system is hotter than another. We say that system $A$ is hotter than system $B$ if when we put them in thermal contact heat starts to flow from system $A$ to system $B$. With these conditions we can say that negative temperatures are hotter than positive ones. We can show this with these following simple examples:
For the first example we have two system: system $A$ not capable of negative temperatures and system $B$ capable of negative temperatures (for the sake of simplicity exactly of the two levels type treated before); the system $B$ is in a state of negative temperature.

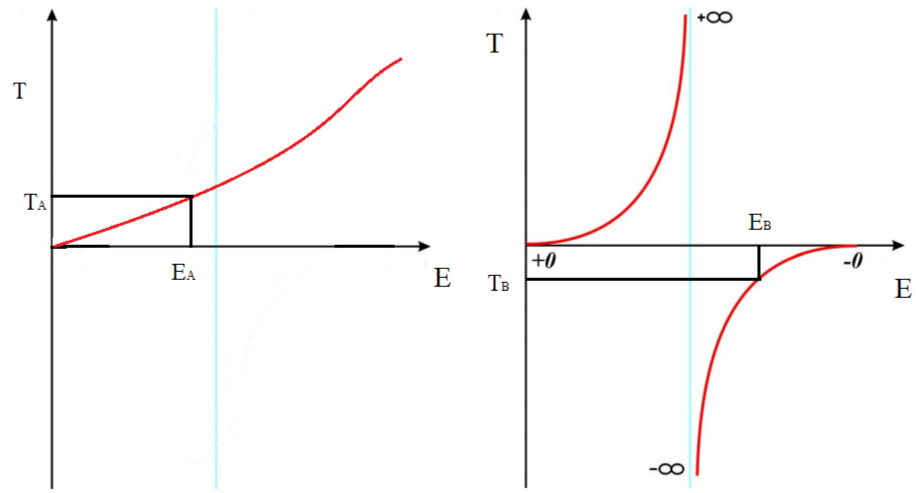

Figure 4: Energy/temperature for system $A$ and system $B$

If we put them in thermal contact they have to reach the same temperature. Because system $A$ can not have negative temperatures $T_{\mathrm{eq}}$ has to be positive. In order to reach a state of positive temperature the system $B$ has to lower his energy. Due to the conservation of energy it is obvious that system $B$ has lost energy in the form of heat and that system $A$ has gained the same amount. We have shown that a system at a negative temperatures is hotter than any system at any positive temperature.

For the second example we still have two system: system $A$ capable of negative temperatures (but in a state of positive temperature) and system $B$ capable of negative temperatures (in a state of negative temperature), for the sake of simplicity we suppose that these two system are exactly identical and of the two level type. The only difference is, indeed, their initial energy:

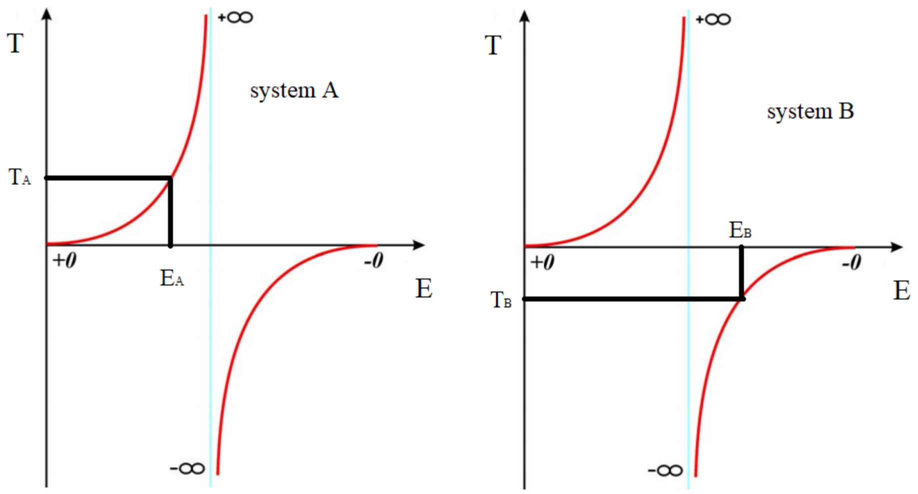

Figure 5: Energy/temperature for system $A$ and system $B$

When we put them in thermal contact there is no reason to think that the total energy should not be divided equally between the two systems (given the symmetry of the situation).So each of the two systems reach an energy of $E = \frac{E_1+E_2}{2}$ that is the point in the middle of the two energies. By varying the position of $E_1$ in the $T$ positive region and $E_2$ in the $T$ negative region we clearly see that the $T_{\text{eq}}$ between a positive and a negative temperature can be a positive temperature higher than the one of the "$T$ positive system" or a negative temperature lower than the one of the "$T$ negative system".
In view of these two examples it seems that the term negative temperature is misleading. it certainly is but the definition of temperature was agreed long ago and the vast majority of physical system don't have these problems. It is worth noticing that for the purpose of negative temperatures the "coldness" scale is in many ways more convenient than the temperature scale. The coldness is defined as $\beta = \frac{1}{kT}$ and the heat always flow from the system with the lower value of $\beta$ to the system with the higher one.

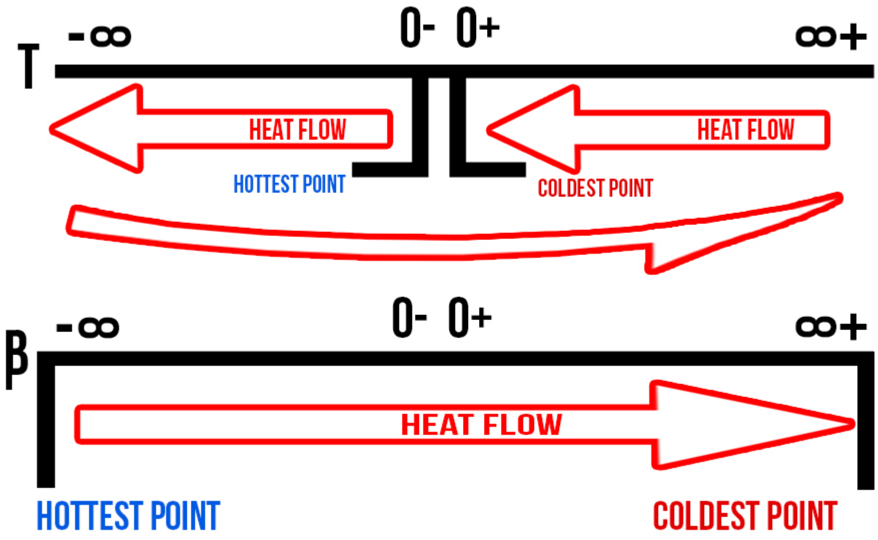

Figure 6: A representation of the heat flow

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To conclude this section we will show in a more formal way that heat flows from negative temperature systems to those at positive temperature. We have:

System 1 with energy $E_1$ and positive temperature $\frac{1}{T_1} = \frac{\partial S_1}{\partial E_1}(E_1) > 0$

System 2 with energy $E_2$ and negative temperature $\frac{1}{T_2} = \frac{\partial S_2}{\partial E_2}(E_2) < 0$

$\Delta$ is the energy that passes from the system 2 to system 1

the total entropy is:

$$S_{\text{tot}} = S_1(E_1 + \Delta) + S_2(E_2 - \Delta)$$

Deriving respect to $\Delta$ we have

$$\frac{\partial S_{\text{tot}}}{\partial \Delta} = \frac{\partial S_1}{\partial E}(E_1 + \Delta) - \frac{\partial S_2}{\partial E}(E_2 - \Delta)$$

which is positive if $\Delta$ is positive. This type of exchange is therefore favorable to reach the state of maximum entropy.

# 6 Nuclear spin system

In this paragraph we want to give an example of a negative temperature system that has been reproduced in an experimental environment. The system we are going to study has been experimentally realized using pure Lithium Fluoride crystals (LiF). More specifically our system consists of the nuclear spins of the crystal subjected to a constant magnetic field. If the spin of the nucleus is $I$ the field forces the nuclear spins to assume one of the $2I + 1$ values of $S_{\mathrm{z}}$ ($z$ is the direction of the magnetic field) ranging form $-I$ to $+I$. Each of the nuclei has an energy of

$$E_{\mathrm{i}} = -B_{\mathrm{z}} S_{\mathrm{z}}$$

So there are only $2I + 1$ states accessible to the "particles" of the system. So there is an upper limit to the possible energies for the elements of the system. Now we have to verify if the other two conditions discussed in the previous paragraph are satisfied. In order that the nuclear spin system can adequately be considered as a thermodynamic system describable by a temperature the various nuclear spins must interact among themselves in such a way that thermodynamic equilibrium is achieved. This occurs by virtue of the nuclear spin-spin magnetic interaction. The last condition that must be satisfied is that this spin system has to be isolated. This is not totally true because of the existence of a spin-lattice interaction but it has experimentally observed that the relaxation time (the relaxation time is a measure of the time it takes for the system to be significantly perturbed by a certain type of interaction ) of the spin-spin interaction is $\approx 10^{-4}$ seconds while the relaxation time of the spin-lattice interaction is $\approx 120$ seconds; so we can consider our nuclear spin system as isolated for short time intervals in which we can neglect the spin-lattice effects.

The last question we have to answer is how we put this system in a negative temperature state. The answer is simple: we open a magnetic field and wait till the nucleus reach the thermal equilibrium with the surrounding environment, since the temperature of the environment is obviously positive we have that the lower energy states of the spin system are more populated than the higher ones. Now we quickly reverse the magnetic field thus forcing an inversion of population between the levels (in reality we are simply swapping the value of the energy of each level with its opposite!). The system ends in a situation in which the high energy levels are the more populated: a negative temperature state. All the observed behaviours of the system are consistent with our analysis.

# 7 Classical definition of Temperature

Throughout the thesis we have used the statistical mechanics definition of temperature but the concept of absolute temperature was already present in thermodynamics (absolute scale: a scale with no negative values). In this chapter we are going to analyze the thermodynamic definition of absolute temperature and see why negative values were not contemplated.

*Classical definition of absolute Temperature*:
The absolute temperature of a system T is the thermodynamic function that makes $dS = \frac{\delta Q}{T}$ a perfect differential ($\Delta S$ depends only on the initial and final state of the system) and it can be measured using a Carnot cycle as a thermometer.

The $S$ function is entropy and it can be shown that it is equivalent to the statistical mechanics one.
The Temperature $T$ can be multiplied by an arbitrary constant, to fix the scale we have to assign a value to the temperature of the triple point of water. The most common absolute temperature scale is the Kelvin scale which assigns to the triple point a $T = 273,2K$.
How can we use a Carnot cycle to measure the temperature of a system?

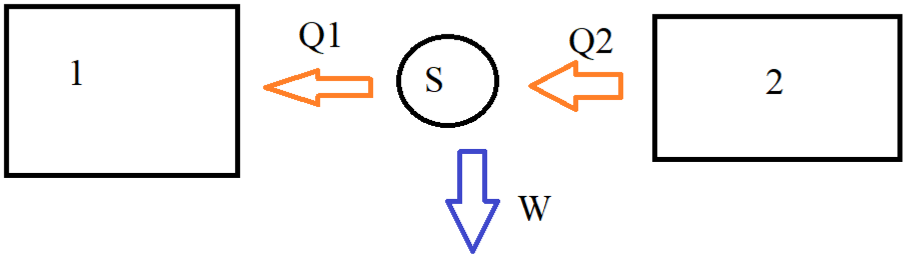

Figure 7: A classical Carnot cycle

A Carnot cycle is a reversible process so it is characterized by a $\Delta S = 0$. Since it is a cycle at the end the system $S$ is in the initial state so the $\Delta S$ is 0 (state function) and we have to consider only the $\Delta S$ of the heat reservoirs. (we are using the convention that heat leaving a system is negative, with $Q_1$ and $Q_2$ we always indicate the absolute value of the heat and we put the plus or minus sign manually)

$$\Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

This has to be zero so:

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

And

$$T_2 = \frac{Q_2}{Q_1} T_1$$

By letting the first heat reservoir consist of water at its triple point we have:

$$T_2 = \frac{Q_2}{Q_1} 273.2K$$

So why are negative temperature not contemplated?
The answer is easy : we have mistakenly assumed that in order to have a reversible cycle (with a $\Delta S = 0$) $Q_2$ must be absorbed by the system $S$ and $Q_1$ must be discharged but if $T_1$ is negative we can also have a reversible cycle like this:

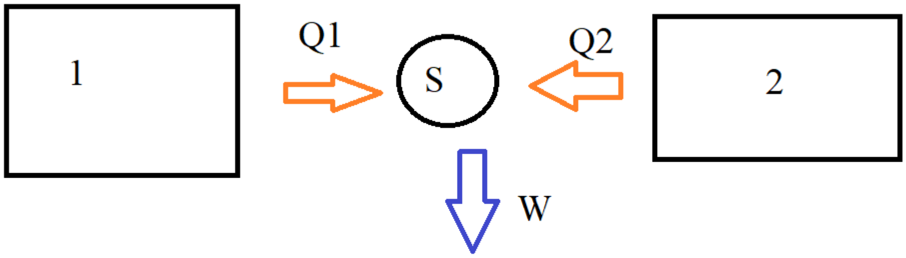

Figure 8: Heat flows from system 2 to system 1

because given the fact that both $Q_1$ and $Q_2$ are absorbed by the system

$$\Delta S = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

can be zero if $T_1$ is negative.
This situation seems to be in contrast with the second principle of thermodynamics (efficiency $> 1$), we will deepen this in the next section.

# 8 Second Principle

Another important thing to study is the effect of the existence of physical systems capable of negative temperature on the theoretical results obtained from the classical thermodynamics, in fact many theorems use implicitly the assumption that the entropy is always an increasing function of energy.
More specifically we will study what happens to the main formulations of the second principle listed below:

*The classical formulation*:
If a thermodynamic system is isolated then $dS \geq 0$

*Kelvin formulation*:
There can't exist a thermodynamic process that has as only result the transformation of heat absorbed from a body in work

*Clausius formulation*:
There can't exist a thermodynamic process that has as only result the flow of heat from a colder to an hotter system

Let's start our analysis with the classical formulation, we can rewrite it as "every process is characterized by a $\Delta S \geq 0$ (of the universe)". This formulation is still valid because it is strictly connected to the principle of maximum entropy and it is crucial in the statistical mechanics that we have extensively used in this study; if the principle would have been invalidated, the whole thesis would have lost its meaning. Given the importance of this formulation we will study what happens to the Kelvin and Clausius formulation leading back to it.

The Clausius formulation also remains true but we have to consider the new definition of "hotter".
We have shown that the most appropriate scale to study the flow of heat is the coldness scale. We show below that any process that has as only result the flow of heat form a system with an higher value of coldness (colder) to a system with a lower one (hotter) is characterized by a $\Delta S < 0$ and is therefore impossible

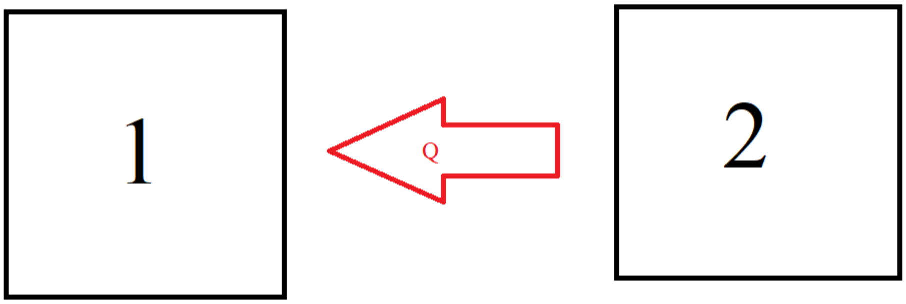

Figure 9: Heat flows from system 2 to system 1

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Remembering that the $\Delta S$ for a system is equal to $\beta Q$ then the $\Delta S$ of the universe is equal to

$$Q\beta_1 - Q\beta_2$$

(Heat is going from system 2 to system 1 and we are using the convention that heat leaving a system is negative) .
If $\beta_2 > \beta_1$ we can clearly see that we always have a $\Delta S < 0$.

The Kelvin formulation loses its validity unlike the other two.
Analyzing the situation we have

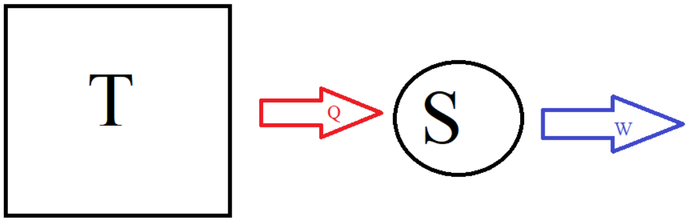

Figure 10: Heat converted in work

Classically the $\Delta S$ in a process like the one in the picture is always negative

$$-\frac{Q}{T}$$

but if we consider a negative temperature system we have that the $\Delta S$ is $> 0$ and so the process is possible. (that is exactly what happened in the Carnot cycle of the previous section)
This formulations of the second principle does not hold anymore and is in fact possible to convert all the heat produced by a negative temperature system in work (and also have reversible cycles with an efficiency $> 1$). It is true that we can produce work simply by cooling a $T < 0$ system but there are some restrictions:

1) Negative temperature systems do not exist in nature and often the energy required to build one is greater than the energy that we can get from it

2) Negative temperature systems will eventually reach a positive temperature state when cooled so only limited amount of work can be produced this way.

3) Negative temperature systems exists only for brief intervals of time as discussed before.

All these limitations make all practical application impossible or useless.

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