Statistical and Low Temperature Physics (PHYS393)

6. Magnetic Cooling

Kai Hock 2013 - 2014 University of Liverpool State the formula for energy levels in a spin 1/2 paramagnetic salt.

Sketch and explain the temperature graphs for energy, heat capacity and entropy of the spin 1/2 salt.

State the distribution of spin 1/2 ions among these levels. Derive the formula for total energy.

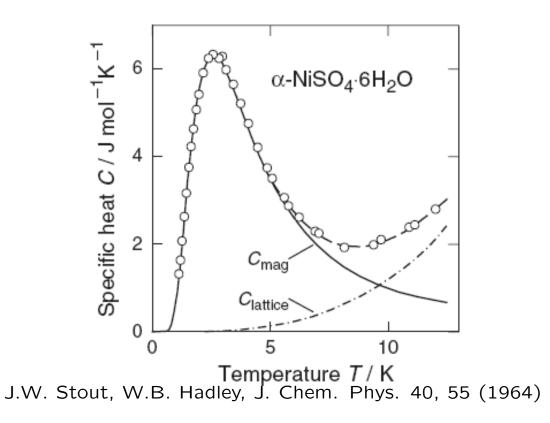
Use the entropy graph to explain magnetic cooling.

Explain how to find the heat of magnetisation, the cooling power, and the final cooling temperature.

Explain what limits the lowest temperature that can be achieved. Explain how nuclear cooling overcomes this problem.

Paramagnetic salts

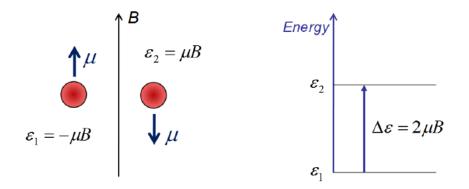
Heat capacities tend to increase with temperature, as we have seen for electrons in metals and phonons in solids. A paramagnetic salt, however, has a heat capacity that goes up to a peak, comes down, then goes up again.



This unusual peak is called the Schottky anomaly.

The Schottky anomaly happens for paramagnetic materials in a magnetic field. At very low temperatures, there is little contribution from electrons and phonons (lattice vibration).

Consider a material with ions that have spin 1/2. This is called a spin 1/2 paragmagnet. When a magnetic field *B* is applied, the energy level of each ion split into two.

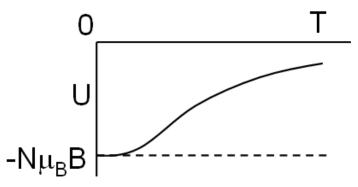


The energy levels are

$$\varepsilon = -\mu \cdot \mathbf{B} = -\mu_B B \text{ or } + \mu_B B$$

Lets see if we can "deduce" the Schottky anomally. At 0 K, all electrons are at the ground state, so the total energy U is $-N\mu_B B$, where N is the number of the ions.

At high temperatures, the thermal energy the electrons is much larger than the difference between the two magnetic energy levels. Then the electrons are equally likely to be in $-\mu_B B$ or $+\mu_B B$, so U is zero



A sketch of U against T would look like this.

In principle, we can now find the heat capacity C using

$$C = \frac{dU}{dT}.$$

However, the gradient of U neat 0 K is not known.

According to one form of the Third Law of Thermodynamics:

"The entropy of a system approaches a constant value as the temperature approaches zero."

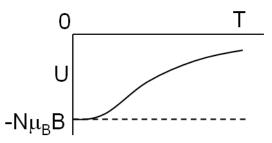
This means that change in entropy dS approaches zero. Since

$$dS = \frac{dQ}{T},$$

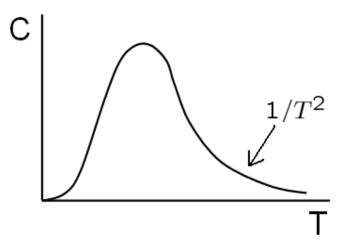
SO

$$C = \frac{dU}{dT} = \frac{dQ}{dT} = T\frac{dS}{dT} \to 0.$$

Now that we know the gradient is zero at both 0 K and high ${\cal T}$



we can sketch the heat capacity, which is the gradient of U.



We have just deduced the Schottky anomaly.

The energy can be obtained quantitatively using the Boltzmann distribution of the number of spin 1/2 ions in the energy levels 1 and 2:

$$n_1 = A \exp\left(+\frac{\mu_B B}{k_B T}\right)$$
 and $n_2 = A \exp\left(-\frac{\mu_B B}{k_B T}\right)$

Using the total number

 $N = n_1 + n_2,$

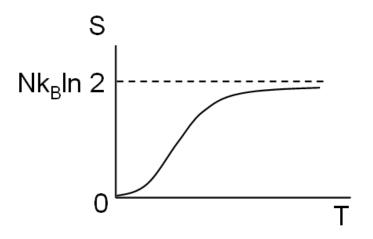
we can solve for A and find the total energy

$$U = n_1(-\mu_B B) + n_2(\mu_B B).$$

The answer is

$$U = -N\mu_B B \tanh\left(+\frac{\mu_B B}{k_B T}\right)$$

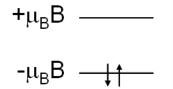
Next, we shall deduce qualitatively the graph for the entropy. It looks like this:



We need to show that at low T, it tends to zero. And at high T, it tends to $Nk_B \ln 2$.

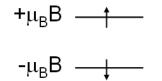
Recall the formula for entropy: $S = k_B \ln \Omega$.

At low temperature, most atoms would be in the ground state.



There is only 1 way to arrange this. So the entropy would tend to $S = k_B \ln 1 = 0$.

At high temperature, the difference between the energy levels would be small compared with the k_BT in $\exp(-\epsilon/k_BT)$.



The atom is equally likely to be in either level. There are 2 possible arrangements for each of the N atoms - 2^N in total.

So the entropy would tend to $S = k_B \ln 2^N = N k_B \ln 2$.

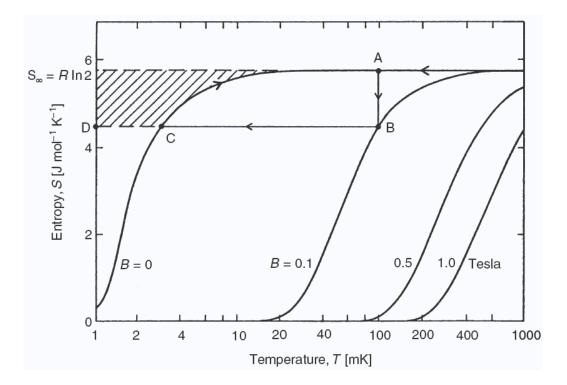
The Principle of Magnetic Cooling

Magnetic cooling can ultimately reach a temperature of microKelvins.

To understand the principles, we start with the paramagnetic salt, which can go down to milliKelvins. This salt contains ions with magnetic moments coming from their electrons.

At milliKelvin temperatures, the magnetic disorder entropy (about 1 J/mol) is large compared to all other entropies, such as lattice and conduction electron entropies, which may be neglected.

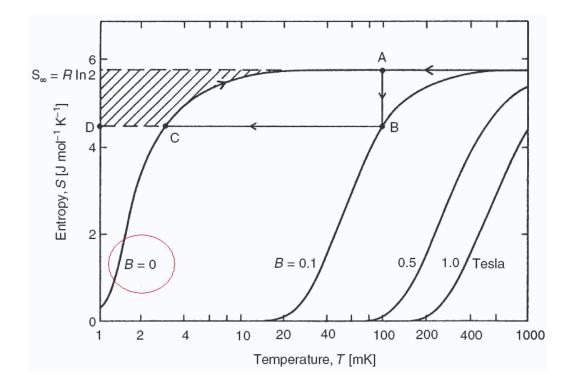
We have seen the properties of a paramagnetic salt. The entropy is a function of the magnetic field applied. We shall look at this and see how it can help us understand magnetic cooling. This graph show the entropy against temperature for a commonly used paramagnetic salt.



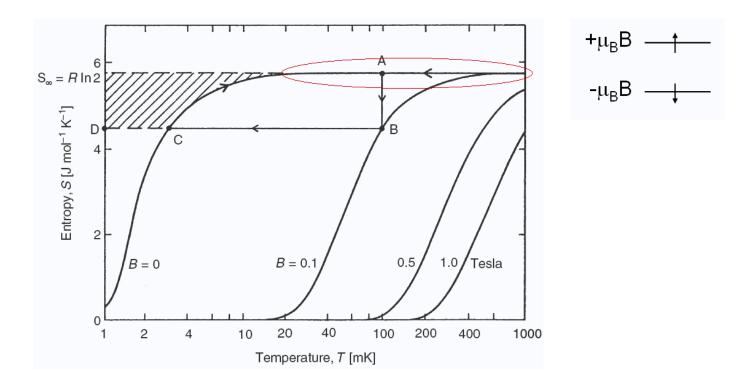
D.S. Betts: An Introduction to Millikelvin Technology (Cambridge University Press, Cambridge 1989)

We start by familiarising ourselves with the various features of the graph.

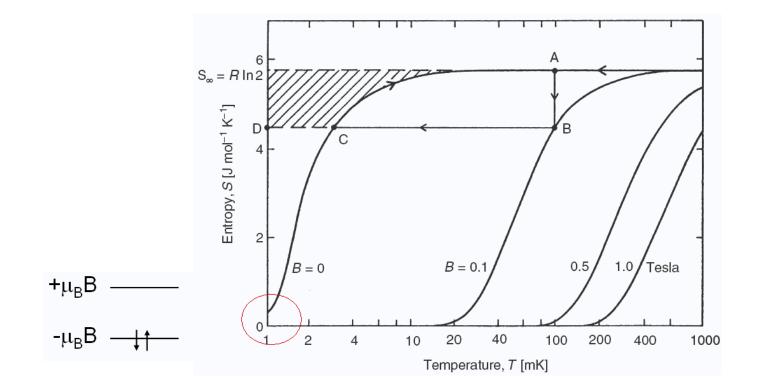
The symbol B is the magnetic field. We start with the graph for zero or low magnetic field.



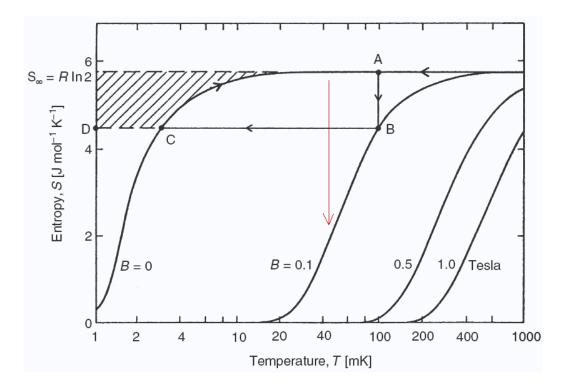
At high temperature, the entropy approaches a constant because it becomes equally likely to be at any of the magnetic energy levels.



At low temperature, the entropy goes to zero because all particles fall to the lowest level.

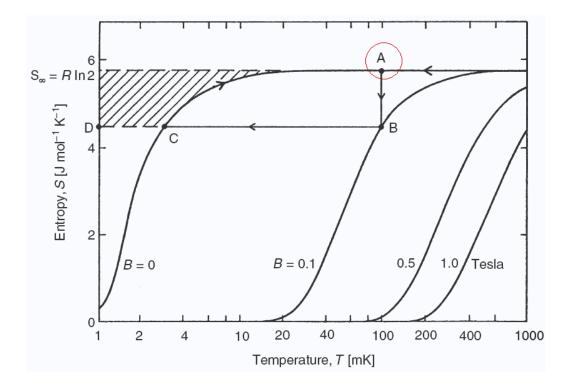


Next, suppose the magnetic field is increased, say from 0 T to 0.1 T. The spacing between energy level would increase.



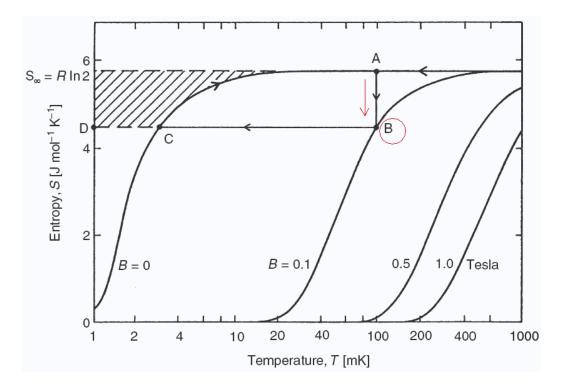
Then it becomes more likely for a particle to be at the lower level. So the entropy would fall.

Point A: To understand how to use the magnetic property for cooling, suppose we start with a temperature at point A, and with a low magnetic field.



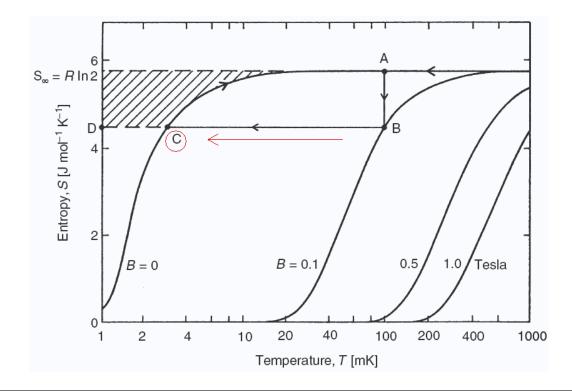
The salt is placed in contact with a precooling bath. This can either be a helium bath, or a dilution refrigerator.

Point B: A magnetic field is then applied. This is done isothermally. The entropy falls to point B at constant temperature.



This process performs magnetic "work" on the salt, which is converted to heat (like compressing a gas). This heat would be absorbed by the precooling bath. The salt is then thermally isolated from the precooling bath (e.g. by using a heat switch).

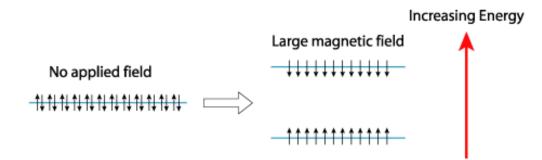
Point C: Demagnetisation now takes place adiabatically (so entropy is constant). The magnetic field is reduced to a very small value. The temperature falls to C.



We have seen how the cooling takes place using thermodynamics. Let us now see how this takes place physically.

The ions in the salt have magnetic dipole moments. Normally, half of the dipoles are spin up, and the other half are spin down.

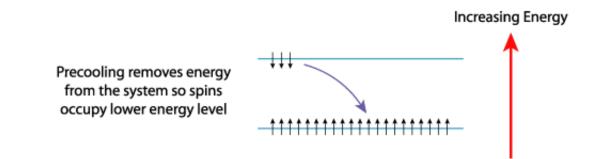
If a strong magnetic field is applied, the energy levels will split into two.



Dipoles in the direction of the field will have lower energy, and dipoles in the opposite direction higher energy.

Remember that a helium bath or a dilution refrigerator is cooling the salt at the same time.

This would remove energy from the higher energy atoms, so that they fall into the lower energy state.

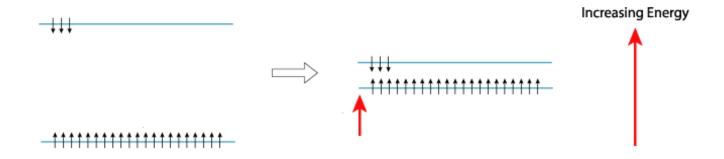


This is the "precooling."

Then, using a heat switch, the salt can be thermally disconnected from the precooling bath.

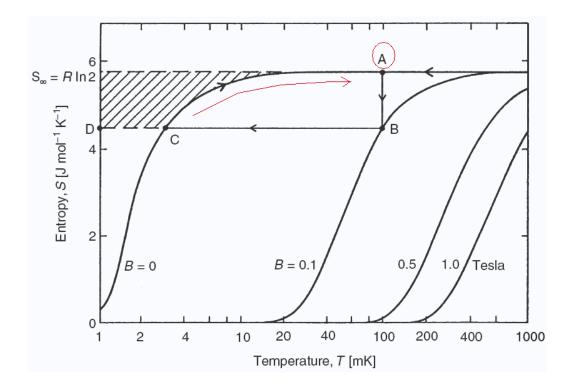
The magnetic field is now slowly reduced.

The lower energy level, which contains most of the atoms, is then forced to increase in energy.



This energy has to come from the surrounding. So the salt cools down.

Point C: After some time, the salt would warm up because of heat leak from the surroundings, since the insulation is not perfect. The temperture returns to point A along the curve from C.



The temperature cannot be maintained, unlike the dilution refrigerator. This is called a "one-shot" technique.

Thermodynamics of Magnetic Cooling

With the help of the entropy graph, we can calculate the heat Q and temperature T in magnetic cooling.

We can divide the cycle into the following stages:

1. Isothermal magnetisation: We shall find the heat given out by the salt.

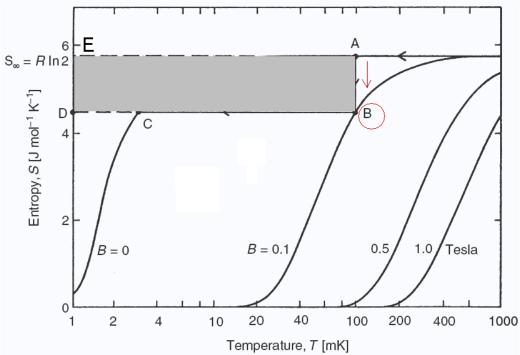
2. Adiabatic demagnetisation: We shall find the lowest temperature reached.

3. Warming up: We shall determine the cooling power.

Isothermal magnetisation takes place from A to B on the graph at the start. Since dQ = TdS, the heat given out is

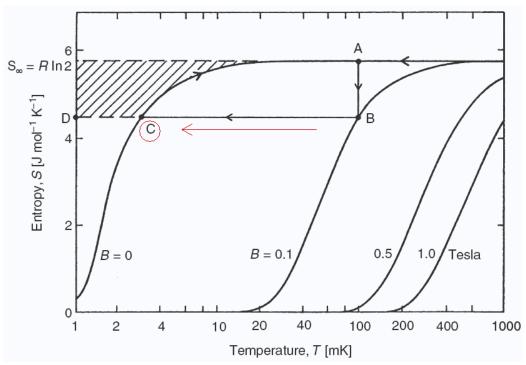
$$Q = \int_{B}^{A} T dS.$$

This is just the area of the rectangle ABDE.



The heat released is usually a few J/mol of the refrigerant (the salt), so it can easily be absorbed by an evaporating helium bath or a dilution refrigerator.

Adiabatic demagnetisation takes place from B to C on the graph.



Later on, we shall derive the formula for magnetic entropy. In that formula, we shall see that the entropy is a function of B/T.

For now, a quick way to understand this is to look at the Boltzmann distribution, $\exp(-\mu_B B/k_B T)$. This is indeed a function of B/T.

Since the entropy should depend on $\exp(-\mu_B B/k_B T)$, we would expect the entropy to be a function of B/T as well.

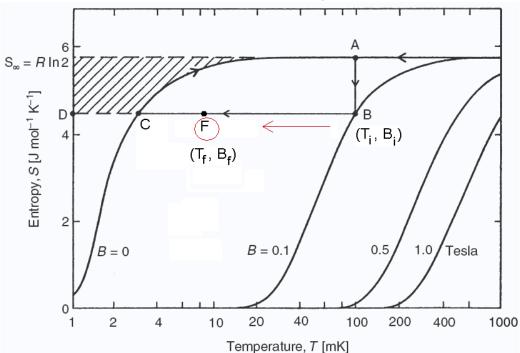
This gives us a quick way to find the coldest temperature reached in this demagnetisation step.

From the graph, we see that the entropy is a simple function of T and B. If T increases, entropy increases. If B increases, entropy decreases.

In the adiabatic process, the entropy is a constant. Since it is a function of B/T, then B/T must also be constant. This is just the equation we need:

$$\frac{B}{T} = \text{constant}$$

Point B: Suppose we start at temperature T_i and field B_i . If this is point B on the graph, then $B_i = 0.1T$ and $T_i = 100mK$



Point F: We then reduce the field to a smaller value B_f . Let T_f be the new temperature.

The equation B/T = constant means that

$$\frac{B_f}{T_f} = \frac{B_i}{T_i}$$

The new temperature is

$$T_f = \frac{T_i}{B_i} B_f$$

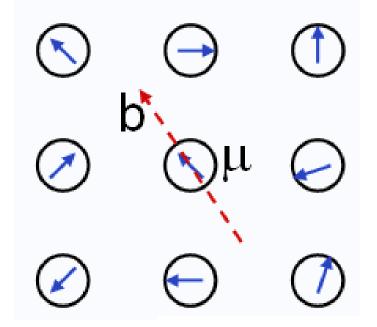
Clearly, we can make T_f very small by reducing the magnetic field B_f to a very small value.

But what if we reduce the magnetic field B_f to zero? Surely the temperature T_f would not go to zero. Something must happen to limit the lowest temperature that we can reach.

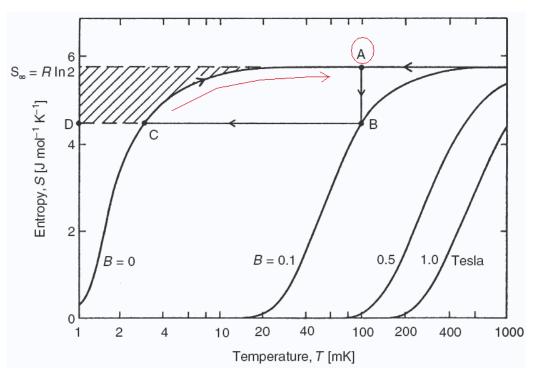
Indeed, this is the case. When the temperature is sufficiently low, the effects of the magnetic fields from neighbouring ions of the salt become important.

Interacting Magnetic Dipoles

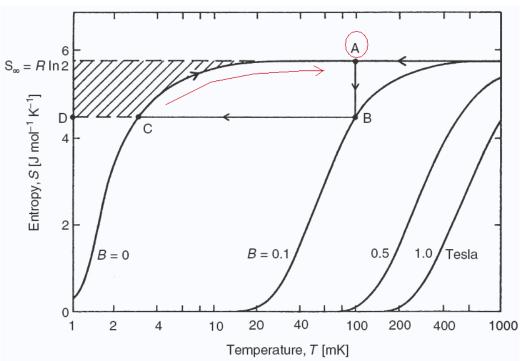
When the temperature is sufficiently low, the mutual interaction would tend to align all magnetic dipoles in the same direction. When this happens, the entropy falls to zero, and the magnetic cooling would stop.



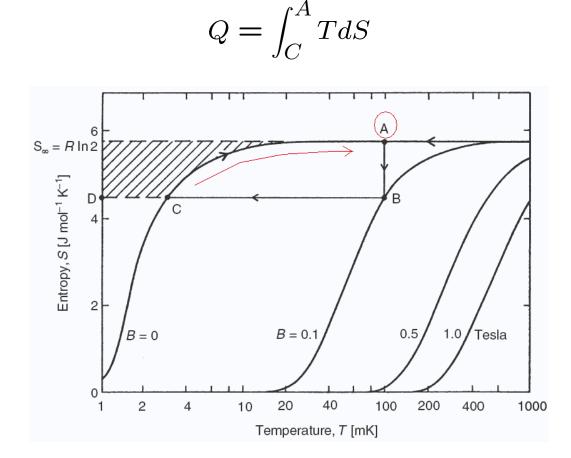
So the mutual interaction limits the lowest temperature that can be achieved using this method. At very low temperatures, the equation would have to be modified to take into account this mutual interaction. We shall come back to this. Point C: We can now see that the graph is misleading. We do not actually demagnetise to a field at point C, which is zero. Rather, we would demagnetise to a very small field, close to C.



To make things simple, we shall still refer to C for the end point of the demagnetisation. Then warming up starts. Remember that the salt is thermally isolated during the demagnetisation. After reaching the lowest temperature at C, the salt remains isolated. We hope that it would stay cold for as long as possible.

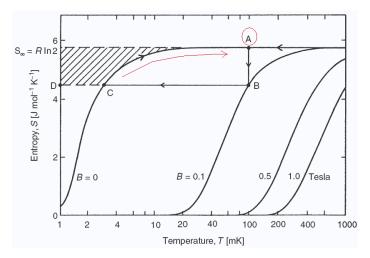


But because insulation is not perfect, the salt starts warming up slowly. Since the magnetic field B is fixed, the temperature and entropy would follow the curve and eventually reach the starting temperature at A. As it warms up, the heat absorbed by the salt can be obtained from the entropy using the same formula as before



We need to integrate along the curve from C to A. So the heat absorbed is given by the shaded region on the graph.

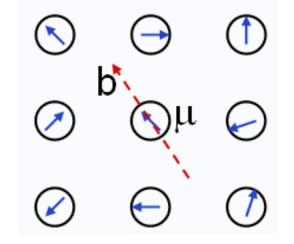
The heat absorbed in warming up also gives the cooling power. If the salt can absorb more of the heat that leaks in through the insulation, then it would be able to remain cold for a longer period of time.



Note that this is a different definition from before. For the dilution refrigerator, the cooling power \dot{Q} is the rate at which heat is absorbed.

The cooling power Q for the magnetic refrigerator is the total heat absorbed.

We have seen that the interaction between magnetic dipoles of the ions in the salt sets a lower limit to the temperature that can be reached by demagnetisation.



This also means that the formula for the lowest temperature

$$T_f = \frac{T_i}{B_i} B_f$$

would not be accurate at very low temperatures. It can be modified to the following form:

$$T_f = \frac{T_i}{B_i} \sqrt{B_f^2 + b^2}$$

Lets try and understand this formula physically.

$$T_f = \frac{T_i}{B_i} \sqrt{B_f^2 + b^2}$$

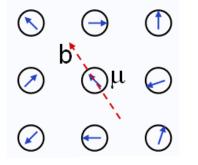
We see that when B_f is reduced to zero,

$$T_f = \frac{T_i}{B_i}b.$$

If we compare this with the original form of

$$T_f = \frac{T_i}{B_i} B_f$$

we see that b corresponds to B_f . This makes sense if we think of b as the field that remains after the applied magnetic field has been reduced to zero. When the applied magnetic field is reduced to zero, there is indeed a remaining field. That would be the resultant field from the neighbouring magnetic dipoles.



We are looking at a temperature T_c at which the effect of this interaction becomes important. This means that $k_B T_c$ is comparable to the interaction energy

$$\varepsilon_d = \mu b.$$

 T_c is called the ordering temperature. It is the temperature below which the neighbouring fields become strong enough to align the dipoles. We may define

$$k_B T_c = \mu b.$$

Magnetic Refrigerators

The performance of a magnetic refrigerator is mainly determined by:

- the starting magnetic field and temperature,
- the heat leaks, and
- the paramagnetic salt that is used.

Typical starting conditions are 0.1 to 1 T and 0.1 to 1 K. These are fairly easy to achieve nowadays.

There a few properties of a paramagnetic salt that are desirable:

- low ordering temperature to reach low temperatures,
- large specific heat to absorb more heat before warming up

The following are paramagnetic salts that have been used:

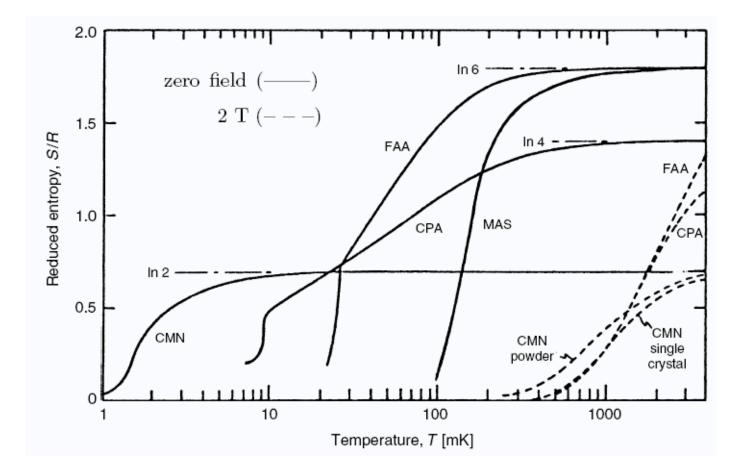
"High"-temperature salts:

$$\begin{split} \mathrm{MAS} &: \mathrm{Mn}^{2+}\mathrm{SO}_4 \cdot (\mathrm{NH}_4)_2 \mathrm{SO}_4 \cdot 6\mathrm{H}_2\mathrm{O}; & T_{\mathrm{c}} \simeq 0.17\,\mathrm{K} \\ \mathrm{FAA} &: \mathrm{Fe}_2^{3+}(\mathrm{SO}_4)_3 \cdot (\mathrm{NH}_4)_2 \mathrm{SO}_4 \cdot 24\mathrm{H}_2\mathrm{O}; & T_{\mathrm{c}} \simeq 0.03\,\mathrm{K} \end{split}$$

"Low"-temperature salts:

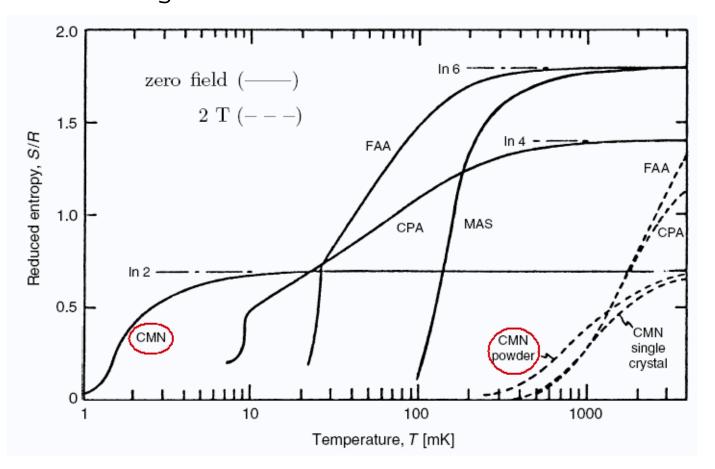
The last one, CMN, has the lowest ordering temperature. This means it can potentially reach the lowest temperature before the interaction between magnetic dipoles become important. CMN has been used extensively and could reach 2 mK.

The follow graphs show the entropies of the actual salts.



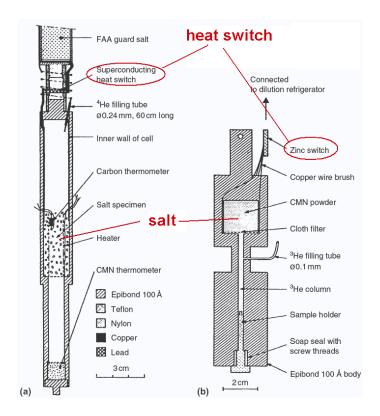
Pobell, Matter and methods at low temperatures (2007)

For example, look at the 2 graphs for the salt CMN: The one to the left is for zero magnetic field. The one to the right is for 2 T.



They look very similar to the entropy graphs that are shown earlier.

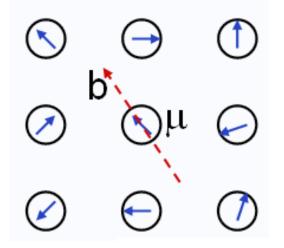
These are examples of actual magnetic refrigerators that have been built.



Pobell, Matter and methods at low temperatures (2007) Notice the heat switch near the top. They are usually connected to a dilution refrigerator. The paramagnetic salt refrigerant is in the middle. Magnetic refrigerators using paramagnetic salts are now largely replaced by the dilution refrigerator, which can reach the same temperatures.

However, they are still useful for small experiments and satellites, where compact refrigerators are required. Examples are in detectors for millimetre wave, X rays and dark matter. **Nuclear Refrigeration**

We have so far looked at the use of the electronic magnetic dipoles for cooling. This is limited to milliKelvin temperatures by the interaction between the electronic dipoles.



It is possible to reach much lower temperatures if we use the nuclear magnetic dipoles. The magnetic dipole moment of the nucleus is much smaller than that of the electron. As a result, the interaction between nuclear dipoles is much weaker. To get some idea of the relative magnitudes, we look at the unit for electronic dipole moment (Bohr magneton) and the unit for nuclear dipole moment (nuclear magneton):

Bohr magneton, $\mu_B = 9.27 \times 10^{-24} \text{ J/T}$ Nuclear magneton, $\mu_n = 5.05 \times 10^{-27} \text{ J/T}$

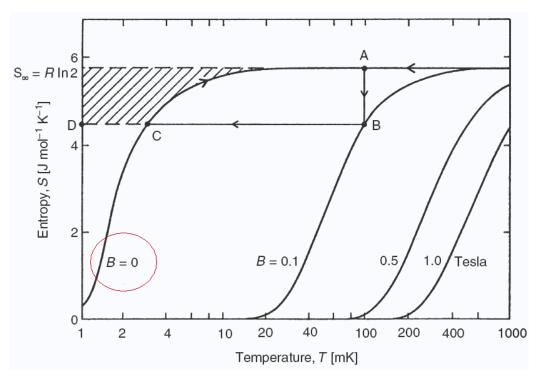
The nuclear magneton is nearly 2000 times smaller. This gives us an idea of how much smaller the nuclear magnetic moment is.

If we use the nuclear magnetic dipole for cooling, we can reach microKelvin temperatures because of the much smaller interaction field. The ordering temperature for the nuclear dipole can be as small as 0.1 μ K.

For nuclear cooling, we can use metal as the refrigerant instead of paramagnetic salts. Metal has the advantage of high thermal conductivity. Although the small nuclear moment offers the potential of reaching much lower temperatures, it also requires much more demanding conditions. The very small moment means that we need very high starting magnetic fields, and very low starting temperatures.

As an example, we look at copper. Copper is a "work horse" of nuclear refrigeration. For copper, we would typically need a starting field of $B_i = 8$ T, and a starting temperature of $T_i = 10$ mK. This is just to reduce the entropy by 9%.

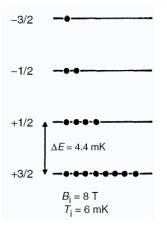
From the earlier explanation on the principle of magnetic cooling, we know that an lower entropy means that a lower temperature can be reached during demagnetisation. It also means a higher cooling power, since more heat can be absorbed during warming up. From the entropy graph, we can see that to reduce the entropy further, even higher fields and lower temperatures would be required.



The 8 T field already requires superconducting magnets, and the 10 mK temperature would require a dilution refrigerator.

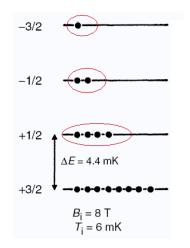
Why would a small magnetic moment require higher starting field and lower starting temperature? Lets try and understand this physically.

Consider the magnetic energy levels of copper. Applying a magnetic field increases the spacing between levels. Because of the small nuclear moment, the spacing would be small even for a high starting field.



Pobell, Matter and methods at low temperatures (2007)

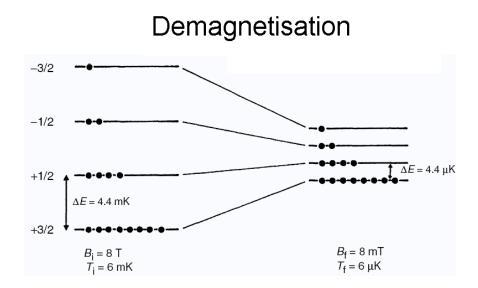
Because the spacing is small, we would get more particles at the higher energy level according to the Boltzmann distribution. This means higher entropy. In order to reduce this, we need a lower starting temperature.



Pobell, Matter and methods at low temperatures (2007)

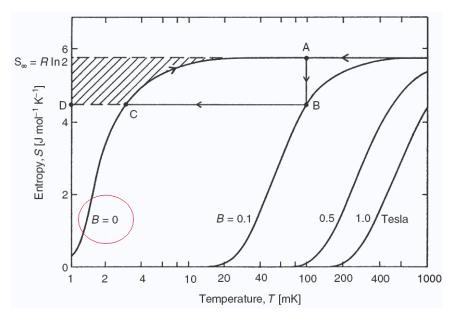
This is difficult. For copper, even at a starting temperature of 10 mK, there is still a substantial fraction of the nuclei at the higher levels. The levels are just too close together because of the small nuclear moment.

Fortunately, because the nuclear moment is small, the interaction field is also small. This means that in the demagnetisation step, it is possible to reduce the temperature to a very small value.



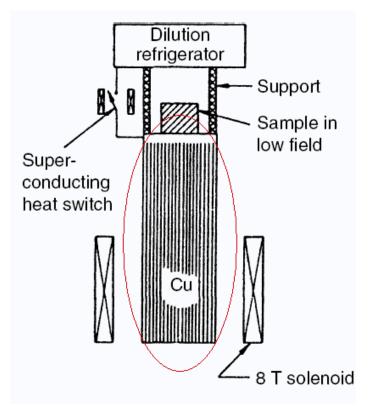
In the case of the copper example, if we reduce the field by 1000 times to 8 mT, the temperature also falls by 1000 times to 6 μ K.

One disadvantage of very low temperatures in magnetic cooling is that the cooling power becomes very small. The cooling power is given by the shaded region in the graph.



The horizontal axis is temperature. So for low temperatures, the horizontal size of the shaded area would also be small. Since nuclear cooling is 1000 times colder than electronic magnetic cooling, the cooling power is also 1000 times smaller. This is a schematic diagram of a nuclear refrigerator. Notice how the main components are connected together.

The refrigerant is a copper block at the centre.



Pobell, Matter and methods at low temperatures (2007)

State the formula for energy levels in a spin 1/2 paramagnetic salt.

Sketch and explain the temperature graphs for energy, heat capacity and entropy of the spin 1/2 salt.

State the distribution of spin 1/2 ions among these levels. Derive the formula for total energy.

Use the entropy graph to explain magnetic cooling.

Explain how to find the heat of magnetisation, the cooling power, and the final cooling temperature.

Explain what limits the lowest temperature that can be achieved. Explain how nuclear cooling overcomes this problem.

Worked Examples

Example 1

There is one mole of a spin 1/2 salt in a magnetic field of 2 T.

(i) Write down the formulae for the magnetic energy levels. Calculate them.

(ii) Write down the formula for the distribution of number of spin 1/2 ions in each level. Find the high temperature limit of each formula.

(iii) Hence find the population in each energy level in the high temperature limit.

Solution

(i) Formulae for the magnetic energy levels are

$$\varepsilon_1 = -\mu_B B$$
, $\varepsilon_2 = \mu_B B$.

Substituting B = 2 T, we get

$$\varepsilon_1 = -1.854 \times 10^{-23}$$
 J, $\varepsilon_2 = 1.854 \times 10^{-23}$ J.

(ii) The particles follow Boltzmann distribution:

$$n_1 = A \exp\left(\frac{\mu_B B}{k_B T}\right)$$
, $n_2 = A \exp\left(-\frac{\mu_B B}{k_B T}\right)$

At high temperatures, T is large and the arguments $\varepsilon_1/k_B T$ and $\varepsilon_2/k_B T$ both tend to zero.

So the high temperature limits are:

$$n_1 = A, n_2 = A.$$

(iii) The total population of spin 1/2 ions is 1 mole.

Since the populations are equal in both levels, the population of spin 1/2 ions in each level is 0.5 mole.

Example 2

There is one mole of a spin 1/2 salt in a magnetic field of 2 T.

(i) Write down the formula for the Boltzmann factor. Find the Boltzmann factor at each energy level when temperature is 0.5K.

(ii) Find the ratio of the population at the higher energy level to the population at the lower energy level.

(iii) Find the population at each energy level in moles.

Solution

(i) The Boltzmann factors at levels 1 and 2 are :

$$\exp\left(\frac{\mu_B B}{k_B T}\right) \text{ and } \exp\left(-\frac{\mu_B B}{k_B T}\right)$$

respectively.

Substituting B = 2 T and T = 0.5 K, we find

$$\exp\left(\frac{\mu_B B}{k_B T}\right) = 14.69 \text{ and } \exp\left(-\frac{\mu_B B}{k_B T}\right) = 0.06809.$$

(ii) The populations are

$$n_1 = A \exp\left(\frac{\mu_B B}{k_B T}\right), \ n_2 = A \exp\left(-\frac{\mu_B B}{k_B T}\right)$$

The ratio is

$$n_1: n_2 = \exp\left(\frac{\mu_B B}{k_B T}\right): \exp\left(-\frac{\mu_B B}{k_B T}\right)$$

is the ratio of the Boltzmann factors.

So the answer is $n_1 : n_2 = 14.69 : 0.06809$.

(iii) The total population of spin 1/2 ions is 1 mole.

This is distributed between the two energy levels in the ratio 14.69 : 0.06809.

So the population in level 1 is

$$n_1 = \frac{14.69}{14.69 + 0.06809} \times 1 = 0.9954$$

and the population in level 2 is

$$n_2 = \frac{0.06809}{14.69 + 0.06809} \times 1 = 0.004615$$

Example 3

There is one mole of a spin 1/2 salt in a magnetic field of 2 T. At first, the salt is at a high temperature where the populations of spin 1/2 ions at each energy level are approximately equal.

(i) When temperature is lowered to 0.5 K, how much of the population falls from higher to lower energy level? (Use results from Example 2.)

(ii) When this happens, how much heat is given out? (Use results from Example 1.)

Solution

(i) The total population is 1 mole. So at the high temperature, there is 0.5 mole at each level:

$$n_1 = 0.5, n_2 = 0.5.$$

From Example 2, there are at 0.5 K the following:

$$n_1 = 0.9954, n_2 = 0.004615.$$

So the amount that falls from higher to lower level is:

 $(n_2 \text{ at high temperature}) - (n_2 \text{ at } 0.5 \text{ K}) = 0.5 - 0.004615 = 0.4954 \text{ mole}$

(ii) From Example 1, the energies of each level are

$$\varepsilon_1 = -1.854 \times 10^{-23}$$
 J, $\varepsilon_2 = 1.854 \times 10^{-23}$ J.

When a particle falls from higher to lower level, the heat it gives out is $\varepsilon_2 - \varepsilon_1$.

0.4954 mole of spin 1/2 ions fall from higher to lower level. This number of spin 1/2 ions is 0.4954 N_A .

So the total heat given out is:

$$0.4954N_A \times (\varepsilon_2 - \varepsilon_1) = 11.06$$
 J.

Example 4

This question follows from Example 3. The salt is now isolated thermally, so that no heat can go out or come in.

(i) Write down the formula for the final temperature in adiabatic demagnetisation, explaining all symbols used. The magnetic field is then lowered from 2 T to 0.2 T. Find the new temperature of the salt.

After some time, the temperature slowly increases because heat leaks in.

(ii) The spin 1/2 ions move from lower to higher level until populations are approximately equal again. Find the heat absorbed.

Example 4

(i) Formula for the final temperature in adiabatic demagnetisation is

$$T_f = \frac{B_f}{B_i} T_i,$$

where T_i is initial temperature, T_f is final temperature, B_i is initial magnetic field and B_f is final magnetic field.

From Example 3, $T_i = 0.5$ K, $B_i = 2$ T.

Given $B_f = 0.2 \text{ T}$. Substituting, we find

$$T_f = \frac{0.2}{2} \times 0.5 = 0.05$$
 K.

(ii) We know from Example 3 that 0.4954 mole of particles has fallen from higher to lower energy.

When the salt warms up, the same amount would move back to higher level. However, the energy spacing between levels is now smaller, because the field has decreased.

The energy spacing is

$$\varepsilon_2 - \varepsilon_1 = \mu_B B - (-\mu_B B) = 2\mu_B B.$$

This spacing is proportional to B.

The field has decreased from 2 T to 0.2 T. This is 10 times smaller.

This means that the energy spacing is also 10 times smaller. Therefore, when the particles move back to higher level, the energy gain would also be 10 times smaller.

From Example 3, the heat given out was 11.06 J. The energy gain now would be 10 times smaller than this.

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So the answer is 11.06/10 = 1.106 J.
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