Thermodynamics third law

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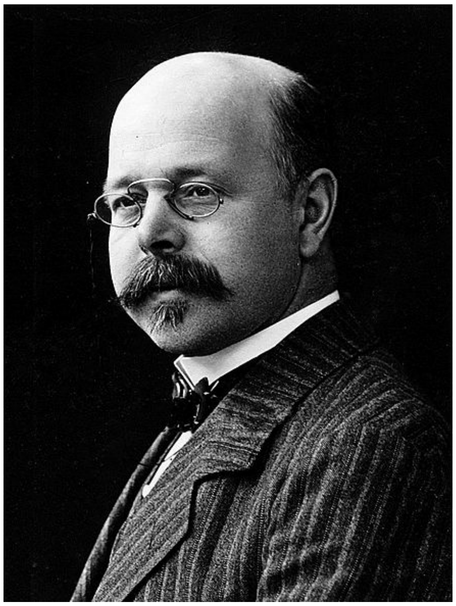
Walther Hermann Nernst, (25 June 1864 – 18 November 1941) was a German chemist who is known for his work in thermodynamics; his formulation of the Nernst heat theorem helped pave the way for the third law of thermodynamics, for which he won the 1920 Nobel Prize in Chemistry. Nernst helped establish the modern field of physical chemistry and contributed to electrochemistry, thermodynamics and solid state physics. He is also known for developing the Nernst equation in 1887.



https://en.wikipedia.org/wiki/Walther_Nernst

1. Overview

The third law of thermodynamics is an axiom of nature regarding entropy and the impossibility of reaching absolute zero of temperature (Nernst's theorem, 1906). As a system approaches absolute zero temperature, all processes cease and the entropy of the system approaches a universal constant (that can be taken to be zero).

$$\lim_{T\to 0} S = 0$$

Alternative statement: It is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations.

Since $S = k_B \ln W$ (Boltzmann), the entropy is related to the number of microscopic states consistent with macroscopic states variables. Third low states that at zero temperature, there is only one microscopic state, i.e., the system can only occupy the ground state at $T = 0K$. In other words,

$$W = 1 \text{ (the ground state, just one state)}, \qquad S = k_B \ln(1) = 0$$

which can be explained only by the combination of quantum mechanics and statistical mechanics (quantum statistical mechanics).

2. The statement of the third law

Nernst's statement

> Near absolute zero, all reactions in a system in internal equilibrium take place with no change in entropy.

Planck's statement

> The entropy of all systems in internal equilibrium is the same at absolute zero, and may be taken to be zero.

Simon's statement

> The contribution to the entropy of a system by each aspect of the system which in in internal thermodynamic equilibrium tends to zero as $T \to 0$.

3. Consequences of the third law

(a) Heat capacity

From the definitions of the heat capacities at constant volume and constant pressure, we have

$$C_{P,V} = T\left(\frac{\partial S}{\partial T}\right)_{P,V} = \left(\frac{\partial S}{\partial \ln T}\right)_{P,V}$$

since $\ln T \to -\infty$ and $S \to 0$ as $T \to 0$.

The heat capacities approach zero as the temperature approaches absolute zero. With respect this behavior, extensive experiments provide a full confirmation of the third law.

(b) Thermal expansion

The thermal expansion is defined by

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Using the Maxwell's relation

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

We have

$$\alpha_V = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T$$

leading to

$$\lim_{T\to 0}\alpha_V = 0$$

The thermal expansion approaches zero as the temperature approaches absolute zero.

(c) No gas remains ideal

For the ideal gas, the entropy S is given by

$$S = C_V \ln T + R\ln V$$

As $T \to 0$, $S \to -\infty$

(d) Break down of the Curie law

From the Maxwell's relation

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B$$

Suppose that the magnetization M is expressed by

$$M = \frac{C}{T}B \qquad \text{(Curie law)}$$

and

$$\left(\frac{\partial M}{\partial T}\right)_B = -\frac{C}{T^2}B$$

As $T \to 0$, $\left(\frac{\partial M}{\partial T}\right)_B \to -\infty$, which is inconsistent with

$$\left(\frac{\partial S}{\partial B}\right)_T \to 0$$

since $S \to 0$ as $T \to 0$.

((**Note**))
The occurrence of the Curie law indicates that the ground state is degenerate in the absence of magnetic field. As $T \to 0$, the ground state is non-degenerate. So the Curie-law does not exist any longer.

(e) Nernst's theorem applied to solids

We consider a solid body which is heated (at constant pressure, for example) until its temperature increases from the absolute zero to a certain value *T*. Let $C(T)$ be its heat capacity (at constant pressure) when its temperature is *T*. Then, if the temperature changes by an amount d*T*, the system will absorb an amount of heat $dQ = C(T)dT$. The entropy of the system at the temperature *T* is therefore given by

$$S = \int_0^T \frac{C(T)}{T} dT . \tag{1}$$

We can obtain the first consequence of the Nernst's theorem from Eq.(1). We observe that if the heat capacity, *C*(0), at absolute zero were different from zero, the integral (1) would diverge at the lower limit. We must therefor have

$$C(0) = 0$$

This result is in agreement with the experiments on the specific heat of solids.

4. Explanation based on quantum mechanics

According to the quantum mechanics, the system is in a lowest state (non-degenerate state) so called the ground state. Mathematically, the absolute entropy of any system at zero temperature is defined by

$$S = k_B \ln \Omega_0$$

where Ω_0 is the number of ground state. When $\Omega_0 = 1$ as $T \to 0$, the entropy $S \to 0$. The entropy tends to zero as the temperature approaches zero.

((**Landau and Lifshitz**))

At absolute zero, any part of the body must be in a particular quantum state, the ground state. In other words, the statistical weights of these parts are equal to unity, and therefore so is their product, i.e, the statistical weight of the macroscopic state of the body as a whole. The entropy of the body, being the logarithm of its statistical weight, is therefore zero. We consequently reach the important result that the entropy of any body vanishes at the absolute zero of temperature. This is called Nernst's theorem (W. Nernst, 1906).

It should be emphasized that this theorem is a deduction from quantum statistics, in which the concept of discrete quantum states is of essential importance. The theorem cannot be proved in purely classical statistics, where the entropy is determined only to within an arbitrary additive constant.

5. Adiabatic demagnetization for spin 1/2 system

Each electron spin has a magnetic moment (μ_B). Note that the direction of spin is antiparallel to that of magnetic moment. There are two spin states which are denoted by the spin state ↓ for positive magnetic moment and by the spin state ↑ for negative magnetic moment. In the presence of an applied magnetic field along the *z* axis, the two orientations of magnetic moments have different energies, and the Boltzmann distribution can be used to calculate the small difference in populations for a given temperature. At higher temperature there will be slightly lower energy ↓ spins than higher energy ↑ spins. If somehow we could contrive to convert some of the ↑ into ↓ spins, then the population difference will correspond to a lower temperature, and we shall have cooled the sample. If we could contrive to make all the spins ↓, then we shall have reached absolute zero. We shall represent the sample at room temperature and in the absence of a magnetic field by . . .↑↓↓↑↓↓↓↑↑↓↑ . . .with a random distribution of ↓ and ↑ spins. These spins are in thermal contact with the rest of the material in the sample and share the same temperature.

Now we increase the magnetic field with the sample in thermal contact with its surroundings. Because the sample can give up energy to its surroundings, the electron spin populations can adjust. The sample becomes . . .↓↓↑↓↑↑↓↓↓↑↓ . . .with a small preponderance of ↓ spins over ↑ spins. The spin arrangement contributes to the entropy, and so we can conclude that, because the spin distribution is less random than it was initially (because we can be more confident about getting a ↓ in a blind selection), the entropy of the sample has been reduced (**Fig.**). That is, by turning up the magnetic field and allowing energy to escape as the electron spins realign, we lower the entropy of the sample. Now consider what happens when we isolate the sample thermally from its surroundings and gradually reduce the applied field to zero. A process that occurs without the transfer of energy as heat is called adiabatic, so this step is the ‘adiabatic demagnetization’ step that gives the process its name. Because the process is adiabatic the entropy of the entire sample (the spins and their immediate surroundings) remains the same. The electron spins no longer have a magnetic field to align against, so they resume their original higher entropy random arrangement like . . .↓↓↑↓↑↑↓↓↓↑↓ . . . .However, because there is no change in the overall entropy of the sample, the entropy of the molecules that carry the electrons must be lowered, which corresponds to a lowering of temperature. Isothermal magnetization followed by adiabatic demagnetization has cooled the sample (originally from **Atkins**)

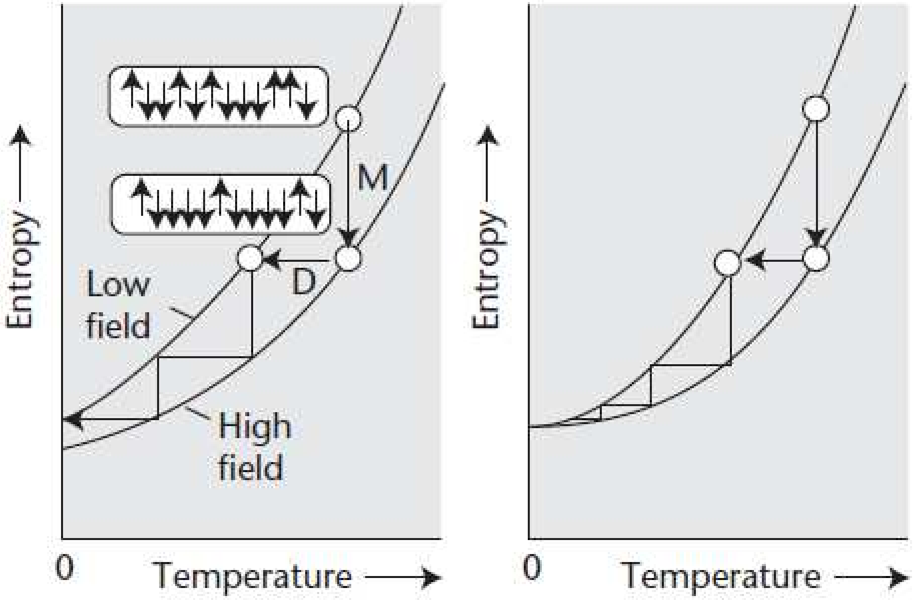


Fig. The process of adiabatic demagnetization for reaching low temperatures. The arrows depict the spin alignment of the electrons in the sample. The first step (M) is isothermal magnetization, which increases the alignment of the spins, the second step (D) is adiabatic demagnetization, which preserves the entropy and therefore corresponds to a lowering of temperature. If the two curves did not meet at $T = 0$, it would be possible to lower the temperature to zero (as shown on the left). That a finite sequence of cycles does not bring the temperature to zero (as shown on the right) implies that the curves meet at $T = 0$ (**Atkins**)

Next, we repeat the process. We magnetize the newly cooled sample isothermally, isolate it thermally, and reduce the field adiabatically. This cycle lowers the temperature of the sample a little more. In principle, we can repeat this cyclic process, and gradually cool the sample to any desired temperature. At this point, however, the wolf inside the third law hurls off its sheep's clothing. If the entropy of the substance with and without the magnetic field turned on were to be like that shown in the left-hand half of Figure, then we could select a series of cyclic changes that would bring the sample to $T = 0$ in a finite series of steps. It has not proved possible to achieve absolute zero in this way. The implication is that the entropy does not behave as shown on the left, but must be like that shown on the right of the illustration, with the two curves coinciding at $T = 0$.

6. Construction of the zig-zag path in the entropy vs temperature diagram

We use the entropy for the spin 1/2,

$$\begin{aligned}\frac{S}{k_B N} &= \ln[2\cosh(\frac{\mu_B B}{k_B T})] - \frac{\mu_B B}{k_B T}\tanh(\frac{\mu_B B}{k_B T}) \\ &= \ln[2\cosh(\frac{b}{t})] - \frac{b}{t}\tanh(\frac{b}{t})\end{aligned}$$

or simplicity we use the form

$$\begin{aligned}f(\frac{t}{b}) &= \ln[2\cosh(\frac{\mu_B B}{k_B T})] - \frac{\mu_B B}{k_B T}\tanh(\frac{\mu_B B}{k_B T}) \\ &= \ln[2\cosh(\frac{b}{t})] - \frac{b}{t}\tanh(\frac{b}{t})\end{aligned}$$

We make a plot of $f(\frac{t}{b})$ as a function of t, where we choose two values of b; one is $b = 1$ and the other value of b (= 3, 1.5, 1.2). We define the points in the $f(t/b)$ versus t for b= 1 and for b.

$$\boldsymbol{a}_n = \{t = \frac{1}{b^n}, f(\frac{t = \frac{1}{b^n}}{b = 1})\} = \{t = \frac{1}{b^n}, f(\frac{1}{b^n})\},$$

$$\boldsymbol{b}_n = \{t = \frac{1}{b^n}, f(\frac{t = \frac{1}{b^n}}{b})\} = \{t = \frac{1}{b^n}, f(\frac{1}{b^{n+1}})\}$$

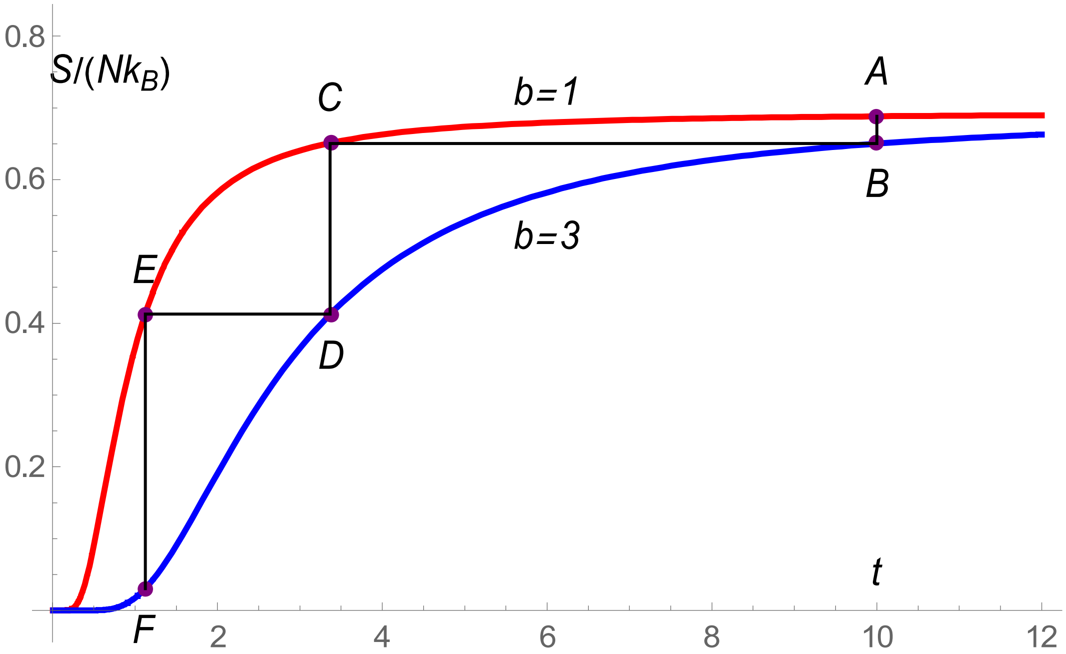
$$\boldsymbol{a}_{n+1} = \{t = \frac{1}{b^{n+1}}, f(\frac{t = \frac{1}{b^{n+1}}}{b = 1})\} = \{t = \frac{1}{b^{n+1}}, f(\frac{1}{b^{n+1}})\}$$

Path $\{\boldsymbol{a}_n \to \boldsymbol{b}_n\}$: isothermal process (the magnetic field decreases from b = 1 to b) which corresponds to the vertical line.

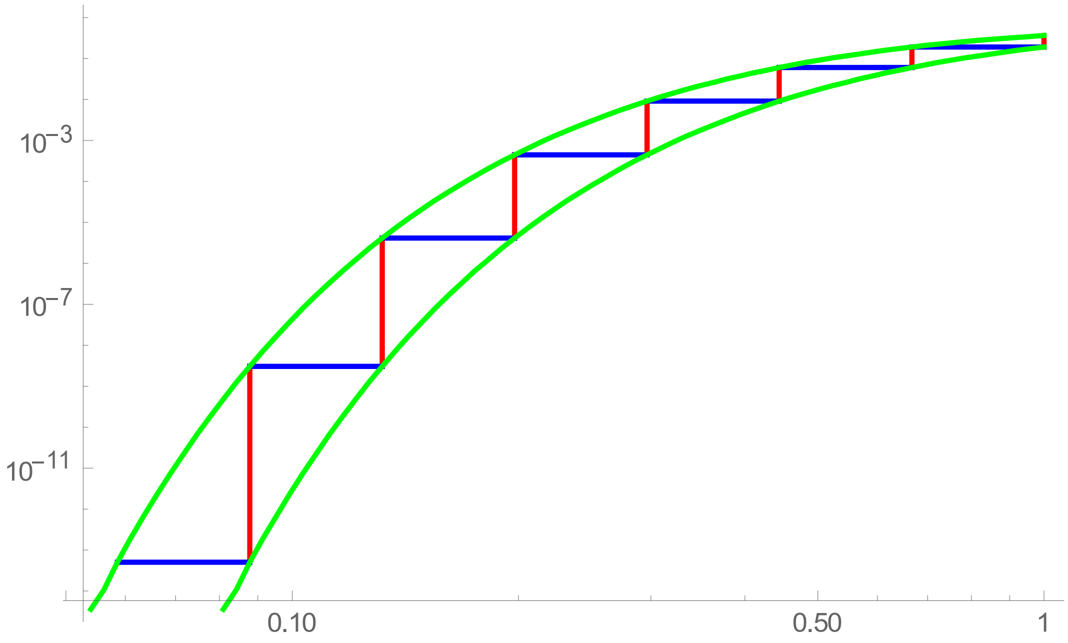
Path $\{\boldsymbol{b}_n \to \boldsymbol{a}_{n+1}\}$: isentropic process (the magnetic field decreases from b to b =1) which corresponds to the horizontal line. The zig-zag path can be obtained by repeating these two processes staring form the point $\boldsymbol{a}_0 = \{t=1, f(\frac{t=1}{b=1})\} = \{1, f(1)\}$;

$$\boldsymbol{a}_0 \to \boldsymbol{b}_0 \to \boldsymbol{a}_1 \to \boldsymbol{b}_1 \to \boldsymbol{a}_2 \to \boldsymbol{b}_2 \to \boldsymbol{a}_3 \to \boldsymbol{b}_3 \to \cdots\cdots\cdots\cdots$$

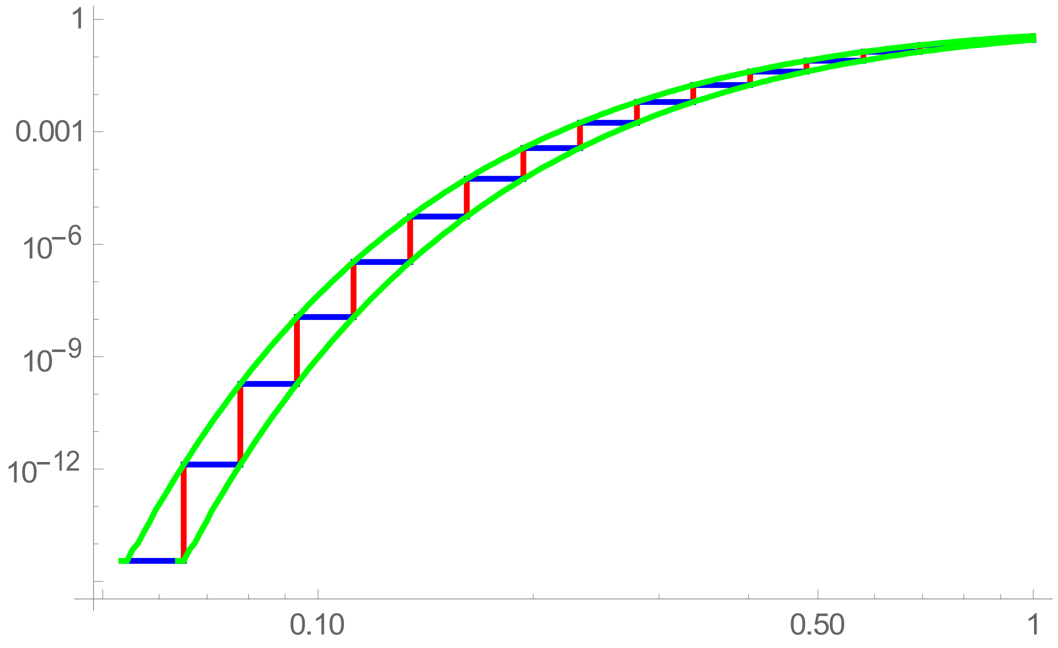
(a) $\boldsymbol{b}$ **= 3**



(b) $\boldsymbol{b}$ **= 1.5**



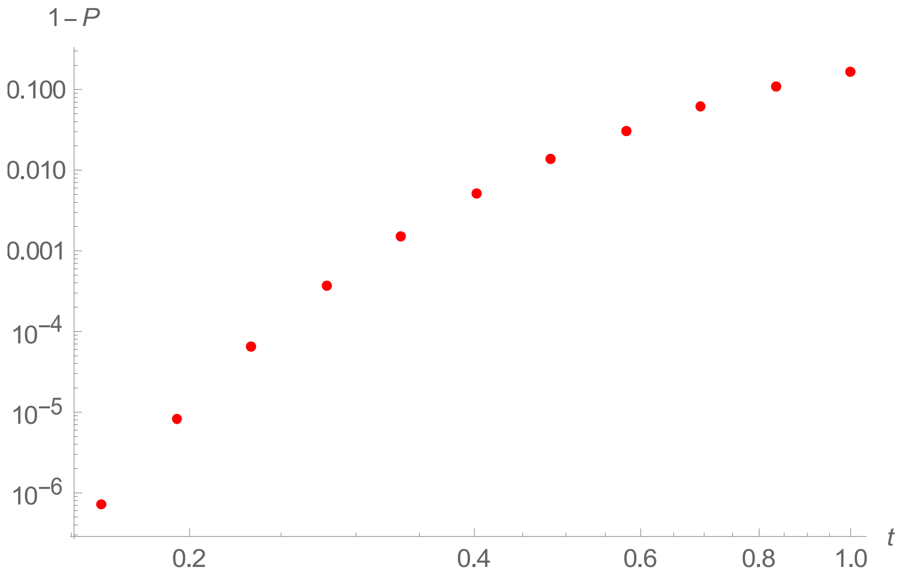
(c) ***b* = 1.2**



We also make a probability $1-P_n$ as a function of *t* for b = 1.2, where

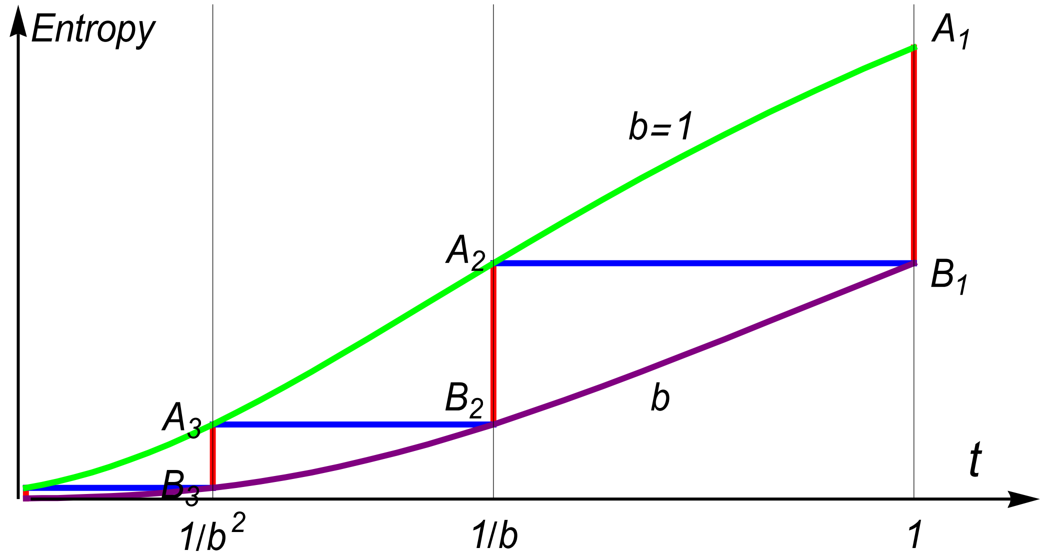
$$t = \frac{1}{b^n}, \qquad 1-P_n = 1-\tanh(b^{n+1})$$

As the temperature t decreases, the probability P approaches very close to unity. This means that the system is nearly in the ground state with ↓↓↓↓↓↓↓↓ ············



7. Physical meaning of the zig-zag path

A series of isothermal and adiabatic processes (demagnetizations) are represented by the zig-zag path. Each successive process reduces the temperature. It is clear, however, that because the curves intersect at $T = 0$, an infinite number of steps would be required of absolute zero by any practical method.



A_1: Stating point. $f(t=1, b=1)$

A_1B_1: Isothermal process (the increase of magnetic field from b = 1 to b) at $t = 1$.

$B_1\,A_2$: Adiabatic demagnetization (isentropic, the decrease of magnetic field from b to $b = 1$). The temperature decreases from $t = 1$ to $t = 1/b$.

A_2B_2: Isothermal process (the increase of magnetic field from $b = 1$ to b) at $t = 1/b$

$B_2\,A_3$: Adiabatic demagnetization (isentropic, the decrease of magnetic field from b to $b = 1$). The temperature decreases from $t = 1/b$ to $t = 1/b^2$.

A_3B_3: Isothermal process (the increase of magnetic field from $b = 1$ to b) at $t = 1/b^2$

Fig. Entropy vs temperature for a cooling process. The unattainability of absolute zero is illustrated by the indefinitely increasing number of staps required to achieve a given temperature reduction as absolute zero is approached.

REFERENCES

P. Atkins, The Law of Thermodynamics A very Short Introduction (Oxford, 2010).
L.D. Landau and E.M. Lifshitz, Statistical Physics (Pergamon Press 1976).

APPENDIX $\frac{S}{k_B N} \to 0$ in the limit of $t \to 0$ for two energy levels.

Noting that $e^{b/t} >> 1$ and $e^{-b/t} << 1$, we can approximate the expression of entropy as

$$
\begin{aligned}
\frac{S}{k_B N} &= \ln[2\cosh(\frac{b}{t})] - \frac{b}{t}\tanh(\frac{b}{t}) \\
&= \ln(e^{b/t} + e^{-b/t}) - \frac{b}{t}\left(\frac{e^{b/t} - e^{-b/t}}{e^{b/t} + e^{-b/t}}\right) \\
&= \ln[e^{b/t}(1 + e^{-2b/t})] - \frac{b}{t}\left(\frac{1 - e^{-2b/t}}{1 + e^{-2b/t}}\right) \\
&\approx \frac{b}{t} + e^{-2b/t} - \frac{b}{t}\left(1 - 2e^{-2b/t}\right) \\
&\approx \frac{2b}{t} e^{-2b/t}
\end{aligned}
$$

where we use the approximation

$$\ln(1+x) \approx x\,, \qquad \frac{1-x}{1+x} \approx 1-2x \qquad \text{for } 0 < x << 1$$

In the limit of $t \to 0$, we have

$$\lim_{t\to 0} S = 0$$
