The First, Second, and Third Law of Thermodynamics (ThLaws05.tex)

A.T.A.M. de Waele

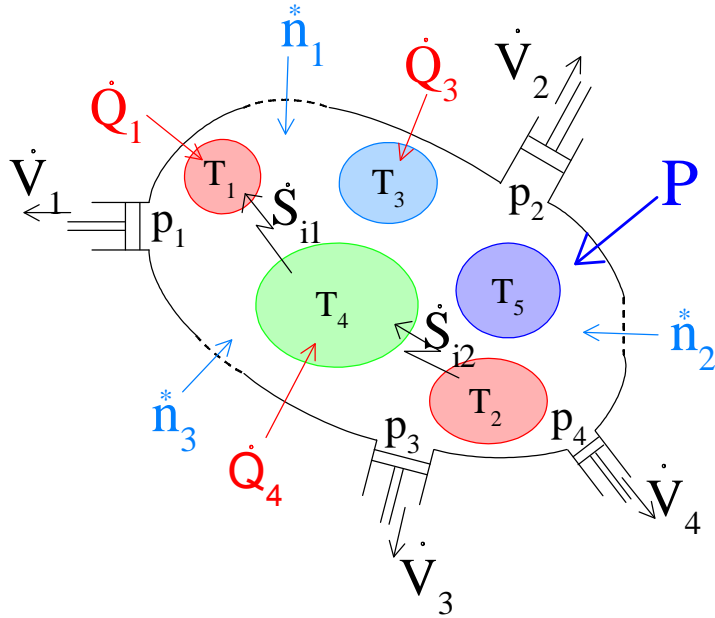September 3, 2009

Contents

1 Introduction

Figure 1: *General representation of a system that consists of a number of subsystems. The interaction with the surroundings of the system can be in the form of exchange of heat, exchange of matter, change of shape, and other exchange of energy. The interactions between the subsystems are of a similar nature and lead to entropy production.*

The laws of thermodynamics apply to well-defined systems. First we will discuss a quite general form of the first and second law. I.e. we consider a system which is inhomogeneous, we allow mass transfer across the boundaries (open system), and we allow the boundaries to move. Fig.1 is a general representation of such a thermodynamic system. In their general form the first and second laws are rather complicated, but in practical cases only a few terms (two or three) play a role. Choosing a clever system is half the solution of many thermodynamical problems.

We will introduce the first and second law for open systems. Why it is important to formulate the law for open systems can be illustrated with Fig.2. This is a schematic diagram of a household refrigerator. It consists of a closed cycle with a compressor, a heat exchanger to room temperature, a condenser, a throttling valve, and a heat exchanger with the cold compartment. If we consider the whole fridge as our system we deal with a closed system. However, if we are interested in the components of the fridge (such as the compressor, heat exchangers, throttling valve) we are dealing with open systems. Therefore the number of open systems is much larger then the number of closed systems.

Secondly we will treat the second law as an equality (see Eq.(4)) and not as an inequality
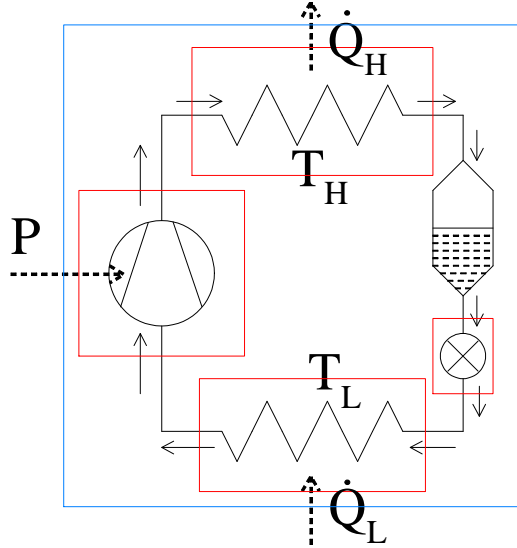
Figure 2: *Schematic diagram of a household refrigerator which consists of a compressor, a heat exchanger to room temperature, a condensor, a throttling valve, and a heat exchanger with the cold compartment. If we consider the whole fridge as one system (blue contour) we deal with a closed system. However, if we are interested in the components of the fridge (compressor, heat exchangers, throttling valve (red contours)) we are dealing with open systems.*

such as in

$$\mathrm{d}S \geq \frac{\mathrm{d}Q}{T}. \tag{1}$$

Unfortunately, Eq.(1) is useless for most practical applications. In order to formulate the second law in the form of an equality we will use the important concept of entropy production.

2   First Law

In the most general form of the first law the various energy fluxes, passing the system boundaries, are integrated over the entire boundary. However, if heat and mass transfer and volume changes are taking place only at some well-defined regions of the system boundaries, the integrals can be replaced by summations. In that case the first law reads

$$\dot{U} = \sum_k \dot{Q}_k + \sum_k \overset{*}{H}_k - \sum_k p_k \dot{V}_k + P.^1 \tag{2}$$

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[1] We use the notation $\overset{*}{Y}$ for the flow of a thermodynamic state function Y and $\dot{Y}$ for the rate of change of Y. Even though the dimensions of $\overset{*}{Y}$ and $\dot{Y}$ are the same their physical meaning is distinctly different.

In Eq.(2)

- U is the internal energy of the system, so $\dot{U}$ is the rate of change of the internal energy. The internal energy is a function of state.

- $\dot{Q}_k$ are the heat flows at the various regions of the boundary which are labeled with k. The convention is that a heat flow is counted positive if heat flows from outside into the system. *Internal* heat flows do not change the internal energy of the system as a whole, so they don't show up in Eq.(2).

- $\overset{*}{H}_k$ are the enthalpy flows into the system defined as

$$\overset{*}{H}_k = \overset{*}{n}_k H_{\mathrm{m}k},\tag{3}$$

where $\overset{*}{n}_k$ is the molar flow of matter flowing into the system and $H_{\mathrm{m}k}$ the molar enthalpy of this matter. Note that the increase of the internal energy $\dot{U}$ is determined by the enthalpy of the added matter $\overset{*}{n}_k H_{\mathrm{m}k}$ and not by the internal energy $\overset{*}{n}_k U_{\mathrm{m}k}$. The difference is $\overset{*}{n}_k p_{\mathrm{k}} V_{\mathrm{m}k}$, which is the work needed to press the matter into the system.

- $\dot{V}_k$ are the rates of change of the volume *of the system* at various moving boundaries, p_k the corresponding pressure behind the moving boundary. Note that $\dot{V}_k$ is not the volume flow of matter which might flow across a certain boundary.

- P takes into account all other forms of work done on the system by its environment (such as electricity, shaft work, etc.).

In the first law work and heat are treated on an equivalent basis.

3 Second Law

The second law reads

$$\dot{S} = \sum_k \frac{\dot{Q}_k}{T_k} + \sum_k \overset{*}{\dot{S}}_k + \sum_k \dot{S}_{\mathrm{i}k} \quad \text{with} \quad \dot{S}_{\mathrm{i}k} \geq 0.\tag{4}$$

Here

- $\dot{S}$ is the rate of change of the entropy of the system.

- T_k represent the temperatures of the subsystems at which the heat flows $\dot{Q}_k$ enter the system.

This is especially clear when these two quantities show up in the same expression such as in the second law of thermodynamics in which the rate of change of the entropy of a system is related to the entropy flow into the system. In the case of heat and work, which are no properties of state, this distinction is meaningless and we will use the dot notation to indicate flow rates.

- $\overset{*}{S}_k$ represent the entropy flows into the system due to matter flowing into the system. The entropy flow is given by

$$\overset{*}{S}_k = \overset{*}{n}_k S_{\mathrm{m}k} \tag{5}$$

  where $S_{\mathrm{m}k}$ is the corresponding molar entropy.

- $\dot{S}_{\mathrm{i}k}$ represent the entropy production rates due to internal irreversible processes. Each of the entropy production rates is always positive. This is an essential aspect of the second law. The summation is over all processes in the system.

The most important irreversible processes are

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  - heat flow over a temperature difference;
  - mass flow over a pressure difference;
  - diffusion;
  - chemical reactions;
  - Joule heating;
  - friction between solid surfaces.

Note that work does not contribute to the entropy change. In the second law work and heat are treated in an essentially different way. In many cases $\dot{Q}/T$ is considered as an entropy flow associated with the heat flow. In this case the second law is a conservation law with flow and source terms.

4 Consequences of the first and second law

4.1 Heat engines

Fig.(3) is a schematic diagram of a heat engine. The machine is a cyclic machine. A heating power $\dot{Q}_{\mathrm{H}}$ enters the engine at a temperature T_{H} and a heat flow $\dot{Q}_{\mathrm{L}}$ leaves it at a temperature T_{L}. Usually T_{L} is around room temperature. A power P is produced. Note that the sign of P differs from the sign in Eq.(2). Due to the irreversible processes inside the engine entropy is produced at a rate $\dot{S}_{\mathrm{i}}$.

In the steady state, after one cycle, the state of the engine is the same as in the beginning of the cycle, thus on average

$$\dot{U} = 0 \tag{6}$$

and

$$\dot{S} = 0. \tag{7}$$

The system is closed so

$$\overset{*}{H} = 0 \tag{8}$$
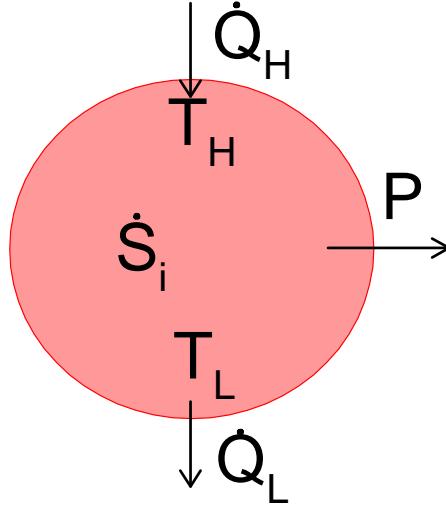
and

$$\overset{*}{S} = 0. \tag{9}$$

Figure 3: *Schematic diagram of a heat engine. A heating power $\dot{Q}_H$ enters the system at some high temperature T_H, and $\dot{Q}_L$ is released at a temperature T_L. A power P is produced and an entropy $\dot{S}_i$ is produced per second.*

The boundaries of the system are fixed so

$$\dot{V}_k = 0. \tag{10}$$

The first law. Eq.(2), with Eqs.(6), (8), and (10), gives

$$\dot{Q}_H - \dot{Q}_L = P. \tag{11}$$

The second law, Eq.(4), with Eqs.(7) and (9) gives

$$0 = \frac{\dot{Q}_H}{T_H} - \frac{\dot{Q}_L}{T_L} + \dot{S}_i \text{ with } \dot{S}_i \geq 0 \tag{12}$$

or

$$\dot{S}_i = \frac{\dot{Q}_L}{T_L} - \frac{\dot{Q}_H}{T_H} \geq 0. \tag{13}$$

Relation (13) already allows a very important conclusion: suppose that there is no heat released at low temperature then

$$\dot{Q}_L = 0. \tag{14}$$

In this case Eq.(13) would reduce to

$$\dot{S}_i = -\frac{\dot{Q}_H}{T_H} \geq 0. \tag{15}$$

As $T_H > 0$ and $\dot{Q}_H > 0$ Eq.(15) is false so our assumption, Eq.(14), must be false. This gives the well-known result that a heat engine can operate only if heat is released at some low temperature. In fact this is the Kelvin formulation of the second law.

Eliminating $\dot{Q}_L$ with Eq.(11) from Eq.(13) gives

$$P = \left(1 - \frac{T_L}{T_H}\right)\dot{Q}_H - T_L\dot{S}_i. \tag{16}$$

As $\dot{S}_i \geq 0$ we must require

$$P \leq \left(1 - \frac{T_L}{T_H}\right)\dot{Q}_H. \tag{17}$$

The efficiency is defined as the ratio

$$\eta = \frac{P}{\dot{Q}_H}. \tag{18}$$

With Eq.(17) follows

$$\eta \leq 1 - \frac{T_L}{T_H}. \tag{19}$$

This famous relation shows that the efficiency of thermal engines has a maximum given by the Carnot efficiency defined as

$$\eta_C = 1 - \frac{T_L}{T_H}. \tag{20}$$
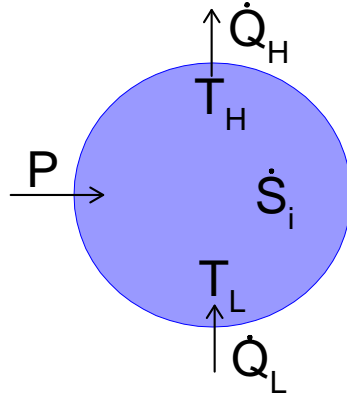
4.2 Refrigerators

Figure 4: *Schematic diagram of a refrigerator. $\dot{Q}_L$ is the cooling power at some low temperature T_L, and $\dot{Q}_H$ is released at a temperature T_H. A power P is supplied to the system and an entropy $\dot{S}_i$ is produced per second.*

Refrigerators, as depicted in Fig.4, can be treated in a similar way as heat engines. The first law, Eq.(2), gives

$$\dot{Q}_H = P + \dot{Q}_L. \tag{21}$$

The second law, Eq.(4), reads

$$0 = \frac{\dot{Q}_\mathrm{L}}{T_\mathrm{L}} - \frac{\dot{Q}_\mathrm{H}}{T_\mathrm{H}} + \dot{S}_\mathrm{i} \text{ with } \dot{S}_\mathrm{i} \geq 0 \tag{22}$$

or

$$\dot{S}_\mathrm{i} = \frac{\dot{Q}_\mathrm{H}}{T_\mathrm{H}} - \frac{\dot{Q}_\mathrm{L}}{T_\mathrm{L}} \geq 0. \tag{23}$$

Eliminating $\dot{Q}_\mathrm{H}$ from Eqs.(21) and (23) gives

$$\dot{S}_\mathrm{i} = \frac{P + \dot{Q}_\mathrm{L}}{T_\mathrm{H}} - \frac{\dot{Q}_\mathrm{L}}{T_\mathrm{L}} \geq 0. \tag{24}$$

If there would be no work done

$$P = 0 \tag{25}$$

then Eq.(24) would reduce to

$$\dot{S}_\mathrm{i} = \left(\frac{1}{T_\mathrm{H}} - \frac{1}{T_\mathrm{L}} \right) \dot{Q}_\mathrm{L} \geq 0. \tag{26}$$

This is false since both $\dot{Q}_\mathrm{L} > 0$ and $T_\mathrm{H} > T_\mathrm{L}$. This means that Eq.(25) must be false: heat cannot flow from a low temperature to a high temperature without doing work. This is Clausius formulation of the second law.

Turning back to Eq.(24) we see that

$$P = \frac{T_\mathrm{H} - T_\mathrm{L}}{T_\mathrm{L}} \dot{Q}_\mathrm{L} + T_\mathrm{H} \dot{S}_\mathrm{i}. \tag{27}$$

As $\dot{S}_\mathrm{i} \geq 0$ we must require

$$P \geq \frac{T_\mathrm{H} - T_\mathrm{L}}{T_\mathrm{L}} \dot{Q}_\mathrm{L}. \tag{28}$$

The coefficient of performance (COP) is defined as the ratio

$$\xi = \frac{\dot{Q}_\mathrm{L}}{P}. \tag{29}$$

With (28) follows

$$\xi \leq \frac{T_\mathrm{L}}{T_\mathrm{H} - T_\mathrm{L}}. \tag{30}$$

This relation shows that the COP of refrigerators has a maximum given by

$$\xi_\mathrm{C} = \frac{T_\mathrm{L}}{T_\mathrm{H} - T_\mathrm{L}}. \tag{31}$$

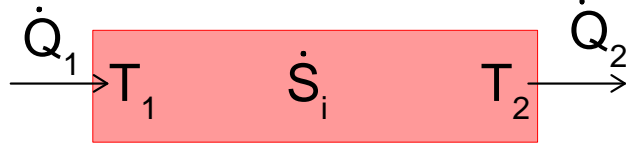This quantity is called the Carnot efficiency of refrigerators.

Figure 5: *Heat conduction experiment. A heat flow $\dot{Q}_1$ enters at T_1 and $\dot{Q}_2$ leaves at T_2.*

4.3 Heat conduction

The third system on which we apply the laws of thermodynamics is a simple heat conduction experiment (see Fig.(5)). The system in consideration is a section of a bar in which a heat flow $\dot{Q}_1$ enters at a temperature T_1 and $\dot{Q}_2$ leaves at T_2. In the steady state the internal energy of the bar section is constant so

$$\dot{U} = 0. \tag{32}$$

The entropy of the bar section is constant as well so

$$\dot{S} = 0. \tag{33}$$

Furthermore the system is closed so

$$\overset{*}{H} = 0 \tag{34}$$

and

$$\overset{*}{S} = 0 \tag{35}$$

and no work is done

$$P = 0. \tag{36}$$

The boundaries of the system are fixed so

$$\dot{V}_k = 0. \tag{37}$$

The first law reduces to the rather trivial relation

$$\dot{Q}_1 = \dot{Q}_2 = \dot{Q}. \tag{38}$$

The second law gives

$$0 = \frac{\dot{Q}}{T_1} - \frac{\dot{Q}}{T_2} + \dot{S}_i \text{ with } \dot{S}_i \geq 0 \tag{39}$$

or

$$\dot{S}_i = \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \dot{Q} \geq 0. \tag{40}$$

or

$$\dot{S}_i = \frac{T_1 - T_2}{T_1 T_2} \dot{Q} \geq 0. \tag{41}$$

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Relation (40) is an expression of the entropy production during transport of heat over a temperature difference. As $\dot{Q} > 0$, Eq.(40) demands that $T_1 \geq T_2$, in other words: heat flows from a high temperature to a low temperature. This is again the Clausius formulation of the second law.

For small temperature differences the heat flow in a bar of length L and with cross-sectional area A can be written as

$$\dot{Q} = \kappa \frac{A}{L} (T_1 - T_2) \tag{42}$$

with κ the thermal conductivity. The entropy production rate can now be expressed as

$$\dot{S}_i = \kappa \frac{A}{L} \frac{(T_1 - T_2)^2}{T_1 T_2}, \tag{43}$$

which shows the quadratic dependence of the entropy production on the "driving force" $(T_1 - T_2)$, which is characteristic for expressions of the entropy production in general.

5 The third law

5.1 Introduction

In the formulation of the third law we consider a closed system $(\overset{*}{n}_k = 0)$ in internal equilibrium. As the system is in equilibrium there are no irreversible processes so $\dot{S}_i = 0$. During the application of heat temperature gradients are generated in the system, but the associated entropy production can be kept low enough if the heat is applied slowly. In that case the second law reduces to

$$\dot{S} = \frac{\dot{Q}}{T}. \tag{44}$$

The increase in entropy due to the supplied heat δQ is given by

$$\delta S = \frac{\delta Q}{T}. \tag{45}$$

The heat capacity C_X is defined by

$$\delta Q = C_X \delta T. \tag{46}$$

The index X is a symbolic notation for all parameters which are kept constant during the heat supply. I.e. when the volume is constant we determine the heat capacity at constant volume C_V, if the pressure is constant we determine C_p, if the magnetic field is constant C_B, etc. In the case of a phase transition from liquid to solid, or from gas to liquid, the parameter X is the fraction of one of the two components. Combining Eqs.(45) and (46) gives

$$\delta S_X = \frac{C_X}{T} \delta T. \tag{47}$$

Integration of Eq.(47) from a temperature T_0 to an arbitrary temperature T gives the entropy at temperature T

$$S_X(T) = S_X(T_0) + \int_{T_0}^{T} \frac{C_X(T')}{T'} dT'. \tag{48}$$

The entropy depends on the parameters X, which are kept constant in the whole range from T_0 to T.

5.2 Mathematical formulation of the third law

First of all the third law states that:
1. the integral in Eq.(48) is finite for $T_0 \to 0$.
So we may write

$$S_X(T) = S_X(0) + \int_0^T \frac{C_X(T')}{T'} dT'. \tag{49}$$

The second important element of the third law is that:
2. the value of the entropy at absolute zero $S_X(0)$ is independent of X.
In mathematical form

$$S_X(0) = S(0). \tag{50}$$

So Eq.(49) can be further simplified to

$$S_X(T) = S(0) + \int_0^T \frac{C_X(T')}{T'} dT'. \tag{51}$$

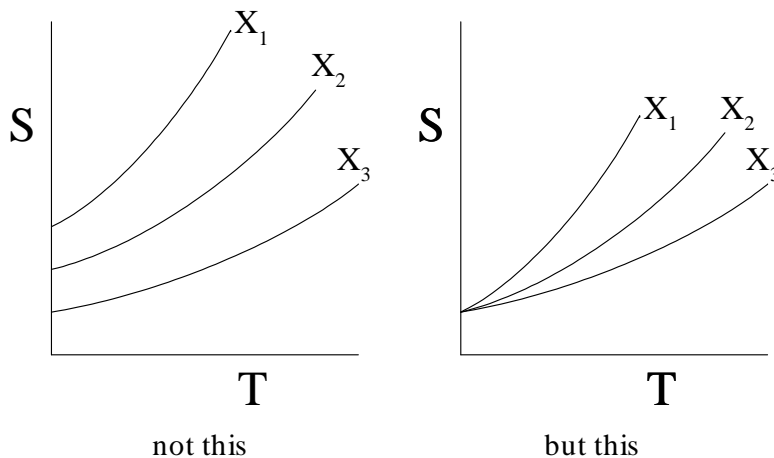Relation (50) is represented in graphical form in Fig.6. The property (50) can also be formulated

not this   but this

Figure 6: *Schematic representation of the temperature dependence for various values of the external conditions X_1, X_2, and X_3. In the left figure the limiting value at $T = 0$ depends on the value of X. This is not the real case. Due to the third law all curves tend to the same value at $T = 0$, as represented in the right figure.*

as

$$\lim_{T \to 0} \left(\frac{\partial S_X(T)}{\partial X} \right)_T = 0. \tag{52}$$

This relation can be seen as the mathematical formulation of the third law. In words: at absolute zero all isothermal processes are isentropic.
3. Take the entropy at 0K equal to zero
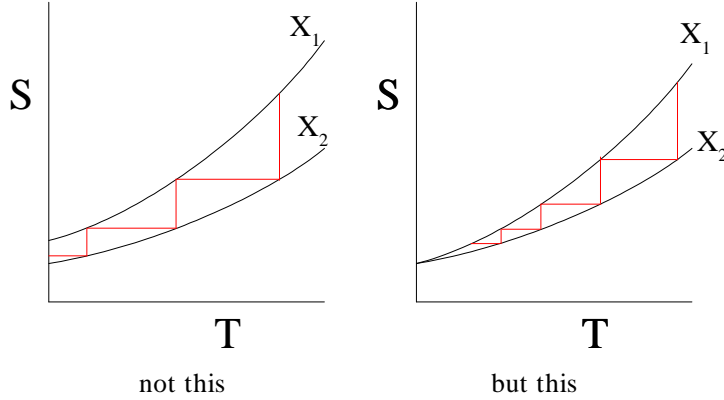
$$S(0) = 0 \tag{53}$$

Figure 7: *In the left figure the limiting value at $T = 0$ depends on the value of X. If this would be true absolute zero could be reached in a finite number of steps. However, this is not the real case. Due to the third law all curves tend to the same value at $T = 0$, as represented in the right figure. Reaching absolute zero requires an infinite amount of steps.*

so that Eq.(51) reduces to its final form

$$S_X(T) = \int_0^T \frac{C_X(T')}{T'} dT'. \tag{54}$$

Eq.(53) has a deep physical meaning, but at this moment it is just a convenient expression for the entropy.

5.3 Consequences of the third law

5.3.1 Can absolute zero be obtained?

The reason that $T = 0$ cannot be reached according to the third law is explained in Fig.7. Suppose that the temperature of a substance can be reduced by an isentropic change by changing the parameter X from X_2 to X_1. In the left figure we see that absolute zero can be reached in a finite number of steps. In reality an infinite number of steps would be needed, as shown in the right figure.

5.3.2 Specific heat

Suppose that the heat capacity of a sample in the LT region can be approximated by

$$C_X(T) = C_0 T^\alpha \tag{55}$$

then

$$\int_{T_0}^T \frac{C_X(T')}{T'} dT' = C_0 \int_{T_0}^T T'^{\alpha-1} dT' = \frac{C_0}{\alpha} (T^\alpha - T_0^\alpha). \tag{56}$$

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The requirement that the integral must be finite for $T_0 \to 0$ implies that

$$\alpha > 0. \tag{57}$$

So the heat capacity of all substances must go to zero at absolute zero

$$\lim_{T \to 0} C_X(T) = 0. \tag{58}$$

However, the molar specific heat at constant volume of a classical monatomic ideal gas (helium) is given by

$$C_V = \frac{3}{2}R. \tag{59}$$

This corresponds with $\alpha = 0$ in Eq.(55). Substitution of Eq.(59) in Eq.(48) gives

$$S_V(T) = S_V(T_0) + \frac{3}{2}R \ln \frac{T}{T_0}. \tag{60}$$

In the limit $T_0 \to 0$ this expression diverges. Clearly Eq.(59) does not satisfy Eq.(58). This means that the existence of a classical ideal gas, with a heat capacity given by Eq.(59), violates the third law of thermodynamics. This reveals the fundamentally quantum mechanical nature of the third law.

The conflict is solved as follows: At a certain temperature the quantum mechanical nature of matter starts to dominate the behavior. This changes the statistics of the system. Fermi particles follow Fermi-Dirac statistics; Bose particles follow the Bose-Einstein statistics. In both cases Eq.(59) is no longer valid. For Fermi gases the molar specific heat at constant volume in the low-temperature limit is given by

$$C_V = \frac{\pi^2}{2}R \frac{T}{T_F} \tag{61}$$

with R the molar ideal gas constant and the Fermi temperature T_F given by

$$T_F = \frac{1}{8.25} \frac{N_A^2 h^2}{MR} \left(\frac{N_A}{V_m}\right)^{2/3}. \tag{62}$$

Here N_A is Avogadro's number, V_m the molar volume, and M the molar mass. For Bose gases

$$C_V = 1.93R \left(\frac{T}{T_B}\right)^{3/2} \tag{63}$$

with T_B given by

$$T_B = \frac{1}{11.9} \frac{N_A^2 h^2}{MR} \left(\frac{N_A}{V_m}\right)^{2/3}. \tag{64}$$

The specific heats given by Eq.(61) and (63) both satisfy Eq.(55).

5.3.3 Vapor pressure

There is still another property of matter that seems to violate the third law. The heat of evaporation of ^{3}He and ^{4}He has a finite limiting value given by

$$L = L_0 + C_\mathrm{p}T. \tag{65}$$

So the entropy of a liquid-gas mixture is

$$S = S_\mathrm{l}(T) + x\left(\frac{L_0}{T} + C_\mathrm{p}\right) \tag{66}$$

where $S_\mathrm{l}(T)$ is the entropy of the liquid and x is the gas fraction. Clearly the entropy change during the liquid-gas transition diverges for $T \to 0$. This violates Eq.(52).

Nature solves the apparent violation of the third law as follows: at low temperatures the vapor pressure p_v is given by

$$p_\mathrm{v} = p_0\left(\frac{T}{T_0}\right)^{C_\mathrm{p}/R}\exp\left[\frac{L_0}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]. \tag{67}$$

Where p_0 is the vapor pressure at some low temperature T_0. For ^{4}He at $T_0 = 1$ K we have $p_0 = 15.6$ Pa and $L_0 = 7.17R$. For ^{3}He at $T_0 = 1$ K we have $p_0 = 1160$ Pa and $L_0 = 2.47R$. The relation (67) for ^{3}He is plotted in Fig.8. Note the highly compressed pressure scale. Also plotted are the $p - T$ relations for fixed particle distance (or fixed molar volume)

$$p = \frac{k_\mathrm{B}T}{\delta_\mathrm{p}^3} \tag{68}$$

with k_B the Boltzmann constant and δ_p the average particle distance

$$\delta_\mathrm{p} = \left(\frac{V_\mathrm{m}}{N_\mathrm{A}}\right)^{1/3}. \tag{69}$$

Plotted are the cases that δ_p is 1 μm, 1 mm, and 1 m respectively. Fig.8 shows e.g. that at about 140 mK the average particle distance in the gas above the liquid ^{3}He is 1 μm. At 65 mK it is 1 mm, and at 43 mK the particle distance is as large as 1 m!

In the interstellar space the average particle distance is about 1 cm. From Fig.8 it can be seen that the average particle distance for the vapor of liquid helium-three is also about 1 cm at a temperature of 60 mK. This means that the particle density above liquid ^{3}He at 60 mK is the same as between hydrogen atoms in space. At a temperature of 40 mK there is one atom in 1 m^3. In other words: the best vacuum in the universe is in the vacuum chamber of a dilution refrigerator below 60 mK.

The very low vapor pressure of helium has still some other unexpected consequence: if there is a leak in a system at very low temperatures the helium leaks to the vacuum space as a liquid. This will be unobserved at room temperature until the layer of liquid at the outside of the system is so thick that a droplet is formed. In the course of time the droplet grows and eventually it falls on the bottom of the vacuum chamber which usually is at a temperature of 4.2 K. There it will evaporate and give rise to a sudden increase in the pressure. Suddenly the thermal insulation is broken between the cold regions of the system and the relatively warm vacuum chamber.
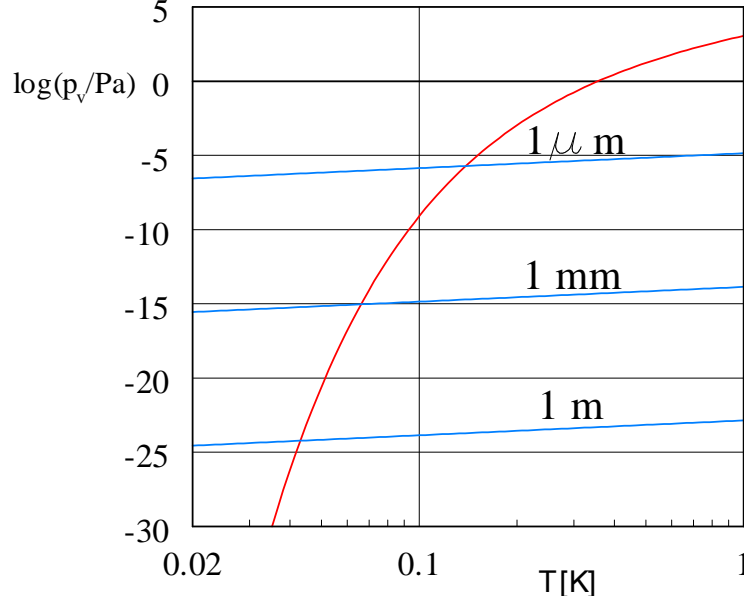
Figure 8: *Vapor pressure of ^3He as function of temperature. Note the highly compressed pressure scale. Also plotted are the $p-T$ relations in the cases that the particle distance is 1 µm, 1 mm, and 1 m respectively.*

5.3.4 Can ^{4}He gas become a superfluid?

At sufficiently low temperatures and sufficiently high densities Bose-Einstein can take place in an ideal gas. We consider now the possibility that BE-condensation can take place in the vapor above liquid ^{4}He. The expression for the Bose-Einstein condensation temperature is given by Eq.(64) or the particle density at the BE-condensation is

$$\left(\frac{N_A}{V_m}\right)_B = \left(\frac{11.9MRT}{N_A^2 h^2}\right)^{3/2}. \tag{70}$$

The particle density at the liquid-vapor transition for helium is with Eq.(67)

$$\left(\frac{N_A}{V_m}\right)_{lv} = \frac{N_A p_v}{RT} = \frac{N_A p_0}{RT_0^{5/2}}T^{3/2}\exp\left[\frac{L_0}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]. \tag{71}$$

Substituting the proper numbers shows that the density at which the gas becomes liquid is always much smaller than the density at which BE condensation would take place

$$\left(\frac{N_A}{V_m}\right)_{lv} \ll \left(\frac{N_A}{V_m}\right)_B. \tag{72}$$

Now suppose that we have gaseous helium at some low pressure p and temperature T. If we now increase the pressure at fixed T there are two possibilities for phase transitions:

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BE condensation or condensation of the gas into the liquid phase. Eq.(72) shows that the condensation into the liquid comes at lower density than the BE condensation. Hence the vapor of helium never reaches a high enough density to show BE-condensation. The vapor always behaves as a classical gas with the specific heat given by Eq.(59) even at the lowest temperatures. The conflict with Eq.(57) is solved simply by the fact that, at low temperatures, there is no gas at all.

5.3.5 Latent heat of melting

The melting curves of ^{3}He and ^{4}He both extend down to absolute zero at finite pressure. At the melting pressure liquid and solid are in equilibrium. We may take for the parameter X in Eq.(52) the fraction of solid. It is a direct consequence of the third law that the entropy of the solid is equal to the entropy of the liquid at $T = 0$. As a result the latent heat of melting is zero and the slope of the melting curve must extrapolate to zero at $T = 0$.

5.3.6 Thermal expansion coefficient

The expansion coefficient is defined as

$$\alpha_{\mathrm{V}} = \frac{1}{V_{\mathrm{m}}} \left(\frac{\partial V_{\mathrm{m}}}{\partial T} \right)_{\mathrm{p}}. \tag{73}$$

Due to the Maxwell relation

$$\left(\frac{\partial V_{\mathrm{m}}}{\partial T} \right)_{\mathrm{p}} = - \left(\frac{\partial S_{\mathrm{m}}}{\partial p} \right)_{\mathrm{T}}. \tag{74}$$

Comparing with Eq.(52) with $X = p$, shows that

$$\lim_{T \to 0} \alpha_{\mathrm{V}} = 0. \tag{75}$$

5.4 Paradox

The Carnot efficiency of refrigerators is given by Eq.(31). This can be used to express the optimum cooling power of refrigerators as

$$\dot{Q}_{\mathrm{L}} = \frac{T_{\mathrm{L}}}{T_{\mathrm{H}} - T_{\mathrm{L}}} P. \tag{76}$$

So we see that the cooling power $\dot{Q}_{\mathrm{L}} \to 0$ when $T_{\mathrm{L}} \to 0$ even for the best refrigerators. Now consider a sample with heat capacity

$$C(T) = C_0 T^{\alpha} \tag{77}$$

(with C_0 a constant) which is cooled with a cooling power $\dot{Q}_{\mathrm{L}}$. Then the rate of change in temperature is

$$\frac{\mathrm{d} T_{\mathrm{L}}}{\mathrm{d} t} = - \frac{\dot{Q}_{\mathrm{L}}}{C(T_{\mathrm{L}})} \tag{78}$$

or, in the ideal case,

$$\frac{dT_L}{dt} = -\frac{1}{C_0 T_L^\alpha} \frac{T_L}{T_H - T_L} P. \tag{79}$$

In the low-temperature limit $T_H \gg T_L$ so

$$\frac{dT_L}{dt} \approx -\frac{T_L^{1-\alpha}}{C_0 T_H} P. \tag{80}$$

Integration gives

$$T_L^\alpha (t) \approx T_{L0}^\alpha - \frac{\alpha P}{C_0 T_H} t. \tag{81}$$

As $\alpha > 0$ (Eq.(57)) Eq.(81) shows that, starting at a some temperature T_{L0}, absolute zero will be reached ($T_L^\alpha (t_0) = 0$) after a time

$$t_0 = \frac{C_0 T_{L0}^\alpha T_H}{\alpha P} = \frac{C (T_{L0}) T_H}{\alpha P}. \tag{82}$$

This is a finite amount of time! So absolute zero can be reached in a finite amount of time.

6   How to measure very low T

If some pioneering experimental group enters a new temperature region for the first time it has no calibrated thermometer for this temperature. At higher temperatures one can use the pressure of an ideal gas in a constant-volume cell and use the ideal gas law. However, we have seen that below about 300 mK there simply is no more gas. So, how does one measure, basically, temperatures below 300 mK? The answer is that one uses on the second law of thermodynamics.

In order to explain the basic principle we will discuss the question for an adiabatic demagnetization experiment where one gets very low temperatures by slowly reducing the magnetic field. Suppose that, in some high-temperature region, the entropy S is a well-known function of temperature T as given in Fig.9. The starting point a of the cycle has entropy S_a, temperature is T_a, and magnetic field B_i.

- now we lower the magnetic field adiabatically and reversibly (so avoiding all possible irreversible processes) to a value B_f. As a result we arrive at point b. The temperature is some unknown low value T_b, but the entropy has remained constant

$$S_b = S_a. \tag{83}$$

- next a small amount of heat δQ is supplied to the system bringing the system in point c. Both the temperature and entropy are increased. In good approximation

$$S_c - S_b = \frac{\delta Q}{T_X}. \tag{84}$$

- Next we increase the magnetic field adiabatically and reversibly (so avoiding all possible irreversible processes) to a the original value B_i and we arrive in point d. The temperature is
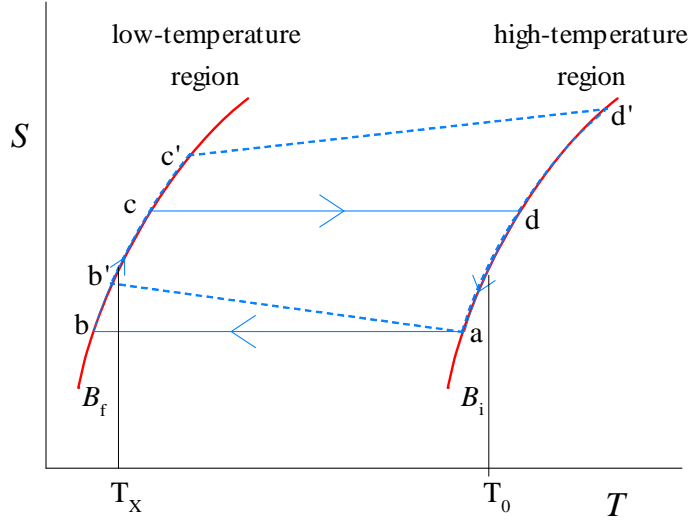
Figure 9: *Thermal cycle to measure the unknown temperature T_X. The solid blue lines give the ideal cycle. The dotted blue lines the cycle with irreversibilities.*

increased from T_c to T_d. while the entropy remains constant

$$S_d = S_c. \tag{85}$$

As T_d is in the high temperature region it can be measured.

- By removing a the heat δQ_0 the cycle is closed. Since the entropy in the high-temperature region is a well known function of T we have

$$\delta Q_0 = T_0 \left(S_d - S_a \right). \tag{86}$$

Combining all these relations leads to

$$T_X = \frac{\delta Q}{\delta Q_0} T_0. \tag{87}$$

Fig.9 also gives a more realistic cycle with entropy production during the steps where the field is changed. The cycle end in point d' with

$$S_{d'} > S_d. \tag{88}$$

The amount of heat to be removed to bring the system back to point a is

$$\delta Q_0' = T_0 \left(S_{d1} - S_a \right) > \delta Q_0. \tag{89}$$

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As a result we will have determined an apparent low temperature

$$T'_X = \frac{\delta Q}{\delta Q'_0} T_0 \tag{90}$$

which is lower than the real temperature T_X.