Faculteit der Natuurwetenschappen, Wiskunde en Informatica

Studiejaar 2019-2020

THERMODYNAMICS
lecture notes

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1. MAIN DEFINITIONS AND LAWS.
WHY ARE HEAT-ENGINES SO INEFFICIENT?

1.1 Introduction

The first step towards understanding thermodynamics is to forget the intuitive understanding of temperature which all of us have. Temperature is a counterintuitive concept. If you have two bodies with masses m_1 and m_2, their mass together will be m_1+m_2. This is not the case, when we talk about temperature. Unlike mass, time or length there is no standard for units of temperature. There is no etalon for 1 Kelvin. Temperature in thermodynamics is an abstract quantity. It acquires a physical meaning only when we apply thermodynamics to a specific area of physics or chemistry.

What is wrong with our intuitive understanding of temperature? The problem is that historically temperature was introduced in a wrong way. The very first philosophers - founders of thermodynamics- started to think why some objects are hot and others are cold. They noticed that when you bring a cold and a hot body in contact, the colder body heats up and the hotter cools down until the bodies become equally hot. The philosophers also noticed that in this final state the bodies can stay very long. The first hypothesis was that the hotness of a body is defined by the concentration in the body of a special type of matter, a hypothetical fluid substance – *caloric*. The caloric can flow as a liquid between two bodies brought in contact until the concentrations of caloric in the bodies are equalized. Obviously, such a concept of temperature is wrong. This is why in modern thermodynamics the definition of temperature does not imply any specific physical meaning. The temperature remains an abstract quantity – something that describes the hotness of bodies and equilibrates when differently hot bodies are brought in contact.

Intermezzo. History of thermometers.

Very first thermometers were built in the 16th century with the aim to measure the concentration of caloric. At that time it was reasonable, because it was known that substances expand upon heating. It was believed that expansion is due to inflow of caloric. To build a thermometer one can take gas or liquid at constant pressure. Supplying heat to the substance will lead to its expansion. The change of the volume is a measure of the concentration of caloric and thus is a measure of temperature. One of the most crucial steps in the development of thermometers was done by Celsius. He was one of the first who introduced a temperature scale. In fact, he measured the volumes of the thermosensitive substance at the temperatures of melting of ice and at the steam point of water, respectively. Afterwards, he divided the range between these two measured points in 100 equal intervals assigning zero Celsius to the point of melting of ice, 100 Celsius to the steam point as well as assigning a linear dependence between the volume and the measured temperature i.e. $V = const * T$. In fact, the very first thermometer pre-defined the law which was "discovered" long afterwards.

A better way to define a temperature scale was suggested by Kelvin. Taking ideal gas of a fixed volume as a thermosensitive substance and measuring the pressure of the gas, one can also quantify temperature, which in the case of ideal gas is defined by the average kinetic energy of the gas atoms. Assigning a linear dependence between the pressure and the temperature $p = const * T$ with 100 units between the temperature of melting of ice (T_0) and the temperature of steam boiling of water

(*T*), we obtain $T - T_0 = 100\ K$. Experiment shows that the ratio of pressures of gas at these two point is $\frac{p}{p_0} = 1.36$. It means that $\frac{T}{T_0} = 1.36$. All together we obtain $1.36T_0 - T_0 = 100$ and $T_0 \approx 273\ K$. The pressure of the ideal gas cannot be lower than 0. At *T*=0 K we achieve the lowest possible temperature, when *p*=0.

1.2 Energy, Work, Heat

One of the first evidences showing that the concept of *caloric* is wrong were experiments in which the hotness of body increased upon exerting a force on it and performing a work. For instance, cold hands can be warmed up by rubbing them. The concept of *caloric* would imply that caloric is generated out of nothing in this case. To solve this problem and avoid total negation of older theories in a transition to modern ones, instead of *caloric* we now use the concept of heat. It is said that heat together with work are forms of energy. Heat can be turned into work and work can be turned into heat. The fundamental law of conservation of energy, also known as the first law of thermodynamics, must be written as

$$\Delta U = W + Q \tag{1a},$$

where *ΔU* is the change of internal energy of body after the body has accepted heat *Q* and experienced work *W* from surroundings.

It is conventionally accepted that if a body performs work, the work is negative (*W*<0) and if the work is performed on the body, the work is positive (*W*>0). Similarly, if the body rejects heat, the heat is negative (*Q*<0) and if the heat is accepted, the heat is positive (*Q*>0).

Very often you can come across the first law of thermodynamics written in the differential form

$$dU = đW + đQ \tag{1b}.$$

Since the heat transferred and the mechanical work done do depend on the process, these are not exact differentials. The notation *đ* is used to emphasize this point.

Intermezzo. Exacte differentialen (zie ook MathWorld Wolfram).

A differential of the form

$$df = P(x, y)\ dx + Q(x, y)\ dy$$

is exact (also called a total differential) if $\int df$ is path-independent. This will be true if

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$$

1.3 Basic definitions

To avoid confusions, we would like to give definitions of the main concepts in thermodynamics.

System. Systems which are the objects in thermodynamics are macroscopic entities. Such a system may consist of a great number of material particles (atoms, molecules, electrons, etc.) or of field quantities such as electromagnetic field.

Isolated system. An independent system with absolutely no interaction with its surroundings.

Closed system. A system which has no material exchange with its surroundings is a closed system. A closed system in classical mechanics would be considered an isolated system in thermodynamics.

Thermal equilibrium[1]. Regardless of the complexity of its initial state, if an isolated system is left standing, the system eventually comes to a final state which does not change. This final state is called the thermal equilibrium state. In the thermal equilibrium, the quantities which describe the state of the system do not change.

Two isolated systems. When two isolated systems *A* and *B* are brought in contact, the total *A+B* eventually comes to thermal equilibrium. It is said that *A* and *B* are in thermal equilibrium with each other.

Temperature. In thermodynamics the temperature is an abstract quantity which prescribes thermal equilibrium between two bodies in thermal contact. If Θ_1 and Θ_2 are the temperatures of two bodies brought in thermal contact, the condition of thermal equilibrium is $\Theta_1 = \Theta_2$. If $\Theta_1 > \Theta_2$, Θ_2 increases when they are brought to thermal contact

Temperature change. Unlike the temperature, temperature change in thermodynamics is less abstract quantity. At least there is a mathematical definition of it. Using the concept of heat capacity we can relate the heat accepted by a body dQ and a change of parameter $d\alpha$. General definition of the heat capacity states

$$C_{\beta,\gamma}^{(\alpha)} = \frac{dQ_{\beta,\gamma}}{d\alpha} \tag{2},$$

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[1] Sometimes authors of different books like to distinguish between thermal equilibrium and thermodynamic equilibrium. They define thermodynamic equilibrium in the same way as we define thermal equilibrium here. When they talk about thermal equilibrium, they mean equilibrium of two systems in thermal contact. I do not see strong reasons to introduce two types of equilibrium in this course. For instance, here we show how to apply thermodynamics to large (not quantum mechanical) objects. Any of these objects can be split into many small, but still classical parts so that these parts are in thermal contact. I do not see why one should distinguish thermal equilibrium of the parts from thermodynamic equilibrium of the whole object.

$C_{\beta,\gamma}^{(\alpha)}$ is general heat capacity upon changing of parameter α; β,γ are physical quantities which in the considered process stay fixed. For instance, $C_V^{(T)} = \frac{dQ_V}{dT}$ is the thermal heat capacity at fixed volume, which relates the heat transferred to a system dQ and temperature change dT. See paragraph 3.6 in "Equilibrium thermodynamics" by C. J. Adkins for more examples of heat capacities.

Reversible process. It is a process the direction of which can be "reversed" by means of infinitesimal changes in some property of the surroundings. During a reversible process, the system is in thermodynamic equilibrium with its surroundings throughout the entire process. This is an idealized process in which it is possible to return both the system and surroundings to their original states. Frictionless motion is an example of a reversible process.

Function of state is a property whose value does not depend on the path taken to reach that specific value. Function of state is meant to describe the equilibrium state of a system. It is easier to understand the meaning of this definition by considering real examples. For instance, among internal energy, heat and work only internal energy is a function of state (see paragraph 1.2).

1.4 Model for idealized engine
In the first half of the 19th century many things about expansion of hot gases were known and people tried to build first heat engines, but those were very ineffective. The development of thermodynamics was greatly motivated by the goal to understand these fundamental limitations. Let's follow the logic of that time and try to build a theoretical model of an engine.

The mission of every heat-engine is to transfer heat into work. The engine will operate in cycles such that in every cycle the heat Q_1 will be supplied from a "hot reservoir" to a working body ($Q_1 > 0$). The working body will use the heat to produce the work W $(W < 0)$. To keep generality of the model, we assume that the heat does not turn into work completely, but a part of the heat Q_2 is rejected ($|Q2| > 0$) by the working body to another body, which we will call "cold reservoir". Obviously after one cycle the total internal energy of the working body should not be affected ($\Delta U = 0$). Otherwise, the body will get exhausted and the engine will stop working. Hence for such an engine using the first law of thermodynamics we obtain $|W| = |Q_1| - |Q_2|$. All these processes and the model itself are summarized using scheme in Fig. 1.1.
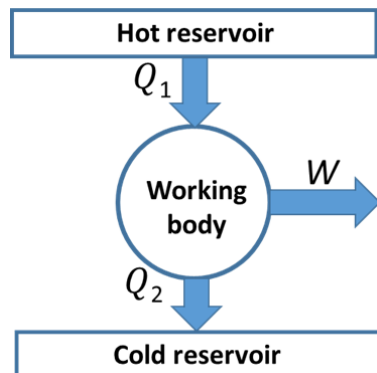
Figure 1.1. *Model for idealized engine.*

We define the efficiency of the heat-engine in the form:

$$\eta = \frac{|W|}{|Q_1|} \tag{2a},$$

which using the first law of thermodynamics becomes

$$\eta = 1 - \frac{|Q_2|}{|Q_1|} \tag{2b}.$$

As this is an idealized heat-engine, we assume that this is a reversible engine. It means that such an engine can be run forwards and backwards. If it runs forwards, the heat flows from the hot towards the cold reservoir and the working body performs a work. If the heat-engine runs backwards, the heat is pumped from the cold to the hot reservoir and this requires performing some work on the working body.

1.5 Second law of thermodynamics: early formulations

Can we imagine in nature a spontaneous heat flow from a colder to a hotter reservoir? Such an phenomenon is obviously impossible as it would mean that the bodies spontaneously go further away from the thermal equilibrium. Clausius formulated this empirical law by the following statement: **It is impossible for heat to transfer spontaneously from a colder to a hotter body without causing other changes.**

If we assume that this is true, we can also show that **no process is possible whose sole result is the complete conversion of heat to work.** This statement was formulated by Thomson (Lord Kelvin) and it can be proven with the help of the simple model of idealized heat-engine. Both these statements made by Clausius and Kelvin are known as early formulations of the second law of thermodynamics. In fact, this law shows that a part of the heat supplied to the working substance must be rejected ($|Q_2| \neq 0$). From Eq. (2b) it is seen that the efficiency will never be equal to 1.

1.6 Proof of the Kelvin statement assuming that the Clausius statement is true
Assume that the Kelvin statement is not true and it is possible to have a process whose sole result is the complete conversion of heat into work. In Fig. 1.2 this processes is realized by the working body on the left. In this case we can take the work produced by the body and use it to feed an idealized heat-engine that runs backwards (in Fig. 1.2 it is the one on the right). It is seen that the combination of these two working bodies implies that the heat spontaneously flows from the cold reservoir to the hot reservoir and this is impossible. Therefore, no process is possible whose sole result is the complete conversion of heat into work.
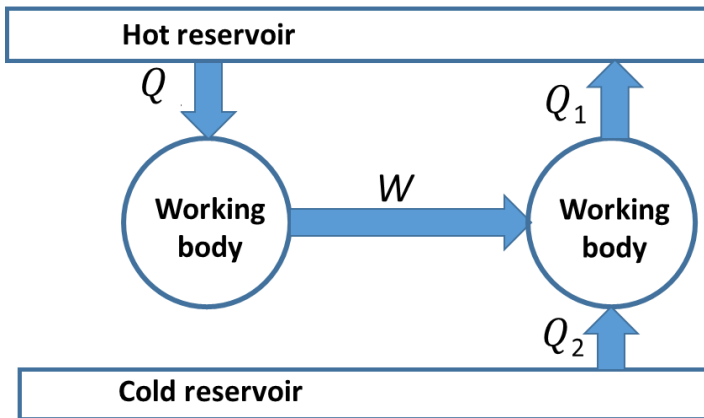
Figure 1.2. *Proof of the Kelvin statement assuming that the Clausius statement is true.*

1.7 Carnot's theorem
Using the simple model of idealized reversible heat-engine one can make another important step. In particular, we can prove that **no heat-engine operating between two given reservoirs can be more efficient than a reversible heat-engine operating between the same two reservoirs.** This statement is also known as Carnot's theorem. To prove it, we will again use the model for idealized engine.
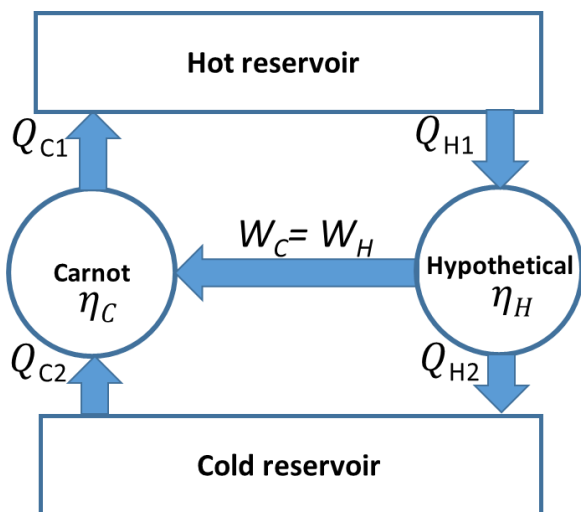
Figure 1.3. *Proof of Carnot's theorem*

In Fig. 1.3 the left working body represents a reversible engine with the efficiency η_C and the right one – hypothetical engine with the efficiency $\eta_H > \eta_C$. It means that $\frac{|W_C|}{|Q_{C1}|} < \frac{|W_H|}{|Q_{H1}|}$. If we use the work produced by the hypothetical engine and feed it to the reversible engine, the reversible engine will run backwards pumping heat from the cold reservoir to the hot one. Since $|W_C| = |W_H|$, we obtain that $|Q_{C1}| > |Q_{H1}|$. It means that the combination of these two engines solely pumps heat from the cold to the hot reservoir and this violates the Clausius statement of the second law of thermodynamics. A situation when $\eta_H = \eta_C$ is still allowed. It also implies that **all reversible heat-engines are equally effective**.

It is remarkable that Carnot formulated this theorem long before Clausius and Kelvin. In his practically philosophical work "Reflections on the motive power of fire", which was lacking mathematics, he treated heat engine as it was a mill that is brought in motion by caloric flowing from the hot to the cold reservoir.

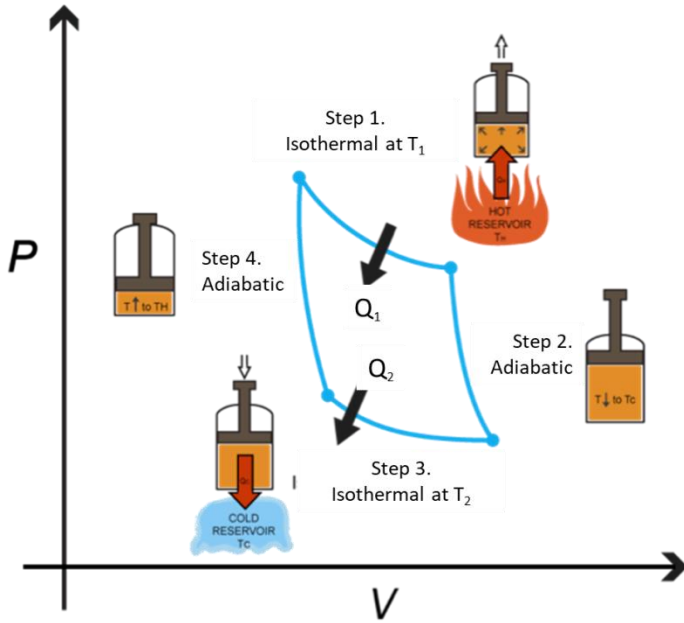*1.8 Carnot's cycle for the case of an ideal gas*
In the particular example of ideal gas temperature acquires a clear physical meaning. It is a measure of the average kinetic energy of particles forming the gas. Let's try to construct a reversible cycle for engine in which the gas plays the role of the working body.

In order to realize a *reversible* cycle which converts heat into work, one must find a sequence of *reversible* processes which perform the conversion such that after the whole cycle the internal energy of the working body does not change $\Delta U=0$. These processes must include transfer of heat from the hot reservoir to the working body, actual production of work, and rejection of heat from the working body to the cold reservoir. According to the Clausius statement of the second law of thermodynamics, a transfer of heat from hot to cold body cannot be reversed. Therefore in order to build a reversible cycle one should avoid any contacts of bodies with different temperatures at any stage of the cycle. Is it possible at all? It was Sadi Carnot who solved this puzzle and realized that such a cycle must consist of two isothermal and two adiabatic processes.

Figure 1.4 shows how the pressure and the volume of ideal gas, which plays the role of the working body in Carnot's engine, change during the cycle. As you know, the cycle consists of 4 steps:

1) Working body is in contact with the hot reservoir. The hot reservoir is in thermal equilibrium with the working body. The temperature of the working body in this process is T_1. The working body, i.e. ideal gas, expands isothermally and reversibly. In this process the working body absorbs heat Q_1 and performs work W_1.

2) Working body got isolated from the reservoirs and expands adiabatically and reversibly. The temperature of the ideal gas changes from T_1 to T_2.

3) Working body is in contact with the cold reservoir. The cold reservoir in this process is in thermal equilibrium with the working body and the temperature of the body is T_2. The working body, i.e. ideal gas, got compressed isothermally and reversibly. In this process the working substance rejects heat Q_2 as a result of work W_2 performed on it.

4) Working body got isolated from the reservoirs and got compressed adiabatically and reversibly. The temperature of the ideal gas changes from T_2 to T_1.

Figure 1.4. *Carnot's cycle with ideal gas as the working body.*

For the case of an ideal gas an isothermal process means that the internal energy does not change. Indeed if we take a gas of atoms, the total internal energy will be given by the sum of potential and kinetic energies of the atoms constituting the gas. The potential energy is given by interatomic interactions. In the case of ideal gas atoms do not interact. It means that the internal energy is fully defined by the kinetic energy of the atoms and thus if the temperature of the gas does not change, the internal energy does not change as well. It is thus clear that $|Q_2|=|W_2|$ and $|Q_1|=|W_1|$ meaning that the net work performed by the heat-engine in this cycle is equal to $|W|=|Q_1|-|Q_2|$.

For an isothermal process of an ideal gas at temperature T_1, one finds that $|Q_1|=|W_1|$. It is known that a gas expanding from volume V_1 to volume V_2 at pressure p performs work $dW=-pdV$. For an ideal gas it is known that $\frac{pV}{T}=const$. Therefore, $Q_1=const\int_{V_1}^{V_2} T\frac{dV}{V} = const\, T_1\ln(\frac{V_2}{V_1})$. Similarly, we find the expression for the second isothermal process of compression from V_3 to V_4: $Q_2=const\int_{V_3}^{V_4} T\frac{dV}{V} = const\, T_2\ln(\frac{V_4}{V_3})$. For an adiabatic processes Poisson's equations state $pV^\gamma = const$ or $TV^{1-\gamma} = const$. It means that $\frac{V_2}{V_1} = \frac{V_3}{V_4}$. Therefore, it is easy to see that in this particular case $\frac{|Q1|}{T1} = \frac{|Q2|}{T2}$. The efficiency of such an engine is $\eta = 1 - \frac{|Q_2|}{|Q_1|} = 1 - \frac{T_2}{T_1}$. As all reversible heat-engines are equally effective, we have the expression for the efficiency of all reversible heat-engines

$$\eta = 1 - \frac{|Q_2|}{|Q_1|} = 1 - \frac{T_2}{T_1} \tag{3}.$$

Moreover, we note that during the first isothermal processes (step 1), the working body and the hot reservoir are in thermal equilibrium. It means that they have equal temperatures. Similarly, the cold reservoir and the working substance have equal temperatures during the second isothermal process. Hence we obtain a definition for the ratio of thermodynamic temperatures of two bodies. **The ratio of thermodynamic temperatures of two bodies is equal to the ratio of the amounts of heat**

exchanged at infinitely large reservoirs at these temperatures by a reversible heat-engine operating between them.

Finally, we can answer the main question of this lecture: why are heat engines so ineffective? As a reversible engine is the most effective engine we can build, the maximum efficiency which we can achieve is given by Eq. 3 and defined by the ratio of thermodynamic temperatures of two reservoirs. If during one cycle of a reversible heat engine the temperature of the working body changes between 300 K and 400 K, its efficiency will not exceed 25%. For real engines it will be obviously much lower.

2. CLAUSIUS' THEOREM. ENTROPY.
SECOND LAW OF THERMODYNAMICS IN TERMS OF ENTROPY

2.1 "Paradox" showing why intuitive understanding of thermodynamics can be wrong

As you can see, a naïve "assumption" that heat is a flow of caloric was good enough to draw rather correct conclusions regarding heat engine. Based on this assumption Sadi Carnot was able to build a model for idealized engine, formulate the theorem about the efficiency of reversible engines, getting very close to formulation of the second law of thermodynamics. The validity of this naïve, but intuitive understanding of heat as a flow of caloric and heat engine as a mill, which uses caloric instead of water, can be easily questioned by the example shown in Fig. 2.1.

Consider a reversible heat engine operating between two reservoirs at temperatures T_1 and T_3, respectively. A part of the heat flowing through the working body is converted into work and the rest is rejected to the cold reservoir (see Fig. 2.1). In the second engine we insert one additional reservoir at temperature T_2 between the working body and the hot reservoir ($T_1 > T_2 > T_3$). Intuitively we think that these two engines must have the same efficiency. Indeed, in the both examples the working body accepts the same amount of heat Q_1. According to Eq. 3, however, the efficiencies of the Carnot's cycles are not equal at all $\eta_1 = 1 - \frac{T_3}{T_2}$ and $\eta_2 = 1 - \frac{T_3}{T_1}$. As $T_2 < T_1$, we obtain that $\eta_1 < \eta_2$. It means that although the working bodies in these two cases obtain equal amounts of heat Q_1, in the second case more heat is rejected by the working substance without performing any work $Q_3 > Q_3'$. This "paradox", however, is purely due to our intuitive understanding of thermodynamics. In order to go beyond this intuitive picture one has to introduce new counter-intuitive quantities such as entropy. There is no device that measures entropy. We have no good feeling of this physical quantity. Why do we need it? How was it introduced in the first place?
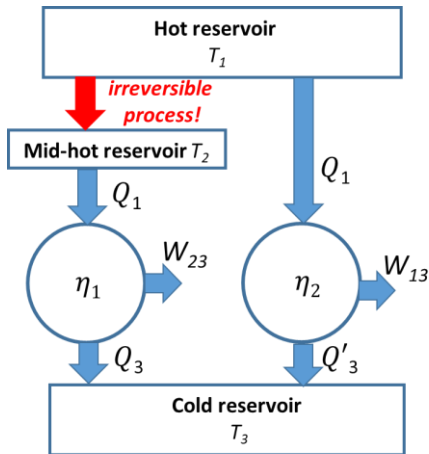
Figure 2.1. *Two heat-engines which accept equal amounts of heat, but perform different amounts of work.*

Let's calculate the difference between the work performed by heat-engine 1 compared to that performed by heat-engine 2. $W_{13} - W_{23} = Q_1 \left(1 - \frac{T_3}{T_1}\right) - Q_1 \left(1 - \frac{T_3}{T_2}\right) = T_3 (\frac{Q_1}{T_2} - \frac{Q_1}{T_1})$. If we introduce new quantity $S = \frac{Q}{T}$, where Q is the heat transferred to body at temperature T, we obtain a very simple expression $W_{13} - W_{23} = T_3 \Delta S$. It means that upon passing through the intermediate reservoir

a part of the energy degrades. The degraded energy cannot be transformed into work and must be rejected to the cold reservoir. The amount of degraded energy is equal to $T_3 \Delta S$. This degradation of energy appeared when the third reservoir was introduced in the chain of heat transfer. In particular, by adding the third reservoir in the chain we also introduced one irreversible process. The heat flow between two reservoirs at temperatures T_1 and T_2 is obviously irreversible. This irreversibility results in an increase of S and eventually leads to the degradation of energy. People started to use this new quantity S calling it "entropy".[1]

2. 2 Enigma of Q/T ratio

Consider two heat engines. The first one is a reversible Carnot's engine with the efficiency η_{rev}. The second is a hypothetical one with the efficiency η. The engines are operating between two reservoirs as shown schematically in Fig. 2.2. According to Carnot's theorem (see Lecture 1) $\eta_{rev} \geq \eta$. It means that $1 - \left|\frac{Q_2}{Q_1}\right| \leq 1 - \left|\frac{Q_{r2}}{Q_{r1}}\right|$ or $\left|\frac{Q_2}{Q_1}\right| \geq \left|\frac{Q_{r2}}{Q_{r1}}\right| = \frac{T_2}{T_1}$. Hence we obtain that for any engine operating between these two reservoirs $\left|\frac{Q_2}{T_2}\right| \geq \left|\frac{Q_1}{T_1}\right|$. As the heat entering the working body is positive (this is conventionally accepted as explained in Lecture 1), we may write that $\sum_i \frac{Q_i}{T_i} \leq 0$ and extend this conclusion to a more general case:

When a system performs a cycle while in contact with the environment and absorbs or rejects heat Q_i (i=1,2,…n) from the heat reservoir at temperature T_i, after completion a cycle the following holds

$$\sum_i \frac{Q_i}{T_i} \leq 0 \qquad \text{(2.1a),}$$

where equality is valid for a reversible cycle.

Rewriting the very same expression in the differential form gives that **for any closed cycle**

$$\oint \frac{dQ}{T} \leq 0 \qquad \text{(2.1b),}$$

where equality necessarily holds for a reversible cycle. This result is called ***Clausius's theorem***.

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[1] The word originates from Greek "*entropē*", which means "turning toward" or "transformation". According to the Oxford Advanced American Dictionary, entropy is the measurement of the energy that is present in the system, but is not available to do work. It was designed to denote that any energy eventually and inevitably turns into a useless heat. The idea was inspired by an earlier formulation by Sadi Carnot of what is now known as the second law of thermodynamics.
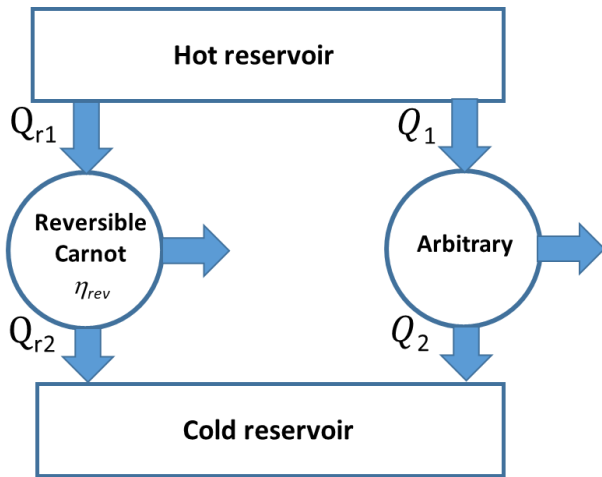
Figure 2.2. *Two heat-engines (reversible and arbitrary) operating between two reservoirs.*

2.3 Entropy

The ratio $\frac{dQ}{T}$ seems to be useful in physics of heat transfer. We now define a new variable, which we will call entropy *S*. It is said that for an infinitesimal reversible change the change of entropy *dS* for a system is defined as

$$dS = \frac{dQ_{rev}}{T} \tag{2.2}.$$

It is easy to show that the entropy is a function of state (see paragraph 5.2 in "Equilibrium Thermodynamics" by C. J. Adkins).

Additivity is probably the most important property of entropy. Using the definition of entropy it is easy to see that if a system consists of two parts with the entropies S_A and S_B, the total entropy of the system is S_A+S_B.

2.4 Second law of thermodynamics in terms of entropy

Since entropy is a function of state, a change of entropy upon a transfer of a thermodynamic system from state A to state B does not depend on the path of the transfer. Let's consider force *F* acting on a thermodynamic system and a response of this system *dx* to the force. The work done on the system is *dW=Fdx*. Work is not a function of state, but performing this work the system is transferred from state A to state B. Imagine that there are two paths of this transfer. One path is reversible and the other is arbitrary. These two paths together form a cycle for which according to Clausius' theorem $\oint \frac{dQ}{T} \leq 0$.

In the case of the reversible process of transfer from B to A the entropy changes as
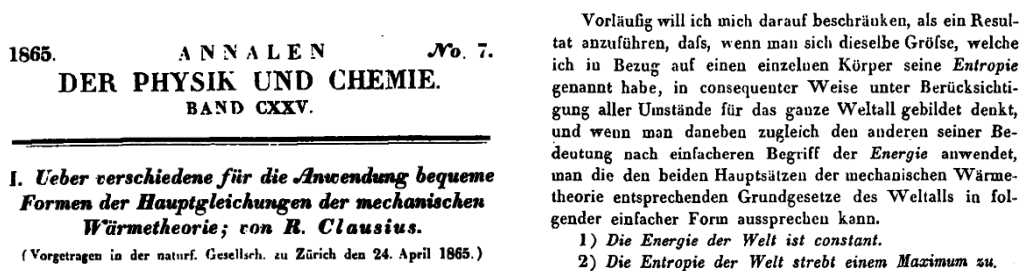
$$\Delta S_{rev} = \int_B^{A_{rev}} \frac{dQ}{T}.$$

According to Clausius' theorem $\int_{A_{irrev}}^{B} \frac{dQ}{T} + \int_B^{A_{rev}} \frac{dQ}{T} \leq 0$ or $\int_{A_{irrev}}^{B} \frac{dQ}{T} \leq \int_{A_{rev}}^{B} \frac{dQ}{T}$.

Taking into account the definition of entropy, one obtains that for an arbitrary process that $\int_{A_{irrev}}^{B} \frac{dQ}{T} \leq S_B - S_A$, where the equality holds for those cases when the process from A to B is reversible. Hence we obtain that for any infinitesimal change in a thermodynamic system the entropy of the system does not change, if the process is reversible, and increases in irreversible processes

$$\frac{dQ}{T} \leq dS \tag{2.3}.$$

For an isolated system ($dQ=0$ and $dS \geq 0$) it means that **the entropy of an isolated system cannot decrease.**

In fact, this is a mathematical formulation of the second law of thermodynamics. In Fig. 2.3 one can see a copy of the original article of R. Clausius in which he formulated this law and even applied it together with the law of conservation of energy to the whole universe.

1865.   A N N A L E N   No. 7.
DER PHYSIK UND CHEMIE.
BAND CXXV.

I. *Ueber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie; von R. Clausius.*
(Vorgetragen in der naturf. Gesellsch. zu Zürich den 24. April 1865.)

Vorläufig will ich mich darauf beschränken, als ein Resultat anzuführen, dafs, wenn man sich dieselbe Gröfse, welche ich in Bezug auf einen einzelnen Körper seine *Entropie* genannt habe, in consequenter Weise unter Berücksichtigung aller Umstände für das ganze Weltall gebildet denkt, und wenn man daneben zugleich den anderen seiner Bedeutung nach einfacheren Begriff der *Energie* anwendet, man die den beiden Hauptsätzen der mechanischen Wärmetheorie entsprechenden Grundgesetze des Weltalls in folgender einfacher Form aussprechen kann.
1) *Die Energie der Welt ist constant.*
2) *Die Entropie der Welt strebt einem Maximum zu.*

Figure 2.3. *Copy of the original article of R. Clausius.*

2.5 Entropy of ideal gas

In this paragraph as an example of calculation of entropy we will derive the entropy of 1 mole of ideal gas. We assume that the molar specific heat of the gas at constant volume is constant, $C_V=C_V^0$. We can also assume that the gas is in a reservoir whose volume V and temperature T can be changed. According to the first law of thermodynamics one can write for internal energy that $dU=dW+dQ$. This law can be rewritten in terms of two variables in the considered experiment (dT and dV) $dU=-pdV+TdS$. It means that

$$dS = \frac{dU + pdV}{T}$$

Upon a temperature increase at constant volume one can expect that $dU = C_V dT$. Moreover, for 1 mole we have $pV=RT$, where R is the universal gas constant. Therefore, we obtain that

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V}.$$

We integrate this expression

$$\int dS = \int C_V \frac{dT}{T} + \int R \frac{dV}{V},$$

and finding the indefinite integrals obtain the expression for the entropy

$$S(T,V) = C_V \ln T + R \ln V + const,$$

where *const* is the constant of integration. It is seen that the entropy increases with an increase of the temperature and the volume of the ideal gas.

2.6 How can we quantify entropy in real experiments?

Entropy is a weird concept. There is no device to measure entropy. Nevertheless, we can try to develop our intuition to "feel" the entropy better. Look at the two situations with 10 hot non-interacting atoms sketched in Fig. 2.4. The internal energies of the gas in these two cases are equal, but the probability of the situation on the left is lower than that on the right. This simple illustration demonstrates for any state of matter that there is a connection between the probability to realize this specific state and disorder. We have shown that in equilibrium the entropy must be maximized. Intuitively we also understand that the equilibrium state must be also the state with the highest probability.

Consider two systems, 1 and 2, in states A and B, respectively. Let's assume that the probability to find system 1 in state A is g_1 and the probability to find system 2 in state B is g_2. Probability theory says that the probability to find systems 1 and 2 in the states A and B is $g = g_1 g_2$. According to the definition of entropy, the total entropy of these two systems taken together is $S = S_A + S_B$. Therefore, it is seen that the entropy and the probability are interconnected such that

$$S = k * \ln(g)$$

where k is a constant.

Consequently, looking at the sketch in Fig. 2.4 it is seen that the entropy of the situation on the left is lower than that on the right. It is also seen that by placing a piston on the position of the dashed line one can harness the internal energy of the gas and let it perform work in the case of the situation on the left, but not in the case of the situation on the right. Hence this illustration shows that the entropy quantifies the energy which is present in the system, but is not available to do work.

10 hot non-interacting molecules

Internal energy is U_1
Lowest g, lowest S

Internal energy is U_2
Highest g, Highest S
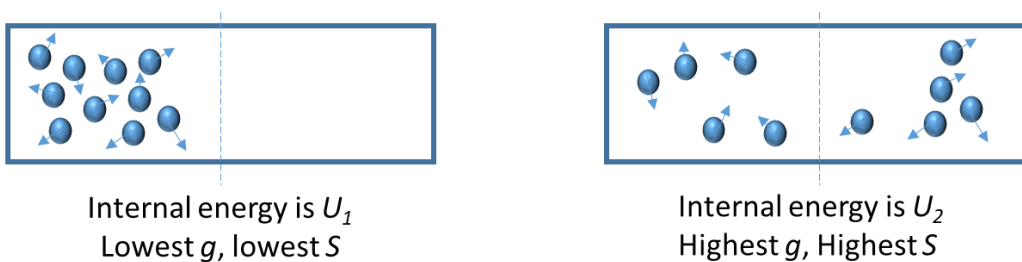
Figure 2.4. *Illustration of statistical meaning of entropy.*

2.7 Modelling noise in experiments using entropy and second law of thermodynamics

Let's consider an experiment that aims to measure quantity x. The measurements are affected by noise. In order to model noise, we assume that fluctuations of the physical quantity are described by a Gaussian distribution. It implies that if the true value of the quantity is $\bar{x}$, the probability that an

outcome of the experiment falls in the range $\bar{x} - \frac{\Delta x}{2} \le x \le \bar{x} + \frac{\Delta x}{2}$ can be calculated as $P\left(\bar{x} - \frac{\Delta x}{2} \le x \le \bar{x} + \frac{\Delta x}{2}\right) = \int_{\bar{x}-\frac{\Delta x}{2}}^{\bar{x}+\frac{\Delta x}{2}} f(x) dx = \int_{\bar{x}-\frac{\Delta x}{2}}^{\bar{x}+\frac{\Delta x}{2}} \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-\bar{x})^2}{2\sigma^2}\right) dx$, where f(x) is a Gaussian probability density function and σ is the dispersion of the distribution.

How do we know that the probability density $f(x)$ is Gaussian? Usually people argue that $f(x)$ is Gaussian in accordance with the Central Limit Theorem. In fact, second law of thermodynamics allows one to demonstrate in a relatively simple way that for a system in thermodynamic equilibrium fluctuations of classical (i.e. not quantum mechanical) physical quantities are described by Gaussian distributions.

The entropy of the system must be a function of the quantity x. As it was shown above, $S(x)=k*ln(g(x))$ and it also means that $g(x)=exp(S(x)/k)$. Note that $g(x = \bar{x})$ is the probability to find the system in the state with $x = \bar{x}$. Therefore we expect that $f(x) \sim g(x)$ and thus aim to find $g(x)$. Expanding function $S(x)$ in Tailor series in the vicinity of $x = \bar{x}$, one obtains

$$S(x) = S(\bar{x}) + (x - \bar{x})\frac{\partial S(\bar{x})}{\partial x} + \frac{1}{2}(x - \bar{x})^2 \frac{\partial^2 S(\bar{x})}{\partial x^2} + \cdots$$

Here we disregard terms of higher order assuming that the fluctuations have so small amplitude that other terms can be neglected. Second law of thermodynamics states that the entropy of a system in thermodynamic equilibrium is at maximum. It means that $\frac{\partial S(\bar{x})}{\partial x}=0$ and $\frac{\partial^2 S(\bar{x})}{\partial x^2} < 0$. If we for simplicity express the second derivative as $\frac{\partial^2 S(\bar{x})}{\partial x^2} = -B$, one obtains that

$$g(x) = \exp\left(\frac{S(\bar{x})}{k} - \frac{B}{2k}(x - \bar{x})^2\right)$$

Hence we can see that the probability density function should have the following form $f(x) \sim \exp\left(-\frac{B}{2k}(x - \bar{x})^2\right)$. This is a Gaussian distribution.

Therefore we have shown that fluctuations of a system around a thermodynamic equilibrium are described by a Gaussian function. The noise can be seen as a result of fluctuations and can be modelled accordingly. This statistical consideration of noise has been adapted from paragraph 110 in L. D. Landau and E. M. Lifshitz "*Statistical Physics*", Third Edition, Part 1:Volume 5 (Course of Theoretical Physics, Volume 5)" (Butterworth-Heinemann, Oxford, 2006).

2.8 Entropy and irreversible processes in operation of heat-engines

To conclude the lecture, we explain the "paradox" in operation of heat-engine described in section 2.1. For this we describe the work of heat-engine using the concept of entropy. For a certain sequence of processes the first law of thermodynamics states $\Delta U = W + Q$ or $Q = \Delta U - W$. For the same sequence of processes the second law of thermodynamics in terms of entropy states $T\Delta S \ge Q$. Using these laws we find that $T\Delta S \ge \Delta U - W$ and $W \ge \Delta U - T\Delta S$. Therefore, we can formulate two statements:

- $W < 0$. In this case the working body performs the work on the environment (the case of heat-engine). The work that can be extracted from such a system in given surroundings is at maximum if the processes are reversible.
- $W > 0$. It means that in the considered sequence of processes the environment does work on the working body (the case of a fridge). The work that must be done by the environment to achieve the required changes is at minimum if the processes are reversible.

3. THERMODYNAMICS AS A METHOD IN PHYSICS. THERMODYNAMIC POTENTIALS. MAXWELL RELATIONS

3.1 Introduction

The goal of this chapter is to show that thermodynamics can be very powerful as a method in magnetism, electricity and mechanics. The diagram shown in Fig. 3.1 depicts different areas of physics and mutual interconnections between them. Using first law of thermodynamics, the concept of thermodynamic potential, the reciprocity and reciprocal theorems we can derive expressions which describe the thermoelastic effect, piezoelectricity, pyroelectricity and the magnetocaloric effect.
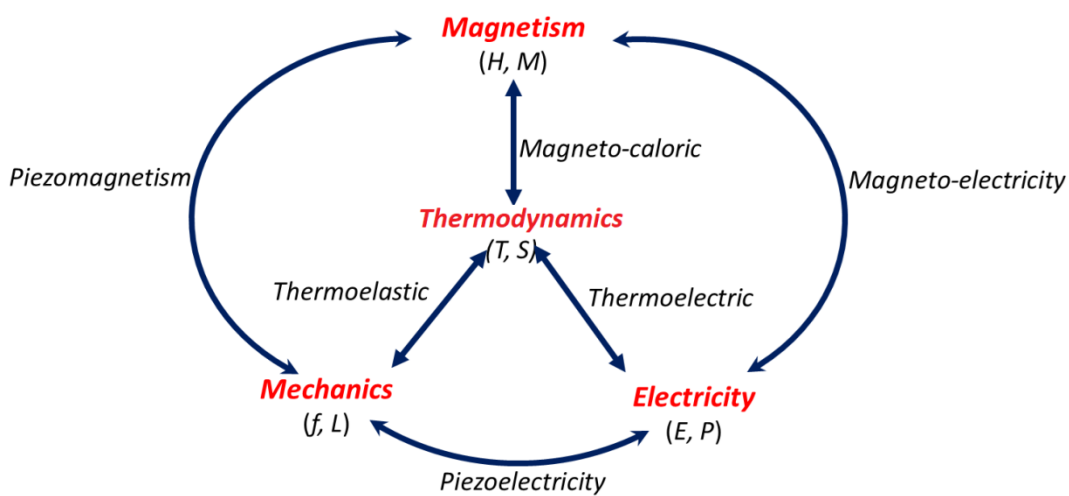
Figure 3.1. *Different areas of physics and typical quantities employed to describe effects in magnetism (H – magnetic field, m - magnetization), electricity (E - electric field, P - polarization), thermodynamics (T - temperature, S - entropy), mechanics (f - force, L - displacement).*

The first law of thermodynamics states that $dU = đW + đQ$. Until now we mainly discussed (ideal) gases. In particular, when we had to define work performed on a system, we always meant ideal gas under pressure. In this case, the work *W* can be calculated integrating *dW=-pdV*. During the lectures I emphasized that thermodynamics is not a science about the physics of (ideal) gases. Ideal gas is just a convenient model system. The power of thermodynamics is in the fact that it can be applied to practically any area of physics. In each of these cases one has to start with first law of thermodynamics, but using a proper expression for work performed on physical system of interest. For instance, in the case of a piece of rubber, work can be performed by tensional force *f* which enlarges the length of the rubber piece by *dL: dW=fdL*. Mechanical force can also perform work against surface tension γ by increasing the surface area by *dA: dW=γdA*. Work can be performed by magnetic field *H* that induces magnetic moment *dm: dW=μ₀Hdm*. An electric field *E* performs work by inducing

polarization *dp*. It means that *dW=Edp*. Derivation of all these expressions for work performed by external stimuli $(F, E, \mu_0 H)$ is beyond the scope of this course. However, for thermodynamics these derivations are not that important. In order to be able to apply the method of thermodynamics, it is sufficient to define an external stimulus (force X_i) on a system and a response of the system (dx_i) such that the product of the stimulus and the response is equal to the work performed on the system (dW). In general, work performed on a physical system can be written as $đW = X_i dx_i$.

## *3.2 An example of real research with the help of thermodynamics. The case of ferromagnetism*

Intermezzo. Ferromagnetism

Normally we assume that the magnetic moment **m** in media is induced by an external magnetic field. Ferromagnetism is the basic mechanism by which certain materials (such as iron) form permanent magnets. We know that every permanent magnet has two sides: a North pole and a South pole. A stronger magnet can bring a weaker magnet in motion and change the orientation of the poles of the latter. This is how electromotor works. It means that the magnetic field of the stronger magnet performs work on the weaker one. In order to describe the magnet, define the orientation of its poles and the strength of the produced magnetic field, we use the concept of magnetic moment **m.** The magnetic moment is defined such that the potential energy of a magnet with moment **m** in external magnetic field **H** equals to $W_{pot} = -\mu_0$**Hm**. It means that if the magnetic field **H** induces magnetic moment d**m** in the direction of the field, the work performed on the magnet equals $dW = \mu_0 Hdm$. What is the origin of the spontaneous magnetic moment **m** in ferromagnets? Electrons have spin and, associated with it, elementary magnetic moment. In ferromagnets (Fe, Co, Ni) quantum mechanical exchange interaction between the spins is so strong that it aligns all the spins in the medium so that the net spin and the net magnetization are not zero even with no external magnetic field. When the temperature is too high, thermal fluctuations are stronger than the exchange interaction and the spin order is destroyed. In physics and materials science, the Curie temperature (T_C), or the Curie point, is the temperature at which permanent magnets lose their permanent magnetic properties. The Curie point for Fe is 1043 K, for Co 1388 K and for Ni 627 K. A typical temperature dependence of the magnetization is shown in Fig. 3.2. Applying a very strong magnetic field one can reverse the magnetization of a permanent magnet. Field dependence of the magnetization on an external magnetic field is often characterized by so called hysteresis loop shown in Fig. 3.3. It is seen that with no magnetic field a ferromagnet can be in one of two states characterized by opposite orientations of the magnetic moment. It is experimental fact that in zero magnetic field these states have equal energies and equal entropies. Switching ferromagnets between these two states with the help of an external magnetic field is the main principle of magnetic recording, where the states magnets with moments "up" and "down" can be used to represent bit-"0" and bit-"1", respectively.

We may know nearly nothing about quantum mechanical origin of ferromagnetism, have very naïve understanding of the phenomenon, but still using the laws and the concepts of thermodynamics we will be able to predict behavior of ferromagnets . Experiments show that the magnetic moment of ferromagnets **m** is a function of temperature. Above the so-called Curie temperature, ferromagnets are in a paramagnetic state. It means that without an external magnetic field **H**, the magnetic moment of the medium is zero (**m** = 0). Application of the magnetic field to a paramagnet induces a magnetization in the medium (**m** = χ**H**). Below the Curie temperature the magnetic moment is not zero, even with no applied magnetic field. Can we theoretically derive the law for **m**(T) using the second law of thermodynamics?
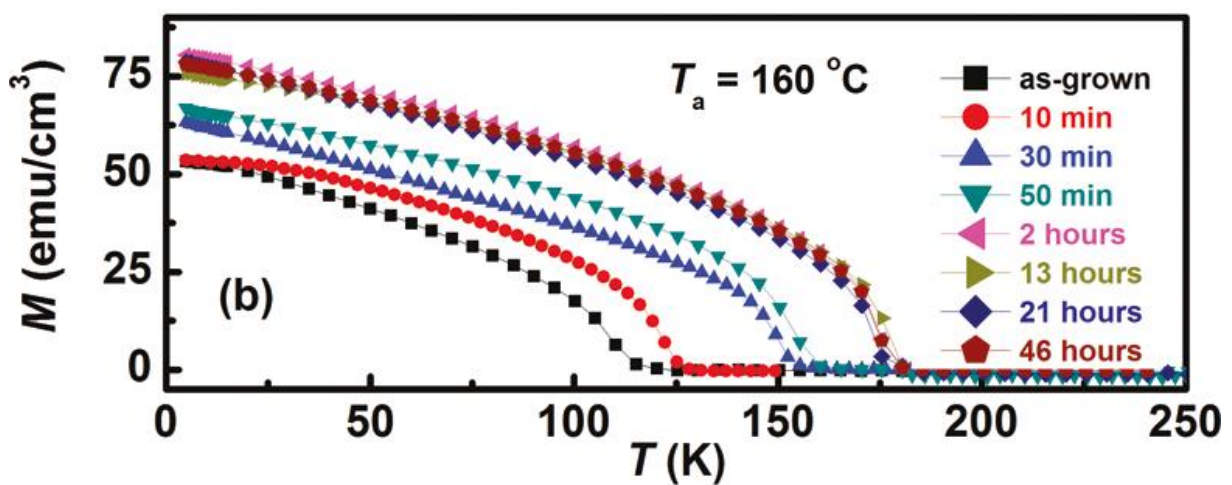
Figure 3.2. *Temperature dependence of the magnetization in of GaMnAs fabricated using different annealing times. GaAs is a non-magnetic magnetic material. Doping the material with Mn-ions induces magnetic order. The material becomes ferromagnetic with the Curie temperature 120 K. Annealing the material at 160 K causes redistribution of the ions, improves the coupling between their magnetic moments and results in an increase of the Curie temperature. It is interesting to note that qualitatively all the temperature dependencies especially about their T_C look the same (data take from* Lin Chen *et al, Nano Lett.,* **11** (7), pp 2584–2589 (**2011**)).
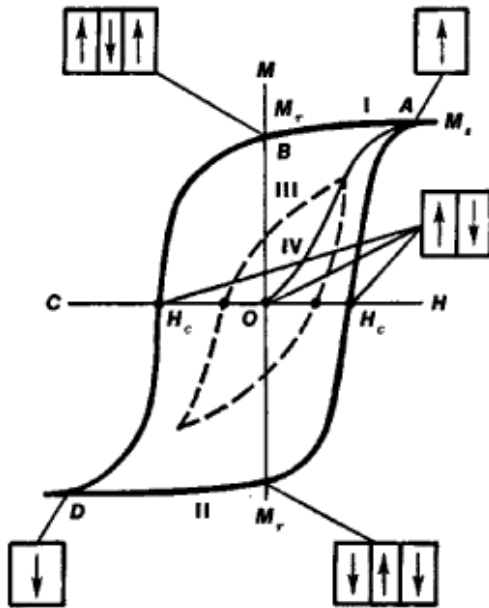
Figure 3.3. *Magnetic hysteresis loop and its description. The loop and the explanation are taken from* http://encyclopedia2.thefreedictionary.com/Hysterisis

Our first step is to define the set of independent variables relevant to this problem. The variables in our case are *m, H, S* and *T*. Secondly, we construct a function which depends on *m, H* and *T*. The only requirement to this function is that it should be at minimum, when at the given *H* and *T* the ferromagnet is in a thermodynamic equilibrium. Intuitively, it is more convenient to work with such a function than with entropy, because the function has a clear analogy classical mechanics - potential energy. A physical system searches for equilibrium by minimizing its potential energy.

Looking for such a function *F*, one can notice that a relatively simple expression satisfies the abovementioned requirements:

$$F = U - TS - \mu_0 \mathbf{mH} \tag{3.1},$$

where *U* is the internal energy and μ_0 is the vacuum permeability. Assuming and **m** and **H** are mutually parallel, one can find that

$$dF = dU - TdS - SdT - \mu_0 m dH - \mu_0 H dm.$$

For the case of fixed *T* and *H* the equation becomes shorter:

$$dF = dU - TdS - \mu_0 H dm \tag{3.2}.$$

According to the first law of thermodynamics ($dU = \text{d}Q + \text{d}W$), the second law of thermodynamics in terms of entropy ($\text{d}Q \leq TdS$) and the expression of the work performed

on a medium by an external magnetic field H ($dW = \mu_0 H dm$), one can write $dU \leq TdS + \mu_0 H dm$. It means that

$$dU - TdS - \mu_0 H dm \leq 0 \tag{3.3}.$$

From Eq. 3.2 and 3.3, we see that $dF \leq 0$. It means that the guessed function F of an isolated system can either decrease or stay constant. If the systems has reached the equilibrium and does not evolve any further, it means that F has found its minimum. Any process that results in an increase of F is forbidden by the laws of thermodynamics and thus the system simply cannot leave this state. At thermal equilibrium F is at minimum.

As the next step we represent $F(m,H)$ in terms of field dependent and field independent parts

$$F(m, H) = F(m, 0) - \mu_0 H m \tag{3.4}$$

and try to figure out what we can say about $F(m, 0)$.

Relying on our experience and intuition, it is reasonable to state that the internal energy of a magnet does not change upon a reversal of **m**. On a hard drive, for instance, magnets representing "0" bits have the same internal energy as magnets representing "1" bits. If one builds an electromagnet which is able to acquire magnetic moment **m** directed either "up" or "down", the electromagnet will consume the same amount of energy for in these two cases independently on the polarity of **m**. It means that the internal energy (and the entropy) of a magnet with the magnetization pointing up is equal to the internal energy (and the entropy) of the same magnet with the magnetization pointing down. Hence the internal U is an even function of the magnetization m. From Eq.3.1 we conclude that the same is true for the function $F(m, 0)$. Representing $F(m, 0)$ in terms of Taylor series gives:

$$F(m, 0) = Am^2 + Bm^4 + \cdots \tag{3.5},$$

where A and B are the corresponding coefficients. From experiments we know that below the Curie temperature the stable state of a ferromagnet corresponds to a state with $m > 0$. At the Curie temperature and above $m = 0$. At thermal equilibrium $F(m, 0)$ is at minimum. Therefore, it is clear that A is negative below the Curie temperature and positive above the Curie temperature. The simplest possible function $A(T)$ that satisfies these requirements is $A(T) = a(T - T_C)$, where T_C is the Curie temperature, a is a proportionality coefficient ($a>0$). Limiting the Taylor series to two terms, one obtains:

$$F(m, 0) = a(T - T_C)m^2 + Bm^4 \tag{3.6}.$$

At thermal equilibrium $F(m, 0)$ is at minimum and $\frac{dF(m,0)}{dm} = 0$. From Eq.3.6 we find that $2a(T - T_C)m + 4Bm^3 = 0$ or, assuming that $m \neq 0$ for the case $T < T_C$, one obtains

$$m(T) = \sqrt{\frac{a}{2B}(T_c - T)} \tag{3.7}.$$

Hence we obtain a simple equation which describes the temperature dependence of the magnetization in a ferromagnet below the Curie temperature. Although this equation has been derived relying on very rough approximations, qualitatively Eq.3.7 reproduces temperature dependence of the magnetization in real ferromagnets very well.

Above the Curie temperature, one observes $m = \chi H$. We can continue in the same fashion and derive the law for temperature dependence of χ. If the field H is not zero, we start from Eq.3.4 and limit the Taylor series given by Eq.3.5 to one term only. As a result, we obtain

$$F(m, 0) = a(T - T_C)m^2 - \mu_0 Hm$$

The condition of having F at minimum gives $\frac{dF(m,0)}{dm} = 0$ and it means that

$$2a(T - T_C)m - \mu_0 H = 0$$

Since the magnetization is induced now by the magnetic field ($m = \chi H$), we have

$$2a(T - T_C)\chi H = \mu_0 H$$

and

$$\chi = \frac{\mu_0}{2a(T - T_C)}$$

This expression predicts that the paramagnetic susceptibility χ must diverge upon approaching the Curie temperature from above. Experimentally it is seen as a sharp peak in the dependence of the susceptibility on temperature.

It is thus convenient to work with functions which, like the potential energy, are at minimum if the system is at equilibrium. Such functions are introduced for simplicity and called thermodynamic potential or thermodynamic functions.

3.3. Examples of thermodynamic potentials

In the case of a gas one can define four thermodynamic potentials. These potentials are:

- internal energy: U
- enthalpy $H = U + pV$
- Helmholtz function or free energy: $F = U - TS$ (3.8)
- Gibbs function or Gibbs free energy $G = U - TS + pV$

Why do we need so many of them? As it is mentioned above, the potentials in the first place were introduced for convenience. Depending on the set of independent variables it is convenient to use one or another potential. For instance, although a gas can be described by many parameters (pressure, temperature, volume and entropy), only two of these variables are independent. According to the first law of thermodynamics for the case of a gas

$$dU = TdS - pdV \tag{3.9}.$$

It means that if in the problem of interest the entropy (S) and the volume (V) are two independent variables, it is convenient to choose the internal energy as a thermodynamic potential.

Similarly, one can show that

$$dH = TdS + Vdp \qquad\qquad (3.10).$$

$$dF = -SdT - pdV \qquad\qquad (3.11).$$

$$dG = -SdT + Vdp \qquad\qquad (3.12).$$

It means that the enthalpy is a convenient thermodynamic potential for the problems in which S and p are the independent variables. The Helmholtz energy was invented for the cases when the variables are T and p. The Gibbs function is used when the variables are p and T. Following a procedure similar to the one described at the beginning of section 3.2, one can show for a physical system that these thermodynamic potentials are at minimum if the system is at thermal equilibrium.

3.4 Reciprocity and reciprocal theorem. Order of differentiation.
(See proofs elsewhere. For instance, in paragraphs 1.9.1, 1.9.2 and 1.9.3 of C. J. Adkins, "Equilibrium Thermodynamics" (Cambridge University Press, Cambridge, 2003))

In this paragraph we provide some useful mathematical expressions. Suppose that three variables x,y,z are related forming such an equation $F(x,y,z) = 0$ that it is possible to express one of the variables in terms the other two independent ones $x = f(y,z)$. According to the reciprocal theorem:

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \qquad\qquad (3.13).$$

The reciprocity theorem states

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \qquad\qquad (3.14).$$

If $f(y,z)$ is a continuous function and its first as well as second derivatives are also continuous (see Schwarz's theorem), one finds that

$$\frac{\partial^2 x}{\partial z \partial y} = \frac{\partial^2 x}{\partial y \partial z} \qquad\qquad (3.15).$$
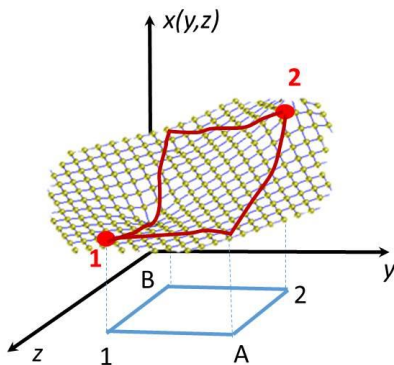
Figure 3.2. *Graphical representation of x(y,z).*

It is rather educative to discuss physical meaning of Eq. 3.15. In fact, it shows that if we perform an experiment and measure x while changing y and z, it does not matter if one first changes y and afterwards z, or first z is changed and afterwards y. It can be seen from Fig. 3.4. We consider a situation when the initial state of quantity x is point "1". Changing y and z we achieve that x reaches the final state given by point "2". There are two ways to proceed from "1"to "2". We use Taylor's series up to the second order assuming that changing y or z does not affect x a lot. With the help of the series we find x in point "2" (x_2) for the route through point "A" i.e. when we first change y and afterwards z:

$$x_A = x_1 + (\frac{\partial x_1}{\partial y})_z \partial y + \frac{1}{2}(\frac{\partial^2 x_1}{\partial y^2})_z (\partial y)^2 + \cdots$$

$$x_2 = x_A + (\frac{\partial x_A}{\partial z})_y \partial z + \frac{1}{2}(\frac{\partial^2 x_A}{\partial z^2})_y (\partial z)^2 + \cdots$$

These expressions give

$$x_2 = x_{A1} + (\frac{\partial x_1}{\partial y})_z \partial y + (\frac{\partial x_1}{\partial z})_y \partial z + \frac{1}{2}(\frac{\partial^2 x_1}{\partial y^2})_z (\partial y)^2 + \frac{1}{2}(\frac{\partial^2 x_1}{\partial z^2})_y (\partial z)^2 + \frac{1}{2}\frac{\partial}{\partial z}(\frac{\partial x_1}{\partial y})_z \partial y \partial z + \cdots$$

Doing the same, but for the case when the changes proceed via point "B", i.e. when we first change z and afterwards y, we find:

$$x_2 = x_{A1} + (\frac{\partial x_1}{\partial y})_z \partial y + (\frac{\partial x_1}{\partial z})_y \partial z + \frac{1}{2}(\frac{\partial^2 x_1}{\partial y^2})_z (\partial y)^2 + \frac{1}{2}(\frac{\partial^2 x_1}{\partial z^2})_y (\partial z)^2 + \frac{1}{2}\frac{\partial}{\partial y}(\frac{\partial x_1}{\partial z})_z \partial z \partial y + \cdots$$

It is seen that in these two cases (i.e. proceeding via "A" or "B") x will arrive to the very same point "2", if

$$\frac{\partial}{\partial y}(\frac{\partial x_1}{\partial z})_z = \frac{\partial}{\partial z}(\frac{\partial x_1}{\partial y})_z \quad \text{or} \quad \frac{\partial^2 x}{\partial z \partial y} = \frac{\partial^2 x}{\partial y \partial z}.$$

3.5 Legendre differential transformation

Assume we have function $f(x)$ and $df = f'(x)dx$. It means that $d(f'x) = f'dx + xdf'$ or $d(xf' - f) = xdf'$. Taking $F = xf' - f$ and $y = f'(x)$ one does the Legendre transformation

$$f(x) \rightarrow F(y)$$

Note that $dF(y) = F'(y)dy$, where $x = F'(y)$. It means that the old variable (x) is the derivative of the new function (F), while the derivative of the old function (f) is now the variable (y).

3.6. Maxwell relations
3.6.1.General principles

Using thermodynamics we can predict behavior of physical system just from general principles i.e. using first law of thermodynamics and the definition of entropy. Let us consider, for instance, the simplest case of a gas under pressure. First law of thermodynamics for the case of the gas under pressure p states:

$$dU = TdS - pdV$$

If we take partial differentials of U, we obtain

$$\left(\frac{\partial U}{\partial s}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial v}\right)_S = -p$$

Differentiating again with respect to the opposite variables gives:

$$\frac{\partial^2 U}{\partial v \partial s} = \left(\frac{\partial T}{\partial v}\right)_S \quad \text{and} \quad \frac{\partial^2 U}{\partial s \partial v} = -\left(\frac{\partial p}{\partial s}\right)_V$$

If U is a continuous function,

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}.$$

The equation means that it does not matter if one first changes volume and afterwards entropy, or first entropy is changed and afterwards volume. The resulting change of the internal energy is always the same. Anyway, after the differentiation one gets

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad (3.16).$$

The equation is an example of Maxwell relations.

Following the same procedure, but using other thermodynamic potentials, we can obtain more Maxwell relations.

From $dH = TdS + Vdp$ one finds

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p \qquad (3.17).$$

From $dF = -SdT - pdV$ one finds

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (3.18).$$

From $dG = -SdT + Vdp$ one finds

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (3.19).$$

Another way to derive Maxwell relations from an expression for a thermodynamic potential is based on the fact that the thermodynamic potential is a function of state and therefore the corresponding function is exact differential. If x is exact differential being a function of y and z, one writes

$$dx = Ydy + Zdz,$$

where $Y = \left(\frac{\partial x}{\partial y}\right)_z$ and $Z = \left(\frac{\partial x}{\partial z}\right)_y$.

Using

$$\frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y},$$

from the last two expressions we obtain

$$\left(\frac{\partial Y}{\partial z}\right)_y = \left(\frac{\partial Z}{\partial y}\right)_z.$$

Finally, it is convenient to remember three simple rules allowing checking correctness of a derived Maxwell relation:

- Cross multiplication of variables always gives the form with the dimensions of energy ($pV, TS, \mu_0 mH$ etc).

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

- Opposite pairs of variables are constant.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

- The sign is positive, if p (pressure) appears on the same side with T.

3.6.2 Thermoelastic effect

Here we consider an example of surface tension. Surface tension is the elastic tendency of a fluid surface which makes it acquire the least surface area possible. If one wants to increase the surface area of a liquid by dA, it is necessary to perform work $dW=\gamma dA$, where γ is the parameter that characterizes surface tension. How does surface tension γ depend on temperature? It means that we have to find an expression for $\frac{\partial \gamma}{\partial T}$.

- **Firstly,** we define the set of relevant variables.
  The variables must be dT and dA.

- **Secondly,** we write first law of thermodynamics for our case assuming that we consider only reversible processes

$$dU = \gamma dA + TdS.$$

- **Thirdly**, we construct a thermodynamic potential with the right set of variable (dT and dA).
  In the expression for internal energy change dU we have to substitute one variable (from dS to dT). If the thermodynamic potential is chosen as $F = U - TS$, we have the required set of variables in the potential:

$$dF = dU - TdS - SdT = \gamma dA - SdT.$$

  This substitution of variables can be seen as a change of the coordinate system. In mathematics this change of variables is called the Legendre differential transformation.

- **Finally,** we derive the Maxwell relation using double differentiation. Assuming that $\frac{\partial^2 F}{\partial A \partial T} = \frac{\partial^2 F}{\partial T \partial A}$, one gets

$$\left(\frac{\partial S}{\partial A}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_A \qquad (3.20a).$$

The same can be also rewritten in terms of heat capacity $C_T^{(A)} = \left(\frac{\partial Q}{\partial A}\right)_T = T\left(\frac{\partial S}{\partial A}\right)_T$.

$$\left(\frac{\partial \gamma}{\partial T}\right)_A = -\left(\frac{\partial S}{\partial A}\right)_T = -\frac{1}{T}\left(\frac{\partial Q}{\partial A}\right)_T = -\frac{1}{T}C_T^{(A)} \qquad (3.20b).$$

3.6.3 Pyroelectricity

Pyroelectricity is the ability of certain materials to generate a temporary voltage when they are heated or cooled. How does the electric polarization of such a medium depend on temperature? To answer this question we must derive an equation for $\left(\frac{\partial p}{\partial T}\right)_E$, where p is the electric polarization and E is the electric field.

- **Firstly,** we define the set of relevant variables.
  The variables must be dT and dE.

- **Secondly,** we write first law of thermodynamics for our case assuming that we consider only reversible processes
  $$dU = Edp + TdS.$$

- **Thirdly**, we construct a thermodynamic potential with the right set of variable (dT and dE).
  In the expression for internal energy change dU we have to substitute two variables (from dS to dT and from dp to dE). If the thermodynamic potential is chosen as $F = U - TS - pE$, we have the required set of variables in the potential:
  $$dF = dU - pdE - Edp - TdS - SdT = -pdE - SdT.$$

- **Finally,** we derive the Maxwell relation using double differentiation. Assuming that $\frac{\partial^2 F}{\partial E \partial T} = \frac{\partial^2 F}{\partial T \partial E}$, one gets

$$\left(\frac{\partial p}{\partial T}\right)_E = \left(\frac{\partial S}{\partial E}\right)_T \qquad (3.21).$$

3.6.4 Magnetocaloric effect

Magnetocaloric effect is an interdependence of the thermal and magnetic properties. Can we control temperature of media T applying magnetic field H? What can we say about $\frac{\partial T}{\partial H}$? Here we would like to note that in accordance with the reciprocity theorem (see Eq. 3.14)

$$\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial T}{\partial S}\right)_H \left(\frac{\partial S}{\partial H}\right)_T \qquad (3.22),$$

where

$$\left(\frac{\partial S}{\partial T}\right)_H = \frac{C_H^{(T)}}{T} \text{ or } \left(\frac{\partial T}{\partial S}\right)_H = \frac{T}{C_H^{(T)}} \qquad (3.23).$$

Here we employed the definition of the heat capacity $C_H^{(T)} = \left(\frac{\partial Q}{\partial T}\right)_H = T\left(\frac{\partial S}{\partial T}\right)_H$.

We have no idea about $\left(\frac{\partial S}{\partial H}\right)_T$ in real magnets. In order to express it differently, we employ Maxwell relations!

- **Firstly,** we define the set of relevant variables.
  The variables are dT and dH.
- **Secondly,** we write first law of thermodynamics for our case assuming that we consider only reversible processes
  $$dU = \mu_0 Hdm + TdS.$$

- **Thirdly**, we construct a thermodynamic potential with the right set of variable (dT and dH).

  In the expression for internal energy change dU we have to substitute two variables (from dS to dT and from dm to dH). If the thermodynamic potential is chosen as $F = U - TS - \mu_0 Hm$, we have the required set of variables in the potential:
  $$dF = dU - \mu_0 m dH - \mu_0 H dm - T dS - S dT = -\mu_0 m dH - S dT.$$

- **Finally,** we derive the Maxwell relation using double differentiation. Assuming that $\frac{\partial^2 F}{\partial H \partial T} = \frac{\partial^2 F}{\partial T \partial H}$, one gets
  $$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial m}{\partial T}\right)_H \tag{3.24}.$$

Bringing together equations (3.22), (3.23) and (3.24), we obtain that
$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H^{(T)}} \mu_0 \left(\frac{\partial m}{\partial T}\right)_H \tag{3.25}.$$

This expression shows that it is possible to control temperature of media with the help of magnetic field.

4. THERMODYNAMICS OF LIGHT

All bodies emit electromagnetic radiation and the character of the radiation depends on how hot the body is. Intuitively we know that a hot body is a source of light and the intensity of the emitted light increases upon a temperature increase. In the 19th century an attempt to estimate the temperature of the sun from analysis of the thermal radiation led to derivation of an equation which is known today as the Stefan-Boltzmann law. Here we review the main steps of this derivation which to a large extent relied on the concepts of thermodynamics.

Imagine that radiation is trapped in a vessel with perfectly reflecting walls. It sounds weird, but the situation is similar to the one when the vessel is filled with an ideal gas: the gas particles (photons) are trapped in the vessel and do not interact with each other (photons do not interact). We first find the internal energy of such a gas.

First law of thermodynamics states

$$dU = dQ + dW$$

For the gas we know that $dW = -pdV$, where p is the gas pressure and V is the volume of the vessel. We also assume that we consider only reversible processes i.e. $dQ = TdS$ and thus

$$dU = TdS - pdV.$$

The total internal energy depends on the size of the vessel, obviously. Therefore we introduce a size independent variable u which states for the internal energy of unit volume $U=uV$.

After differentiation of the equation for internal energy with respect to V, one obtains

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

and

$$u + V\left(\frac{\partial u}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

Since we talk about ideal gas and thus particles of the gas do not interact with each other, we can state that $\left(\frac{\partial u}{\partial V}\right)_T = 0$[1]. To find a possible substitute for $\left(\frac{\partial S}{\partial V}\right)_T$, we find a Maxwell relation for it. Using the procedure described in the previous lecture one gets:

---

[1] If particles do not interact, the internal energy is given by the sum of kinetic energies of the particles. If m is the mass of a single particle , v is the average speed of the particles, for the internal energy one finds $U = \frac{mv^2}{2}nV$, where n is the concentration of the particle in the gas. The internal energy per unit volume does not depend on the volume $u = \frac{U}{V} = \frac{mv^2}{2}n$ and $\left(\frac{\partial u}{\partial V}\right)_T = 0.$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Therefore we find that

$$u = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{4.1}$$

Using the kinetic theory (see "molecular model of an ideal gas" from Physics for Scientists and Engineers by R. A. Serway and J. W. Jewett), one can show that

$$p = \frac{1}{3}u$$

In this way Eq.4.1 turns into

$$u = T\frac{1}{3}\left(\frac{\partial u}{\partial T}\right)_V - \frac{u}{3}$$

or

$$4u = T\left(\frac{\partial u}{\partial T}\right)_V$$

After integration one obtains

$$u = BT^4 + const \tag{4.2}$$

The gas is ideal. It means that at zero temperature ($T=0$ K) the internal energy must be also zero. Therefore we can state that for an ideal gas or for electromagnetic radiation in a vessel

$$u = BT^4 \tag{4.3}$$

Now we take few more expressions from the kinetic theory of gases and find relation between the internal energy stored in the vessel and the ability of the vessel to emit light. According to the kinetic theory, the number of the gas particles (atoms or molecules) striking unit area of the vessel wall per second is given by

$$N = \frac{1}{4}nc,$$

where n is the concentration and c is the mean speed of particles. If the photon energy is equal to η, the average power incident on unit area of the vessel wall is

$$P = \eta N = \frac{1}{4}\eta nc = \frac{1}{4}uc.$$

If a small hole area dA is cut in the wall, the energy escaping the container per second is

$$dP = \frac{1}{4}\, uc\, dA \qquad\qquad (4.4).$$

The rest of the derivation is a question of definitions. We now introduce:

Spectral density u_λ. This quantity is defined such that $u_\lambda d\lambda$ is the energy contained in radiation in the wavelength range between λ and $\lambda+d\lambda$;
- Spectral absorptivity of a surface α_λ is the absorbed fraction of the incident radiation at the wavelength λ.
- Spectral emissive power of a surface e_λ, is quantity defined such that $e_\lambda d\lambda$ is the power emitted in the form of radiation per unit area of the surface in the wavelength range between λ and $\lambda+d\lambda$.
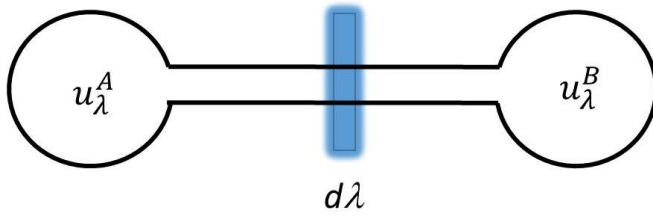
Figure 4.1. *Two reservoirs of energy interconnected with a channel allowing energy transfer in both directions. We assume that energy carriers (photons) cannot change their wavelengths. To account for it, in the model we insert a filter (blue rectangle) in the channel which allows photons transfer between the reservoirs only in the range of wavelengths limited to $d\lambda$. Thermodynamic equilibrium between the reservoirs thus implies $u_\lambda^{(A)} = u_\lambda^{(B)}$.*

We assume that the emitting body is in equilibrium with the environment. In this case the environment and the body can be represented by two reservoirs: *A* and *B*. To account for mutual interactions between the body and the environment, we interconnect the reservoirs with a channel allowing energy flow in both directions. The equilibrium of the reservoirs implies that the internal energies per unit volume of the reservoirs are mutually equal. Assuming that the energy of a photon cannot be changed we obtain that $u_\lambda^{(A)} = u_\lambda^{(B)}$. According to the definition given above, the energy emitted by the body per second in the range of wavelengths $d\lambda$ is $e_\lambda d\lambda$. According to Eq.4.4, the energy coming to the emitting body from the environment per second in the range of wavelengths $d\lambda$ is $\frac{1}{4} c u_\lambda^B d\lambda$. Thermodynamic equilibrium implies the equality

$$e_\lambda d\lambda = \alpha_\lambda \frac{1}{4} c u_\lambda^B d\lambda$$

Taking into account $u_\lambda^{(A)} = u_\lambda^{(B)}$ one obtains

$$e_\lambda d\lambda = \alpha_\lambda \frac{1}{4} c u_\lambda^A d\lambda$$

For absolutely black body we have $\alpha_\lambda = 1$ and thus
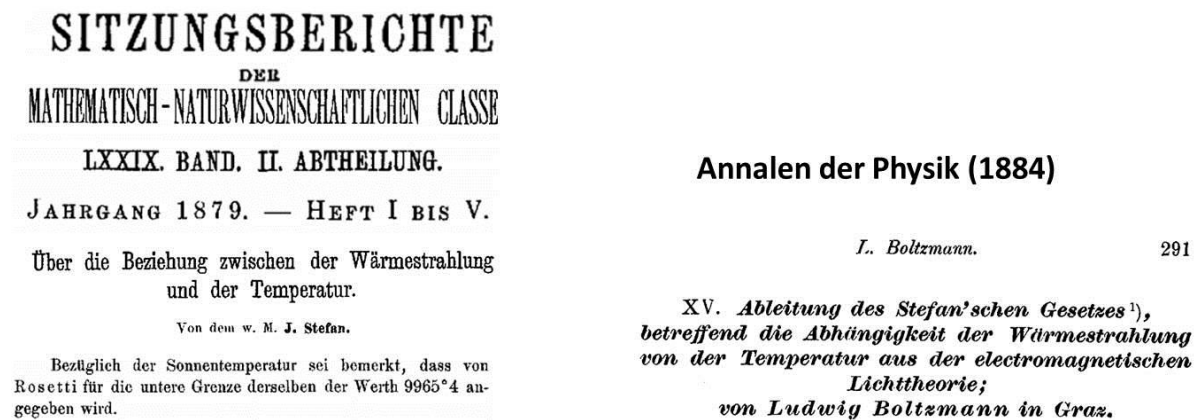
$$e_\lambda = \frac{1}{4} c u_\lambda^A$$

Using Eq. 4.3 we arrive to an expression for spectral emissive power of an absolutely black body

$$e_\lambda = \frac{B}{4} c T^4$$

Integrating over all wavelengths we obtain the total power radiated per unit area by a black body

$$e = \sigma T^4 \tag{4.5},$$

where σ is Stefan's constant. Josef Stefan found this law analyzing experimental data and estimated the temperature of the Sun's surface. This was the first sensible value for the temperature of the Sun. Five years later Ludwig Boltzmann explained the law theoretically.

SITZUNGSBERICHTE
DER
MATHEMATISCH-NATURWISSENSCHAFTLICHEN CLASSE

LXXIX. BAND. II. ABTHEILUNG.

JAHRGANG 1879. — HEFT I BIS V.

Über die Beziehung zwischen der Wärmestrahlung
und der Temperatur.

Von dem w. M. **J. Stefan.**

Bezüglich der Sonnentemperatur sei bemerkt, dass von
Rosetti für die untere Grenze derselben der Werth 9965°4 an-
gegeben wird.

Annalen der Physik (1884)

L. Boltzmann. 291

XV. *Ableitung des Stefan'schen Gesetzes[1]),*
betreffend die Abhängigkeit der Wärmestrahlung
von der Temperatur aus der electromagnetischen
Lichttheorie;
von Ludwig Boltzmann in Graz.

Figure 4.2. *Front pages of the original papers of Josef Stefan and Ludwig Boltzmann reporting about the law known today as the Stefan-Boltzmann law.*

5. THERMODYNAMICS OF PHASE TRANSITIONS

5.1 Introduction

Equilibrium of ice and water is the probably most known example of co-existence of two phases of the very same compound. Changing the temperature of the mixture of ice and water or atmospheric pressure we can change the ratio between masses of water and ice. Such a change of the ratio, i.e. mass transfer between two states of matter, is called a phase transition. A substance which is physically and chemically homogeneous is considered a single **phase**. Different states of aggregation as gas, liquid, or different crystalline states are different phases. Transition of matter from one phase to another is called **phase transition**. Consider two coexisting phases (ice and water). Coexistence means that the phases are in thermodynamic equilibrium. How does the phase boundary change, if we change pressure or temperature?

We consider the mixture in thermodynamic equilibrium. Pressure p and temperature T are two quantities discussed in the problem. If the phases are in thermodynamic equilibrium, temperatures of the phases are equal($T_1 = T_2$) and the phases act on the phase boundary with

equal pressures $(p_1 = p_2)$. Therefore, it is natural to choose Gibbs function as thermodynamic potential in our model. The Gibbs function of the mixture is

$$G = m_1 g_1 + m_2 g_2 \qquad (5.1),$$

where m_1, m_2 are the masses of phase 1 and phase 2. g_1, g_2 are specific Gibbs functions of the phases. The specific Gibbs function of the mixture is thus $g = G/(m_1 + m_2)$. The fact of thermodynamic equilibrium as well as fixed p and T imply that $dG = 0$, $dg_1 = 0$ and $dg_2 = 0$. Therefore,

$$dG = g_1 dm_1 + g_2 dm_2 \qquad (5.2).$$

The total mass is conserved and $dm_1 + dm_2 = 0$. It means that from Eq. 5.2 we obtain that

$$g_1 = g_2 \qquad (5.3).$$

It means that in thermodynamic equilibrium the phases have equal specific Gibbs functions. If the line of equal specific Gibbs functions is crossed, one of the phase expands and another one shrinks. The expanding phase is the one with the smaller specific Gibbs function.

*5.2 Ehrenfest's classification of phase transitions*
There is a plenty of different phase transitions: solid-liquid, liquid-gas, ferromagnet-paramagnet, superconductor-metal. Ehrenfest suggested an elegant way to classify all these phase transitions. Consider two co-existing phases. In thermodynamic equilibrium of two phases one finds $g_1 = g_2$. It means that if we consider 3D-graphs $g_1(p, T)$ and $g_2(p, T)$, the specific Gibbs functions of two phases would correspond to two surfaces. The intersection of the surfaces corresponds to the phase boundary. Although at the phase boundary $g_1 = g_2$, $g_1(p, T)$ and $g_2(p, T)$ are different surfaces. Ehrenfest suggested to assign an order to phase transition. **The order of a transition is defined as the order of the lowest differential of the Gibbs function or other thermodynamic potential which shows a discontinuity at the transition.**
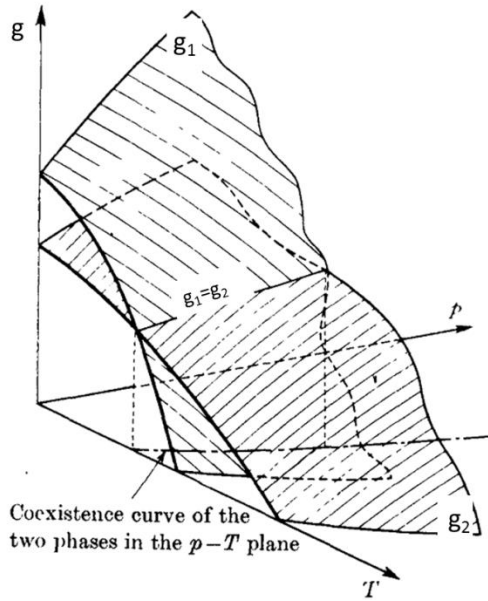
Figure 5.1. *Specific Gibbs functions of two phases. Intersection of the planes corresponds to a first-order phase transition.*

Figure 5.1. represents a first order phase transition. In thermodynamic equilibrium of two phases, the specific Gibbs functions are equal ($g_1 = g_2$), but their first derivatives are not ($\frac{\partial g_1}{\partial T} \neq \frac{\partial g_2}{\partial T}$ and $\frac{\partial g_1}{\partial p} \neq \frac{\partial g_2}{\partial p}$). This is why it is first order phase transition. From the definition of the Gibbs function one can easily see that in the case of first order phase transitions crossing the boundary of equal specific Gibbs functions is accompanied by a step-like change in entropy (ΔS) and volume (ΔV).

The line of equal specific Gibbs functions, i.e. intersection between the planes corresponding to $g_1(p, T)$ and $g_2(p, T)$, can be projected onto pT-plane (see Fig. 5.2).
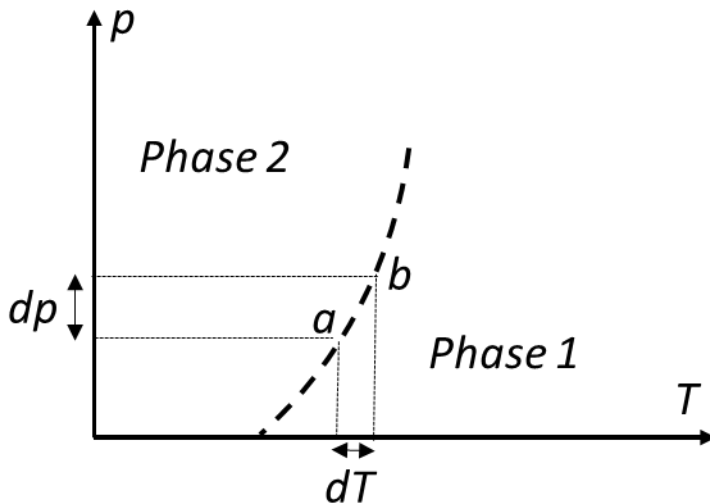
Figure 5.2. *Phase boundary projected onto pT-plane.*

Consider two points a and b at the phase boundary. Passing from a to b will affect the specific Gibbs functions and cause the following changes:

$$dg_1 = \left(\frac{\partial g_1}{\partial p}\right)_T dp + \left(\frac{\partial g_1}{\partial T}\right)_p dT = v_1 dp - s_1 dT$$

and

$$dg_2 = \left(\frac{\partial g_2}{\partial p}\right)_T dp + \left(\frac{\partial g_2}{\partial T}\right)_p dT = v_2 dp - s_2 dT,$$

where v_1, v_2 are volumes of the phases per unit mass (specific volumes) and s_1, s_2 are entropies of the phases per unit mass (specific entropies). Everywhere along the phase boundary $g_1 = g_2$ meaning that $dg_1 = dg_2$. As a result one obtains that $v_1 dp - s_1 dT = v_2 dp - s_2 dT$. It laso means that $V_1 dp - S_1 dT = V_2 dp - S_2 dT$ and

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T \Delta V} \tag{5.4},$$

where ΔS is the change in entropy and ΔV is the change in volume on passing across the phase boundary. L is the latent heat i.e. heat absorbed or rejected upon the phase transition. Equation 5.4 is the Clausius-Clapeyron equation.

First order phase transition is characterized by abrupt change of volume because $\left(\frac{\partial g_1}{\partial p}\right)_T \neq \left(\frac{\partial g_2}{\partial p}\right)_T$ and abrupt change of entropy. It can be also seen that first order phase transitions are characterized by divergence of heat capacity $C = \frac{dQ}{dT} = \frac{T dS}{dT} \to \infty$, coexistence of phases and hysteresis.

What is hysteresis? An example of hysteresis was shown in Fig. 3.3. In the case of first order phase transition from water to vapor one can observe temperature hysteresis in the dependence of mass density on temperature. It means that upon heating up the transition from water to vapor occurs at higher temperature than the transition from vapor to water upon a cooling down. Thermodynamics predicts that if there is a boundary between two phases (gas and water), a temperature increase will promote expanding of gas-phase and shrinking of liquid-phase. However, if one takes a can with perfectly clean surface and starts to increase the temperature slowly, making sure that bubbles are not formed, water can still be in the liquid phase even if the liquid is characterized by a larger specific Gibbs function than the gas-phase. Only when the first bubble, and thus a phase boundary, is formed, the bubble (gas-phase) starts to expand and the larger the difference between the specific Gibbs functions of the two phases, the faster expansion is. One may like to learn about overheated water (https://www.youtube.com/watch?v=2FcwRYfUBLM) and supercooled water (https://www.youtube.com/watch?v=pTdiTe3x0Bo), which are examples of temperature hysteresis during first order phase transition.

5.3 First order phase transition in ferromagnets

Magnetic hysteresis is also a signature of first order phase transition. In this case two coexisting phases are the states with two opposite orientations of the magnetization. The thermodynamic potential relevant for this case is $F = U - TS - \mu_0 \mathbf{m} \mathbf{H}$ (see Eq. 3.1, where $\mathbf{m}$ is the magnetic moment). For the case of parallel $\mathbf{m}$ and $\mathbf{H}$ as well as for fixed T and H one gets $dF = dU - TdS - \mu_0 H dm$ (see Eq. 3.2). At the phase boundary separating two states with opposite magnetizations, i.e. at the domain wall, $\left(\frac{\partial F_1}{\partial H}\right)_T \neq \left(\frac{\partial F_2}{\partial H}\right)_T$ meaning that $m_1 \neq m_2$ i.e. at the domain wall the magnetic moment m experiences a discontinuity.
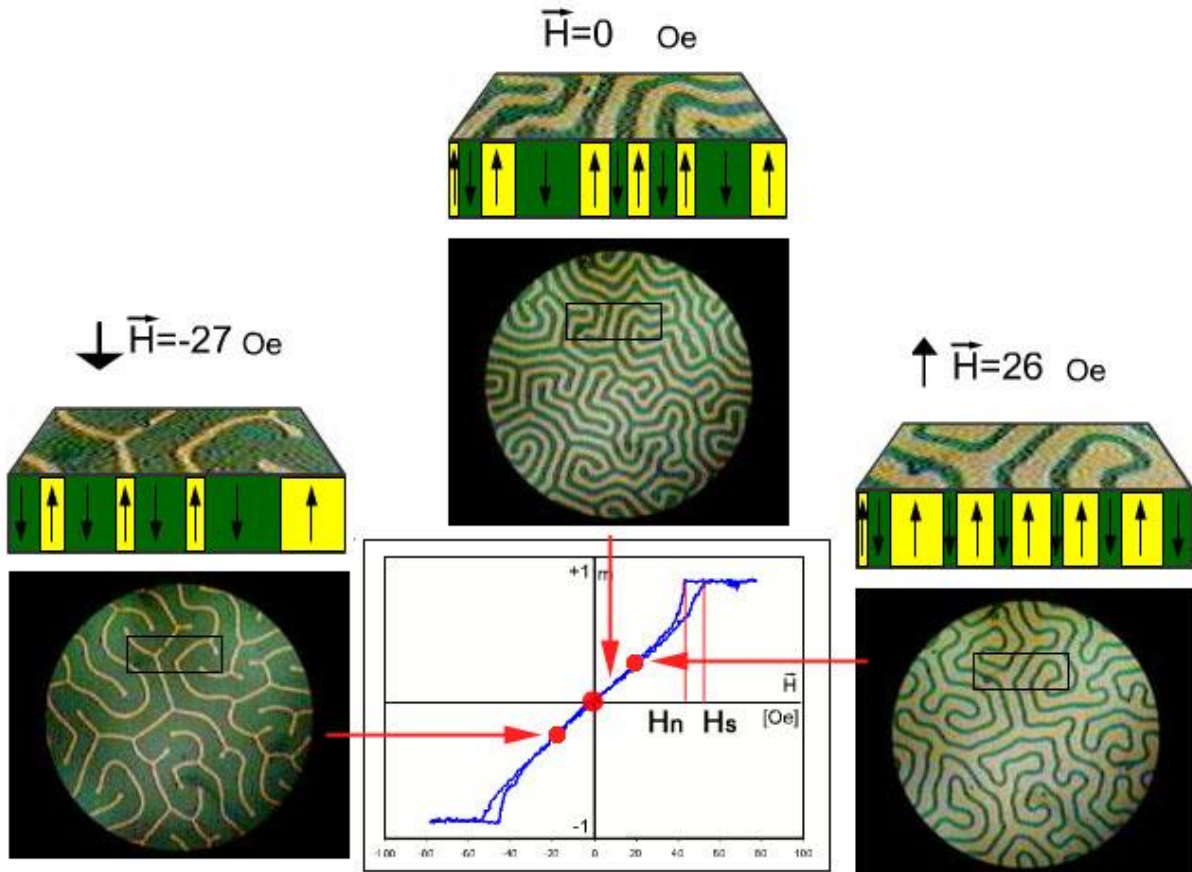
Figure 5.3. *Coexistence of phases (magnetic domains with magnetizations "up" and "down") and manifestation of the existence in magnetic hysteresis loop.http://labfiz.uwb.edu.pl/lab/magmicroscope/?page_id=45&lang=en*

5.4 Second order phase transitions

For second order phase transitions one may also derive an equation similar to Eq. 5.4. Assume that $\frac{\partial g_1}{\partial T} = \frac{\partial g_2}{\partial T}$ $(s_1 = s_2)$ and $\frac{\partial g_1}{\partial p} = \frac{\partial g_2}{\partial p}$ $(v_1 = v_2)$.

First we consider the equality of entropies. For entropy we know that $ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$. If temperature or pressure changes and if the phases are still in mutual equilibrium, the changes of entropies of the two phases are also equal $(ds_1 = ds_2)$. Therefore

$$\left(\frac{\partial s_1}{\partial T}\right)_p dT + \left(\frac{\partial s_1}{\partial p}\right)_T dp = \left(\frac{\partial s_2}{\partial T}\right)_p dT + \left(\frac{\partial s_2}{\partial p}\right)_T dp.$$

Introducing specific heat $c_p^{(T)} = \left. C_p^{(T)} \middle/ mass \right. = \frac{1}{mass}\frac{dQ_p}{dT}$, isobaric cubic expansivity $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and applying Maxwell relation $\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$, we obtain

$$\frac{1}{T}c_{p1}dT - \left(\frac{\partial v_1}{\partial T}\right)_p dp = \frac{1}{T}c_{p2}dT - \left(\frac{\partial v_2}{\partial T}\right)_p dp$$

or

$$\frac{dp}{dT} = \frac{c_{p2} - c_{p1}}{vT(\beta_2 - \beta_1)} \tag{5.5a}.$$

Starting from another equality for second order phase transition $\frac{\partial g_1}{\partial p} = \frac{\partial g_2}{\partial p}$ ($v_1 = v_2$) and after introducing isothermal compressivity $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ we obtain

$$\frac{dp}{dT} = \frac{\Delta\beta}{\Delta\kappa} = \frac{\Delta c}{vT\Delta\beta} \tag{5.5b}.$$

Equations (5.5a) and (5.5b) are called Ehrenfest's equations. In the spirit of Ehrenfest's classification Table 5.1 summarizes behavior of physical quantities in the vicinity of the phase transitions.

It is important to note that the diagram, shown in Fig. 5.1, is unfortunately not applicable to second order phase transitions. If $\left(\frac{\partial g_1}{\partial T}\right)_p = \left(\frac{\partial g_2}{\partial T}\right)_p$ and $\left(\frac{\partial^2 g_1}{\partial T^2}\right)_p > \left(\frac{\partial^2 g_2}{\partial T^2}\right)_p$, we always have that $g_2 < g_1$ meaning that the system must always stay in the phase with g_2.

Note that according to Ehrenfest there must be phase transitions of third, fourth and higher order. However, soon after Ehrenfest proposed his classification, it was realized that it is rather incomplete.

Table 5.1. *Behavior of physical quantities in the vicinity of phase transitions of first and second order according to the classification of Ehrenfest.*

	Quantity	First order transition	Second order transition
First derivatives of thermodynamic potential	volume V, entropy S, magnetization M, electric polarization P i.e observables	*Jump at the phase transition*	*No discontinuity at the phase transition*
Second derivatives of thermodynamic potential	heat capacities c, compressibility κ, expansivity β, susceptibility χ, Permeability χ_m, i.e response functions	*Diverge at the phase transition*	*Jump at the phase transition*

5.5 Modern classification of phase transitions

The classification of Ehrenfest is logical and can be convenient, but it appears that in practice it is incomplete. It can be seen using the example of phase transition from ferromagnetic to paramagnetic state. Such a transition was considered in paragraph 3.2. Substituting Eq. 3.7 into the expression for thermodynamic potential F (Eq.3.6) and differentiating we find that $\frac{\partial F_1}{\partial T} = \frac{\partial F_2}{\partial T}$. It means that this is not a first order phase transition. At the same time, according to table 5.1 the phase transition does have signatures typical to transitions of first order, because magnetic susceptibility $\chi = \left(\frac{\partial M}{\partial H}\right)_T = \left(\frac{\partial^2 F}{\partial H^2}\right)_T$ diverges at the transition point (see paragraph 3.2 that shows that $\chi = \frac{\mu_0}{2a(T-T_C)}$). In short, although the classification of Ehrenfest works well for transitions of first order, description of other phase transitions (non-first order) is incomplete.

For a more general classification, it was decided to consider only the behavior of the first derivative of thermodynamic potential. Based on it we can distinguish discontinuous and continuous phase transitions:

a) Discontinuous phase transitions are characterized by a jump in the first derivative of thermodynamic potential at the phase transition. The transitions are thus equivalent to first order phase transitions in the classification of Ehrenfest.
b) Continuous phase transitions are such that the first derivative of thermodynamic potential upon crossing the phase boundary changes continuously. Phenomenological theory of continuous phase transitions was developed by L. Landau (see Fig. 5.3).

The question about continuous phase transitions (without latent heat) is investigated from the general thermodynamical point of view. In doing this, it becomes clear that such transitions can take place when the symmetry of the lattice changes. There are two possible types of transition, namely: (1) Curie points with a discontinuity in the specific heat which lie on a curve in the p, T-diagram, (2) isolated points in the p, T-diagram which lie in a certain way on intersections of curves of normal phase transitions.

Figure 5.3. *Original article of L. Landau on continuous phase transitions.*

Phase transition from the ferromagnetic to the paramagnetic state is continuous. It can be confusing but it is now conventionally accepted to call discontinuous and continuous phase transitions as transitions of first and second order, respectively.

6. CHEMICAL POTENTIAL. THERMODYNAMICS OF DIFFUSION. THERMODYNAMICS OF CHEMICAL REACTIONS

After thermodynamics of phase transitions, where we discussed equilibrium between different phases of the same compound, we would like to make the next step and develop thermodynamic theory of equilibria between different substances. We start with equilibrium of substances which can get mixed but do not combine chemically. It means that the constituting substances retain their original properties and can be physically separated. In short, we will talk about mixtures. Diffusion is one of the key phenomena in every mixture. Can we understand diffusion thermodynamically?

6.1. Gibbs paradox

We consider a mixture of two ideal gases. Two different gases in a box separated by a partition (see Fig.1). The gases have the same temperatures (T) and pressures (p). The numbers of moles of the gases are n_1 and n_2, respectively. V_1 and V_2 are the volumes occupied by the gases. As it was shown in Chapter 2, the entropy of 1 mole of ideal gas is equal to

$$S(T, V) = C_V \ln T + R \ln V + const,$$

where *const* is the constant of integration and C_V is the molar specific heat of the gas at constant volume. If the partition is removed, the gases diffuse. The total entropy change after the diffusion is equal to

$$\Delta S = \Delta S_1 + \Delta S_2 = n_1 R \ln \frac{V_1 + V_2}{V_1} + n_2 R \ln \frac{V_1 + V_2}{V_2} \qquad (6.1)$$

It is seen that as a result of the diffusion the entropy increases. The fact of such an entropy increase could also be predicted, because both gases expand and diffuse irreversibly. It is not a surprise that the diffusion of different gases leads to an increase of entropy. We will call this entropy change entropy of mixing.

Suppose now that we have filled the two volumes with the same gas. The equation implies a paradoxical increase of the entropy upon removing the partition. We know, however, that removing the partition between two volumes filled with the very same gas, at the very same pressure and temperature will not launch any irreversible processes. This contradiction is now called Gibb's paradox after J. W. Gibbs who proposed this thought experiment in 1875.

Resolving the paradox does not seem to be a difficult problem today. Equation (6.1) was derived for the case of different i.e. distinguishable gases. People may argue that if the gases become more and more alike, upon the gradual disappearance of differences the entropy of mixing should experience a paradoxical jump. To resolve the paradox it is enough to realize that a gradual change from identical to different gases is not possible. Today, with all available knowledge of atomic structure, it is obvious that there is no continuous transition from hydrogen to helium, for instance. In the 19th century, i.e. before the discovery of electron and the development of quantum mechanics, interpretation of such a thought experiment was often a subject of intense debates.
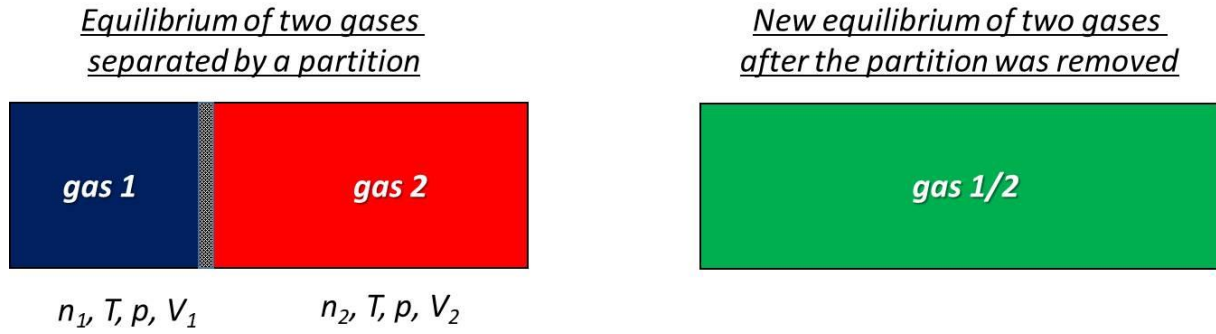
Figure 1. *The thought experiment demonstrating Gibbs' paradox.*

6.2 Chemical potential

In this paragraph we aim to understand how to account for diffusion in thermodynamic theory of mixtures. We again consider a container separated by a partition. Both parts of the container are filled with the very same gas. The gas in these two parts of the container has the very same temperature. The left part having the volume V_1 contains N_1 of gas particles. The right part with the volume V_2 contains N_2 gas particles. Two parts are interconnected with a valve facilitating diffusion of the gas particles in both directions. If G is the Gibbs function of the gas ($G = U - TS + pV$, see Chapter 3), it is clear that $G = G_1 + G_2$, where G_1 and G_2 are the Gibbs functions of the gas in the right and the left parts of the container, respectively. As a result of diffusion the total number of the particles does not change and $dN_1 = -dN_2$. Naturally, the Gibbs function G_1 is a function of N_1 and G_2 is a function of N_2 . We notice that

$$\Delta G = \left(\frac{\partial G_1}{\partial N_1}\right)_T \Delta N_1 + \left(\frac{\partial G_2}{\partial N_2}\right)_T \Delta N_2$$

Using the fact that $\Delta N_1 = -\Delta N_2$, the equation can be written with less variables i.e.

$$\Delta G = \left(\frac{\partial G_1}{\partial N_1}\right)_T \Delta N_1 - \left(\frac{\partial G_2}{\partial N_2}\right)_T \Delta N_1$$

If the mixture reaches thermodynamic equilibrium, the Gibbs function should be at the minimum i.e. the equilibrium requires that $dG = 0$ or $\Delta G = 0$. Therefore at equilibrium one should observe that

$$\left(\frac{\partial G_1}{\partial N_1}\right)_T = \left(\frac{\partial G_2}{\partial N_2}\right)_T \tag{6.2}$$

The derivative of the thermodynamic potential with respect to the number of particles is called the chemical potential. More particularly, the chemical potential for N gas particles at the temperature T with the Gibbs function G is defined as

$$\mu(T, N) = \left(\frac{\partial G}{\partial N}\right)_T \tag{6.3}$$

From Eqs. 6.2 and 6.3 it is seen that the equality of chemical potentials expresses the condition for diffusive equilibrium

$$\mu_1 = \mu_2 \qquad (6.4).$$

The chemical potential of an ensemble of particles shows how the Gibbs function changes upon adding a single particle to the ensemble. In order to explicitly emphasize this dependence, the earlier introduced definitions of thermodynamic potentials must be slightly changed. For instance, if we have a mixture of several gases, the changes of the total internal energy and the total Gibbs function are written as $dU = -pdV + TdS + \sum_i \mu_i dN_i$ and $dG = Vdp - SdT + \sum_i \mu_i dN_i$, where μ_i is the chemical potentials of the i-gas. Expressions for other thermodynamics potentials are upgraded accordingly by adding $\sum_i \mu_i dN_i$ term.

With the help of chemical potential we enrich thermodynamic theory. It is seen that a difference in chemical potentials acts as a driving force for the transfer of particles just as a difference in temperature acts as a driver for a transfer of energy. In short, with the help of chemical potentials diffusion can be understood thermodynamically.

As an exercise, one can calculate chemical potential for the case of ideal gas. We consider a mixture of several gases at the temperature T with the total pressure p. Each i-th gas is an ideal gas under pressure p_i. If n_i is the number of moles of the i-th gas, we can also define the concentration of the i-th component as

$$c_i = \frac{n_i}{\sum_i n_i}$$

It is clear that

$$c_i = \frac{n_i}{\sum_i n_i} = \frac{p_i}{p} \qquad (6.5).$$

From the definition of the Gibbs function ($G = U - TS + pV$ and $dG = -SdT + Vdp$), it is seen that

$$\left(\frac{\partial G_i}{\partial p}\right)_T = V_i,$$

where V_i is the volume occupied by the i-gas. For n_i moles of the i-th ideal gas we have $V_i = n_i \frac{RT}{p_i}$ and

$$\left(\frac{\partial G_i}{\partial p}\right)_T = n_i \frac{RT}{p_i}$$

Integrating the last expression, for 1 mole of the i-th ideal gas we obtain

$$G_i(T, p_i) = G0_i(T) + n_i RT \ln p_i,$$

where $G0_i(T)$ is the constant of integration. This part of the Gibbs function does not depend on the pressure p_i. The same expression can be written differently

$$G_i(T, p_i) = G0_i(T) + n_i RT \ln p + n_i RT \ln c_i$$

In an ideal gas particles do not interact. Therefore, the Gibbs function of ideal gas is the sum of the Gibbs potentials of the particles or simply the chemical potential times the number of particles. If the gas has N_i particles, one can find this number from $N_i = n_i N_A$, where N_A is the Avagadro constant. Therefore, the chemical potential of the i-th ideal gas is $\mu_i(T, p_i) = \frac{G0_i(T) + RT \ln p + RT \ln c_i}{N_A}$. The same expression can be written in a simpler form

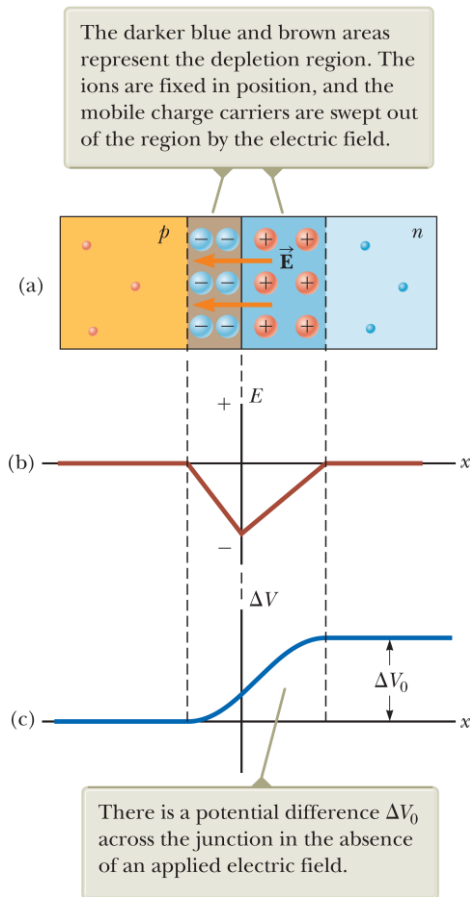$$\mu_i(T, p_i) = \mu0_i(p, T) + kT \ln c_i \qquad (6.6),$$

where k is the Boltzmann constant ($k = \frac{R}{N_A}$) and $\mu0_i(p, T)$ is the part of the chemical potential which depends only on the total pressure and temperature.

6.3 Examples of employing the concept of chemical potential in physics problems

6.3.1 Semiconducting p-n junction

The best way to understand chemical potential is to discuss diffusive equilibrium in the presence of a step of potential energy. Here we use a semiconductor, such as silicon (Si) or germanium (Ge), as an example. Using ion implantation it is possible to change electrical properties of these media. For instance, at low temperatures pure Si does not conduct electric current because of the lack of mobile charge carriers. Implanting a single ion of phosphorus (P) into Si it is possible to create a single mobile electron in the semiconductor. Implanting a single atom of Boron (B) takes one immobile electron from a Si atom and in this way creates a vacancy in the ensemble of Si electrons. This vacancy is called "hole". The hole can be seen as a mobile positively charged particle. Such an implantation is called doping. Therefore using dopants (i.e. implanted ions) it is possible to fabricate semiconductors with high concentration of excess mobile electrons (n-type semiconductor) and holes (p-type semiconductor). Bringing n-type and p-type semiconductors in contact with each other results in a phenomenon called p-n junction. In such a junction free electrons and holes will diffuse. Excess electrons will diffuse from the n-type semiconductor into the p-type semiconductor, while the holes will diffuse into the opposite direction. Upon the diffusion of the electrons and the holes, the p-type semiconductor charges negatively, while the n-type semiconductor acquires a positive charge. In this way at the interface of the n- and p-type semiconductors the diffusion builds up an electric field corresponding to the electric voltage ΔV. When the electric voltage becomes too large, the diffusion stops. The phenomenon can be easily understood in terms of chemical potentials. Thermodynamically the diffusion of electrons from the n-type to the p-type semiconductor is launched due to the initial difference of the chemical potentials of the electron gas in this two types of semiconductors $\Delta\mu_{in}$. At the moment when the diffusion stops the chemical potentials are equalized and the final difference between the chemical potentials is null $\Delta\mu_{fin}=0$. It occurs because the initial difference between the chemical potentials got compensated by an increase of the potential energy of mobile electron in the p-type semiconductor i.e. $\Delta\mu_{in} = |q|\Delta V$, where q is the charge of the mobile particle (electron). In short, the chemical potential in thermodynamics is equivalent to the potential energy in mechanics.

The darker blue and brown areas represent the depletion region. The ions are fixed in position, and the mobile charge carriers are swept out of the region by the electric field.

There is a potential difference ΔV_0 across the junction in the absence of an applied electric field.

Figure 2. *(a) Physical arrangement of a p–n junction. (b) Internal electric field magnitude versus x for the p–n junction. (c) Internal electric potential difference ΔV versus x for the p–n junction (the figure is taken from R. A. Serway, J. W. Jewett, Physics for Scientists and Engineers with Modern Physics (eighth edition).*

6.3.2 Finding the variation of the concentration of oxygen with attitude

Another easy example of diffusive equilibrium between systems in different external potentials is the equilibrium between layers at different heights of the Earth's atmosphere. The chemical potential of the oxygen can be written as the chemical potential of ideal gas (Eq. 6.5) in the gravitational field Mgh

$$\mu_i(T, p_i) = \mu 0_i(p, T) + kT ln(c_i) + Mgh,$$

where M is the atomic mass of oxygen, g is the gravitational acceleration and h is the height. Thermodynamic equilibrium between layers of air at the height h and at the surface of the Earth $h = 0$ implies the equality of the chemical potentials for the layers

$$kT ln\big(c_i(h)\big) + Mgh = kT ln\big(c_i(0)\big),$$

where $c_i(h)$ and $c_i(0)$ are the concentrations of the oxygen at the height h and 0, respectively. Assuming that the layers have the same temperature, we get

$$\ln\big(c_i(h)\big) - \ln\big(c_i(0)\big) = -\frac{Mgh}{kT}.$$

or after converting this logarithmic equation into exponential one

$$c_i(h) = c_i(0)\exp\left(-\frac{Mgh}{kT}\right).$$

The expression is also known as the Boltzmann distribution.

6.4 Phase transitions in mixtures. Gibbs phase rule

In this paragraph we will develop thermodynamic theory of equilibrium in mixtures. In order to account for chemically different constituting substances we introduce the term of "component".

Components are chemically different and chemically independent parts of mixture. Water is just one component. Solution of salt in water is a two component system. If a part of salt in the solution is crystallized, it means that salt in the solution can be found either in liquid or in solid phase.

We consider thermodynamic equilibrium in a mixture which consists of C components and each of the components can be in R different phases. In the theory of phase transitions discussed in the previous chapter one can also use chemical potentials instead of specific Gibbs functions. If $\mu_i^{(k)}$ is the chemical potential for the i-th component in the k-phase, the condition of equilibrium between phases "1" and "2" of the i-th component will be given by the equality of chemical potentials of these two phases

$$\mu_i^{(1)} = \mu_i^{(2)}.$$

If we write the condition of equilibrium for each of the components, we obtain *C(R-1)* equations:

$$\mu_1^{(1)} = \mu_1^{(2)} = \cdots = \mu_1^{(R)},$$

$$\mu_2^{(1)} = \mu_2^{(2)} = \cdots = \mu_2^{(R)},$$

$$\dots\dots\dots\dots\dots\dots\dots\dots, \qquad\qquad (6.7).$$

$$\mu_C^{(1)} = \mu_C^{(2)} = \cdots = \mu_C^{(R)}$$

Each of the chemical potentials in this system depends on the temperature of the mixture T and the pressure p. These are two independent parameters. Moreover, the chemical potential $\mu_i^{(k)}$ depends on the concentrations of the i-th component in the k-phase. The equilibrium described by Eqs.6.7 implies that there is no transfer of particles between different phases of the same component. It means that the masses of the phases are fixed and if the concentration of the k-th component in the i-phase is defined as

$$x_i^{(k)} = \frac{N_i^{(k)}}{\sum_i N_i^{(k)}},$$

where $N_i^{(k)}$ is the number of particles of the k- th component and in the i-th phase, it is seen that not all the concentrations are mutually independent. It follows from the fact that

$$\sum_i x_i^{(k)} = 1.$$

Therefore in each of the R-phases we will find $C - 1$ mutually independent concentrations. Such a mixture has in total $(C - 1)R + 2$ independent variables, where "+2" stays for pressure and temperature.

To summarize, a mixture of C components and R phases has $(C - 1)R + 2$ independent parameters and in thermodynamic equilibrium these parameters must obey $C(R - 1)$ equations.

The system of equations has solutions only if the number of equations does not exceed the number of parameters $(C - 1)R + 2 \geq C(R - 1)$ or

$$R \leq C + 2 \tag{6.8a}$$

This condition says that for any mixture which consists of C components, the number of phases that can maintain mutual equilibrium is equal to $C + 2$ or less. This expression is called Gibbs phase rule. In particular, the equation shows that although Helium can exist in 4 different phases, maximum three of those phases can be simultaneously in equilibrium with each other. The very same phase rule is often given in a different form

$$DoF = 2 + C - R \tag{6.8b}$$

where DoF is the number of degrees of freedom i.e. parameters that can be freely changed without destroying the equilibrium.

For instance, we can consider a solution of KCl and NaCl in water. The solution (liquid phase) can be in an equilibrium with the gas phase (vapor) and three different solid phases can also emerge (KCl crystals, NaCl crystals and ice). How many phases of this mixture can be in equilibrium at the same time? In the problem we have 3 components (KCl, NaCl and water). Applying the Gibbs' phase rule we obtain $R \leq C + 2$ i.e. the number of phases which can simultaneously be found in equilibrium is no more than 5.

6.4 Thermodynamics of chemical reactions

Finally, we discuss thermodynamic theory of chemical reactions. In particular, we focus on a chemical reaction that can go both ways i.e. directly (from-left-to-right) or inversely (from-right-to-left). An example of such a reaction is

$$3H_2 + N_2 \leftrightarrow 2NH_3$$
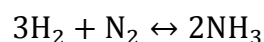
When the speeds of the direct and the inverse reactions are the same, the chemical equilibrium is reached and the masses of the participants of the reaction do not change anymore. The reaction effectively stops. Can we find the condition for the equilibrium?

We express the equilibrium between the compounds participating in the reaction in the following form[1]

$$2NH_3 - 3H_2 - N_2 = 0$$
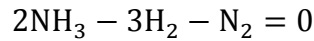
Or being more general

$$\sum_i \nu_i A_i = 0$$

where A_i is a symbol for the i-th chemical compound participating in the reaction and ν_i is the coefficient showing how many molecules of the i-th compound participate in the reaction. If ν_i is positive, it means that this substance is produced as a result of the direct reaction. If ν_i is negative, it means that this substance is consumed as a result of the direct reaction. In the example given above $\nu_{NH3} = 2, \nu_{H2} = -3, \nu_{N2} = -1$. If the reaction proceeds at the given pressure p and temperature T, it is convenient to work further with the Gibbs function.

$$dG = Vdp - SdT + \sum_i \mu_i dN_i$$

Thermodynamic equilibrium between the direct and the inverse reaction implies that $dG = 0$ and at constant pressure and temperature it means that $\sum_i \mu_i dN_i = 0$. After one act of the reaction we obtain $dN_i = \nu_i$. Therefore the condition for equilibrium for a chemical reaction states that

$$\sum_i \nu_i \mu_i = 0 \qquad\qquad (6.9).$$

We assume that the participants of the reaction are ideal gases. As it was shown above (see paragraph 6.2), for the Gibbs function of 1 mole of ideal gas in a mixture we have

$$G_i(T, p_i) = G0_i(T) + RT \ln p_i,$$

Therefore for the chemical potential we obtain

$$\mu_i = \mu0_i(T) + kT \ln p_i,$$

According to the Dalton law $p = \sum_i p_i$ and using Eq.6.5 we obtain

$$\mu_i = \mu0_i(T) + kT \ln(pc_i)$$

The equation for the equilibrium of chemical reaction can thus be written as

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[1] This is not a chemical reaction, but a way to demonstrate that all these compounds are in equilibrium.

$$\sum_i v_i(\mu 0_i(T) + kT \ln(pc_i)) = 0$$

or

$$kT \sum v_i \ln(c_i) + kT \sum v_i \ln(p) + \sum v_i\mu 0_i(T) = 0$$

or
$$\sum \ln(c_i{}^{v_i}) = -\sum v_i \ln p - \frac{1}{kT}\sum v_i\mu 0_i(T)$$

Converting the logarithmic equation to exponential one

$$\prod c_i{}^{v_i} = p^{-\sum v_i} exp\left(-\frac{1}{kT}\sum v_i\mu 0_i(T)\right) \qquad (6.10)$$

This expression is known as the law of mass action. The law was first proposed in 1864 by C. M. Guldberg and P. Waage. J. H. van 't Hoff independently came to the similar conclusions in 1877. The law is often written as

$$\prod c_i{}^{v_i} = K(T, P) \qquad (6.11),$$

where $K(T, P)$ is the equilibrium constant[2]. It is interesting to discuss three possible cases:

- $\sum v_i > 0$. In this case, the direct reaction results in an increase of the number of molecules. The law of mass action predicts that an increase of the pressure results in a decrease of the equilibrium constant and the amount of the reaction products should decrease.
- $\sum v_i < 0$. In this case, the direct reaction results in a decrease of the number of molecules. The law of mass action predicts that an increase of the pressure results in an increase of the equilibrium constant and the amount of the reaction products should increase.
- $\sum v_i = 0$. In this case, the number of molecules in the reaction does not change. The law of mass action predicts that pressure should not affect the outcome of the reaction.

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[2] In high school courses on chemistry you described chemical equilibrium with the help of so-called evenwichtconstante (Dutch). You were also told that this constant is a function of temperature and pressure. The derivation given above explains the origin of these dependencies.

7. THIRD LAW OF THERMODYNAMICS. CONCLUDING REMARKS.

Until now we have used the definition of entropy in terms of differential dS. Such a definition leaves an uncertainty about the absolute value of the entropy. In principle, it does not constitute a drawback, because in applications of thermodynamics to physical problems we practically always deal with differences in entropy. The same is also true for the internal energy U. However, when we discuss thermodynamics of chemical reactions, absolute values of the Gibbs function $G = U - TS + pV$ becomes important. Hence, it is clear that in order to fully benefit from the law of mass action, for instance, one would need to know how entropies of different chemical substances depend on temperature. Aiming to develop quantitative theory in chemistry, W. Nernst formulated the principle what is now known as the third law of thermodynamics. According to the law, the entropy of a system at absolute zero is a well-defined constant.

7.1. Third law of thermodynamics

First of all, we note that the value of entropy change ΔS for any process is finite at all temperatures. Secondly, we look at the behavior of enthalpy ($H = U + pV$) and Gibbs function ($G = U - TS + pV$) at low temperatures. It is seen that

$$H - G = ST$$

and, if S is finite,

$$\lim_{T \to 0}(H - G) = 0$$

According to the definitions of the thermodynamic potentials

$$dH = TdS + Vdp \text{ and } dG = -SdT + Vdp.$$

It also means that

$$\Delta H = T\Delta S + V\Delta p \text{ and } \Delta G = -S\Delta T + V\Delta p.$$

For an isotropic process we also have that $\lim_{T \to 0}(\Delta H - \Delta G) = 0$. Note that upon a temperature increase the entropy cannot decrease. Hence we must conclude that at absolute zero the enthalpy and the Gibbs function are not only equal but also asymptotically tangent to each other and

$$\lim_{T \to 0}\left(\frac{\partial \Delta H}{\partial T}\right)_p - \lim_{T \to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_p = 0 \tag{7.1}.$$

Again according to the definitions of the thermodynamic potentials

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{7.2}$$

L'Hôspital's rule states that for functions f and g which are differentiable on an interval I except possibly at a point c contained in I, if $\lim_{x \to c}(f(x)) = 0$, $\lim_{x \to c}(g(x)) = 0$, $g'(x) \neq 0$ for all x in I with $x \neq c$ and $\lim_{x \to c}\left(\frac{f'(x)}{g'(x)}\right)$ exsists, $\lim_{x \to c}\left(\frac{f'(x)}{g'(x)}\right) = \lim_{x \to c}\left(\frac{f(x)}{g(x)}\right)$.

Applying L'Hôspital's rule to Eq. 7.2 and afterwards using Eq.7.1 one obtains

$$\lim_{T \to 0}(\Delta S) = \lim_{T \to 0}\left(\frac{\left(\partial \Delta H / \partial T\right)_p - \left(\partial \Delta G / \partial T\right)_p}{1}\right) = 0$$

In 1906 W. Nernst stated that for any isothermal process

$$\lim_{T \to 0}(\Delta S) = 0 \qquad\qquad (7.3).$$

It means that upon approaching the absolute zero entropies of substances approach a well defined constant.

7.2. Unattainability of absolute zero

Nernst did not like the concept of entropy. Therefore in 1912 he reformulated Eq.7.3 as the law of unattainability of absolute zero. In the following we show that the statement of constant entropy at very low temperatures is equivalent to the statement of unattainability of absolute zero.

In order to see it, one has to realize first that:

1. ***The most efficient process of cooling down is adiabatic cooling down.*** Let's consider the case when the entropy of a system depends on temperature and some parameter X. To be more specific, we can talk about ideal gas as a system and volume V as the parameter. The most efficient way to perform work on a system is to do it in a reversible way (i.e. entropy does not increase). The most efficient cooling down is a reversible cooling down. In the case of ideal gas, the most efficient (i.e. reversible) way to cool the gas down is to do it via adiabatic expansion.
2. ***Upon a temperature increase entropy can only increase.*** It follows from the fact that heat capacity ($C_X = \left(\frac{\partial Q}{\partial T}\right)_X$) is positive

$$\left(\frac{\partial S}{\partial T}\right)_X = \frac{C_X}{T} > 0$$

Let's assume that third law of thermodynamics is wrong and at $T = 0\,K$ the entropy is not a well-defined constant, but a function of X. In this case, it is easy to show that absolute zero is attainable. Qualitative plots of *S(T)* for *X=X₁* and *X=X₂* in Fig. 7.1show how the cooling may work.

Fig. 12.2. Hypothetical entropy diagrams.

The system represented in (a) violates the third law and may be cooled to absolute zero in a finite number of operations. The third law is satisfied by (b) and absolute zero cannot be reached in a finite number of steps.

(a) (b)
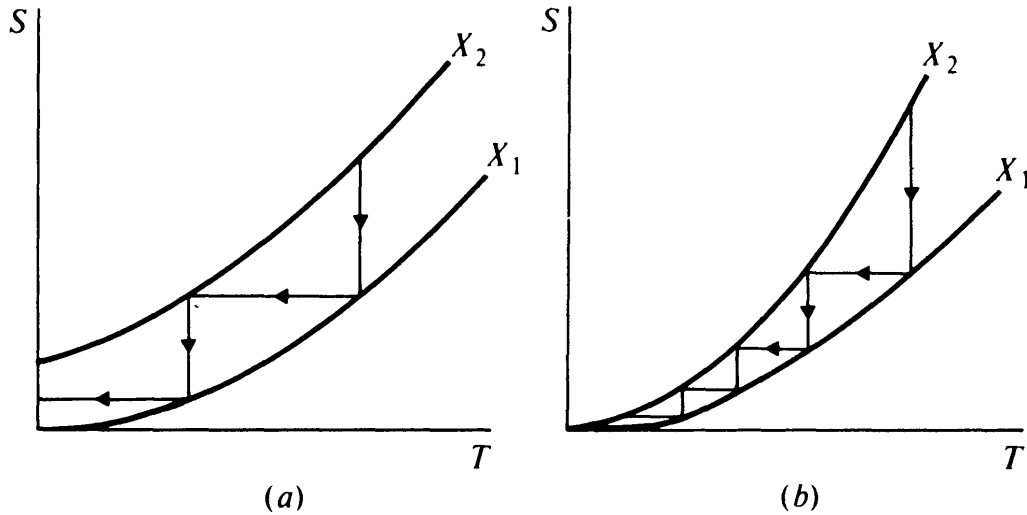
Figure.7.1. *Hypothetical entropy diagrams demonstrating unattainability of absolute zero. The figure is taken from C. J. Adkins "Equilibrium thermodynamics" Page 247).*

Alternatively, we can start the proof assuming that it is possible to achieve T=0 K. If this is performed in an adiabatic way, taking into account the properties of entropy (it increases together with temperature and does not change in an adiabatic process), it would automatically mean that the entropy at T=0 K must depend on some parameter X i.e. entropy is not a well-defined constant.

One can also try to obtain a better insight into Fig. 7.1(b) that corresponds to the case when the entropy is a well-defined constant. Consider a process in which we are attempting to decrease the temperature from T_1 to T_2 by change some parameter X from X_1 to X_2 (a horizontal line of the cooling path in Fig.7.1b). Using the second law of thermodynamics, we obtain the entropies of the initial and final states

$$S(T_1, X_1) = S(0, X_1) + \int_0^{T_1} \left(\frac{\partial S}{\partial T}\right)_{X=X_1} dT$$

$$S(T_2, X_2) = S(0, X_2) + \int_0^{T_2} \left(\frac{\partial S}{\partial T}\right)_{X=X_2} dT$$

Adiabatic cooling implies that $S(T_1, X_1) = S(T_2, X_2)$ and according to the third law of thermodynamics we have $S(0, X_1) = S(0, X_2)$. It means that

$$\int_0^{T_1} \left(\frac{\partial S}{\partial T}\right)_{X=X_1} dT = \int_0^{T_2} \left(\frac{\partial S}{\partial T}\right)_{X=X_2} dT$$

If we assume that $T_2 = 0$, it means that $T_1 = 0$. It means that there is no adiabatic path to T=0, which does not start from T=0.

Nernst has also proposed his "proof" of third law thermodynamics based on a Carnot's cycle. If we assume that absolute zero can be reached, a Carnot's cycle operating between a hot reservoir at temperature T_1 and a cold reservoir at T_2=0 K would have the efficiency 1. This would contradict the second law of thermodynamics (heat coming from the hot reservoir will be fully transformed into work). This is impossible! W. Nernst proposed this logic as a proof of third law of thermodynamics from second law of thermodynamics. This approach was criticized by A. Einstein. In fact, this is not a proof of unattainability of absolute zero, but a proof that a Carnot's cycle with a cold reservoir at T_2=0 K is impossible.

7.3 Consequences of third law of thermodynamics

7.3.1. Heat capacity

Applying L'Hôspital's rule to $S = \frac{H-G}{T}$, one obtains

$$\lim_{T \to 0}(S) = \lim_{T \to 0}\left(\frac{\left(\partial H/\partial T\right)_p - \left(\partial G/\partial T\right)_p}{1}\right)$$

According to the definitions of the thermodynamic potentials

$$dH = TdS + Vdp \text{ and } dG = -SdT + Vdp.$$

In this way, if no work is performed on the system and thus $dU = dQ$, we obtain that $\left(\partial H/\partial T\right)_p = \left(\partial U/\partial T\right)_p = C_p$, where C_p is the heat capacity of at constant pressure. It is also clear that $\left(\partial G/\partial T\right)_p = -S$. Therefore, we see that

$$\lim_{T \to 0}(S) = \lim_{T \to 0}(C_p + S).$$

The equation together with third law of thermodynamics implies that $\lim_{T \to 0}(C_p) = 0$.

Alternatively, one can simply use the definition of the heat capacity

$$C_x = \left(\frac{\partial Q}{\partial T}\right)_x \text{ or } C_x = T\left(\frac{\partial S}{\partial T}\right)_x.$$

From the latter it follows that

$$C_x = T\left(\frac{\partial S}{\partial T}\right)_x = \left(\frac{\partial S}{\partial \ln T}\right)_x$$

Upon approaching the absolute zero S is a constant and $\ln T \to -\infty$. It is seen that

$$\lim_{T \to 0}(C_x) = 0.$$

7.3.2 Response functions

Many response functions such as isobaric cubic expansivity ($\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$) and compressibility ($\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$) can be expressed in terms of derivatives of entropy. For instance, one can derive the Maxwell relation showing

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

According to third law of thermodynamics $\lim_{T \to 0}(\Delta S) = 0$. It means that $\lim_{T \to 0}\left(\frac{\partial S}{\partial p}\right)_T = 0$, $\lim_{T \to 0}\left(\frac{\partial V}{\partial T}\right)_p = 0$ and the isobaric cubic expansivity tends to zero $\lim_{T \to 0}(\beta) = 0$.

According to the reciprocity theorem $\left(\frac{\partial V}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V$. As it was shown above using third law of thermodynamics, $\lim_{T \to 0}\left(\frac{\partial V}{\partial T}\right)_p = 0$. It means that $\lim_{T \to 0}\left(\frac{\partial V}{\partial p}\right)_T = 0$ and the compressibility tends to zero $\lim_{T \to 0}(\kappa) = 0$.

Another example is the phenomenon of surface tension. In Chapter 3 we showed that

$$\left(\frac{\partial \gamma}{\partial T}\right)_A = \left(\frac{\partial S}{\partial A}\right)_T,$$

where A is surface area and γ is surface tension. According to third law of thermodynamics

$$\lim_{T \to 0}\left(\frac{\partial S}{\partial A}\right)_T = 0$$

It also means that

$$\lim_{T \to 0}\left(\frac{\partial \gamma}{\partial T}\right)_A = 0.$$

The results of these mathematical exercises with Maxwell relations were confirmed experimentally soon after formulation of third law of thermodynamics (see Fig. 7.2)

§ 5. *Discussion.*
From Fig. 2 it is seen that the line which represents the surface
tension as a function of temperature has a curvature which first appears
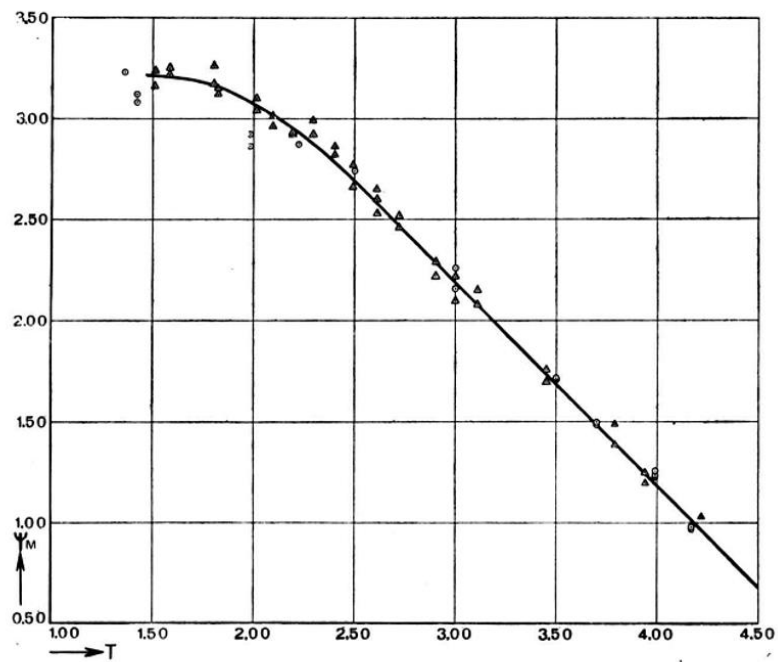at 2.4° K. Above this temperature the line appears to be quite straight.

Fig. 2.

Figure 7.2. *Scan of the original paper by H. Kamerlingh Onnes and co-authors reporting about surface tension of liquid He at low temperatures.*

7.3.3 Phase transitions

Third law of thermodynamics also predicts anomalies in the behavior phase transitions.

According to the Clausius-Clapeyron equation (see Eq.5.4) for first order phase transition one expects

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}.$$

Third law of thermodynamics predicts that for such a transition $\lim_{T\to 0} \frac{dp}{dT} = 0$.

The laws derived for temperature dependencies of physical quantities may become invalid at very low temperatures. As an example one can mention the law for temperature dependence of the magnetic moment in ferromagnet (see Chapter 3 Eq. 3.7). The law derived from first and second laws of thermodynamics fails upon approaching the absolute zero. While Eq.3.7 works very well at high temperatures confirming that $m \sim \sqrt{T_c - T}$, at low temperatures one should take into account the following Maxwell relation

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial m}{\partial T}\right)_H.$$

According to third law of thermodynamics $\lim_{T\to 0} \left(\frac{\partial S}{\partial H}\right)_T = 0$. It means that upon approaching the absolute zero, the law for temperature dependence of magnetic moment in ferromagnet, which we derived based on first and second law of thermodynamics, must fail to obey third law of thermodynamics $\lim_{T\to 0} \left(\frac{\partial m}{\partial T}\right)_H = 0$.

7.4 Concluding remarks

This lecture concludes the course. The goal of this course was to show that thermodynamics is a powerful and universal method in physics. If you feel that you still do not understand thermodynamics, I would like to encourage you not to give up and remember the quote assigned to A. Sommerfeld (professor of many Nobel laureates):

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don't understand it, but by that time you are so used to the subject, it doesn't bother you anymore...";-).