

THERMODYNAMICS. An alternative to the textbook version.

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Abstract

We present an alternative description of the basic aspects of the thermodynamic theory. The purpose is firstly to highlight the assumptions about the physical reality that one makes in the theory and secondly to describe the connection to other physical theories like (quantum) mechanics and statistical mechanics. The most essential parts of the treatment is: to consider the concept of equilibrium as an explicit fundamental part of the theory; to use the equation of state as a central theoretical concept; consider the “first law” of the conventional theory as primarily a definition of heat; to eliminate from the theory components like “quasi-static processes “ and the “zeroth law” that have their basis in operationalism. The theory is described in terms of three basic components; “fundamental concepts”, “propositions” (German “ansatz”) and “laws”

Introduction

Thermodynamics was developed during the 19th century with Carnot as the most important pioneer. The theory was improved and put into a self-contained unit by Clausius, Helmholtz and several others. Towards the end of the century important contributions were made by Gibbs, who, for example, described the important coupling between macroscopic perspective of thermodynamics and the microscopic atomistic description of matter that developed into statistical mechanics. The theory established by 1900 was based on two basic laws; the first law, which prescribes the energy to be constant and the second law that states what processes are “spontaneous”. During the early 1900s to additional laws entered the theory. The third law stated that the entropy was zero at the zero point for the temperature and the zeroth law gives a statement about the equilibria between three separate systems (If A is in equilibrium with B and B is in equilibrium with C then A and C are also in equilibrium).

The way the thermodynamic theory is built has occasionally been presented as an model for how physical theories preferably should be constructed. It is not based on quantitative equations, but rather on more general principles that can be communicated through the ordinary language. The theory appears as “simple” by this criterion. However, teachers know that it is difficult to get the theory across to the students. It is a common remark by experienced scientists that they came to “understand” thermodynamics first when they had penetrated the statistical mechanical theory. One reason why, in my opinion, it is difficult to teach thermodynamics is that the conventional textbook version of the theory contains logical flaws at the same time as it has pretensions of being formally strict.

In currently used elementary thermodynamics textbooks one usually proceeds in line with the classical formulations of the theory in terms of the first, second and usually third law. However, there is a modern discussion of the topic that contains a critique of the classical theory. This critique is typically based on two different circumstances. The most obvious is that our understanding of the microscopic, atomistic, world has changed qualitatively during the last hundred years. It then seems reasonable, if for no other reasons than didactic, to encompass this understanding also into the thermodynamic theory. The theory is based on a macroscopic perspective, but it is more often than not

applied under circumstances where we strive to obtain an understanding of the relation between macroscopic properties and the microscopic description. A second circumstance is that textbook writers, in their ambition to make thermodynamics more accessible, have avoided more fundamental difficulties. When you know the answer to a problem there is always a temptation to provide simple arguments that make the conclusion appear plausible at the cost of logical consistency.

How is thermodynamics used today?

One approach to the thermodynamic theory is to notice for what it is used. The theory has a broad scope and it provides statements of a general character. In the typical case these statements become concrete and specific first when thermodynamics is combined with results and concepts from other physical theories.

The historical root of thermodynamics can be traced back to Carnot's ambition to understand and describe heat engines in general and the steam engine in particular.

This application, somewhat generalized, is still an important aspect of the thermodynamic theory. It is today highly relevant to analyze how much "useful" energy one can maximally extract from different energy conversion processes. The understanding and description of phase equilibria has a central application in materials science. The consideration of chemical equilibria is a standard element in chemistry and molecular biology. Thermodynamics provides a fundamental tool for understanding the relation between the atomic/molecular behavior and the macroscopic properties of a system.

These examples provide an illustration of how thermodynamics play an important role in current science and technology. However, there are limited research efforts focused on thermodynamics as such. The theory is rather seen as an integrated well understood part of a larger field where statistical mechanics, quantum mechanics and other physical theories play a more central role.

Another trend during the second half of the 1900th century is that one has generalized the thermodynamic theory to also describe transport and other dynamic processes.

These efforts are often connected to the term "irreversible thermodynamics". During the 1950 and 60ties great efforts were made along this line. It turned out that are difficulties to arrive at consistent, simple and still useful results. However, it is essential to

understand thermodynamics proper in order to use the theory of irreversible processes in a fruitful way.

A modern thermodynamics?

A good physical theory should give answers to concrete questions and but it should also provide a basis for a conceptual understanding of reality. Understanding is a delicate thing. The fruitful communication of understanding relies on a delicate interplay between the communicator and the recipient. The roles of communicator and recipient should preferably alternate in the form of a dialogue in a direct personal encounter. However, in a written account like the present one, as well as in a textbook, the communication is directed from the author to the reader. The text to follow is written under the assumption that the reader has an elementary, conceptual, knowledge of thermodynamics as well as of classical, statistical and quantum mechanics. The way that thermodynamics was formulated hundred years ago appears as outdated when using the perspective these latter theories provide. It is in practice difficult to understand how thermodynamics is related to the other theories. There has been a tendency to keep thermodynamics “clean” relative to influences from the outside, but such an attitude appears as highly questionable.

The text below should be seen as an attempt to communicate an alternative view of thermodynamics. This view is based on a personal conceptual understanding. An important goal is to clarify the fundamental arguments that lead to concrete statements about reality. Such a way of reasoning is for some of us an important step towards a conceptual understanding of the theory. In the modern literature on the fundamentals of thermodynamics the emphasis is typically on the formal mathematical-logical basis of the theory. This is an important aspect. However, the present text is focused on the conceptual aspects.

Basic concepts, essential propositions and fundamental laws.

Physical theories are often presented as strict logical constructions based on a number of well-defined entities entering into strict logical/mathematical relations. Such a view contains a mix-up between ideal and reality. In science theories are there to describe and understand the complex physical reality. Conflicts necessarily arise when the exact mathematical/logical language is confronted with the complexity of reality. In practice

such conflicts are typically solved through compromises. In undergraduate teaching there are good pedagogical reasons to avoid the difficulties that are created by these compromises. However, a big danger with this approach is that students, who proceed to a research career brings with them too much of indoctrination and too little of a critical analysis of the difficulties that are always present. One important purpose with this text is to unravel some of the difficulties that might have been hidden and as far as possible provide suggestions of how these could be handled.

It is of considerable help to specify the conceptual framework when analyzing the foundations of a theory like thermodynamics. Below we will discuss the theory as being built from three basic ingredients. These are *central concepts*, *essential propositions* and *basic laws*. To do so is a subjective choice. *Central concepts* are quantities that are there to connect the theory with the observable physical reality. The concepts can be more or less useful, but they are not true or false. An *essential proposition* is a condition we put on the theory. Typically propositions are formal requirements on the theory. Some are tacit, like the one that the laws of logic and mathematics, are obeyed by all physical theories. Below we only discuss propositions that are reasonably specific for thermodynamics. Like the concepts basic propositions should not be considered true or false. The *basic laws* constitute the heart of the theory. They express relations that are not obvious and sometimes unexpected. Their value is judged by comparing empirical observations with theoretical predictions. In this sense the laws can be considered true or false. However, it is important to realize observations are influenced by theory so it is in the end a complex matter to decide whether or not a theory is compatible with certain observation. With the strategy clearly stated the next step is to explicitly describe the thermodynamic theory.

The foundations of thermodynamics

Classical mechanics predates thermodynamics by approximately two hundred years. From a current viewpoint one can say that also quantum mechanics, statistical mechanics, electromagnetism and the theory of relativity is a part of the general framework of physical theories within thermodynamics also plays a role. The purpose of thermodynamics is not to replace these theories but to provide an alternative way of describing and understanding reality. The robustness of thermodynamics can be seen from the fact that the theory survived intact during the transition from classical

mechanics to quantum mechanics/theory of relativity that occurred during the first decades of the 20th century. Thermodynamics is based on mechanics and it includes all the quantities/concepts of mechanics that can be applied to macroscopic systems. Such quantities include amounts of matter, volume, pressure, work, and energy. The usefulness of the theory is then accomplished by introducing quantities specific to thermodynamics. Typical examples are temperature, entropy, heat, and free energy. These latter are specified within the theory, while mechanical quantities are considered as known. The “system” is a central concept within thermodynamics. It refers primarily to a (macroscopic) part of reality specified by quantities known from mechanics (amounts, volume, pressure, energy). In the developed theory systems can also be partly specified using also quantities specific to thermodynamics. We now have the background to present the theory in a formalized way:

Law 1 (Equilibrium law): For a given macroscopically specified system there exists a state of equilibrium with unique values of all macroscopic quantities. All systems adopt their equilibrium state if given sufficient time. Once the equilibrium state has been reached the properties of the system remain time independent as long as the defining properties remain unchanged.

From mechanics we know that microscopically seen a system can adopt a large number of physical states. It is an essential aspect of thermodynamics that this multitude of states can be captured using only a few variables. The condition of equilibrium is the key feature that makes it possible to reduce from a multitude of microscopic states to the macroscopic description. In conventional texts on thermodynamics the existence of the equilibrium state is tacitly assumed, while in this presentation this existence is explicitly considered as a fundamental aspect of the theory. The theoretical concept of equilibrium is practically relevant first when we state that all systems reach equilibrium given sufficient time to relax. It is not possible to give a quantitative criterion for “sufficient time”. Experience have shown that for some systems this time is very short, while for others it is very long and the system remains in a non-equilibrium state over the accessible time-scale. In this latter case the properties of the system can be analyzed in terms of a conditional equilibrium. The physical reality behind this is that the system is captured in a metastable state with a very long lifetime. The material properties of

diamond are, for example, well-defined in spite of the fact that graphite is the equilibrium state under normal pressure.

Can one argue that the law¹ is instead a proposition? Is it possible for reality to behave differently? The law contains one feature that makes thermodynamics qualitatively different from the other physical theories. By stating that systems relax to an equilibrium state there is an arrow of time in thermodynamics, while equations in (quantum) mechanics are time reversible.

Proposition 1: The equilibrium condition can be formally described through an equation of state.

Assume that a system at equilibrium can be characterized by N variables $\{X_i\}$, $i=1, \dots, N$. The equation of state can be expressed in a non biased way relative to these variables in the form $f(\{X_i\})=0$. An alternative is then to choose one variable X_j as dependent so that $X_j=f_j(\{X_{i \neq j}\})$ with $N-1$ independent variables. The equation of state has a central role in many practical applications of thermodynamics. It is usually assumed that equation of state can be differentiated. However, it turns out that this does not apply to certain subspaces of the total variable space. This “anomalous” behavior is usually discussed in terms of phase equilibria.

Proposition 2: The variables in the equation of state are either extensive or intensive.

An extensive quantity, E_x , changes linearly with the size of the system so, for example,
 $E_x(\mu V, p, \mu n) = \mu E_x(V, p, n)$,

Where V is volume, p pressure and n amount. An extensive quantity has furthermore the property that the value for the total system is the sum of the values of the parts even if they are not in equilibrium with one another. An intensive quantity, I , on the other hand, is independent of the size of the system so that

$$I(\mu V, p, \mu n) = I(V, p, n).$$

The proposition 2 provides a significant limitation on the character of the variables that enter the equation of state. It is in certain applications desirable to include surface effects in the description of a bulk system. However, the surface doesn't scale linearly with system size and we have a deviation from the basic requirement. A consistent way to analyze the total system is to divide it into a bulk part and a surface part. These can

then separately be described by variables that scale in the correct way with the systems size.

Proposition 3: In an infinitesimal change between two equilibrium states the relation $TdS=dU-dw_{eq}$ applies.

Here U is the energy of the system at equilibrium and dw_{eq} is the work, for example pdV , done on the system under the condition that the system remains at equilibrium during the change. These quantities are defined in mechanics. The two quantities, T , temperature, and, S , entropy, that are introduced through the proposition 3 are specific to thermodynamics. It follows that S is extensive since U and w are extensive quantities. Consequently T must be intensive. It follows from the relation that T and S are undefined with respect to a proportionality constant so that $T' = \alpha T; S' = \frac{S}{\alpha}; T'dS' = TdS$. The relation remains intact at the addition of a constant to S , so the absolute value is unspecified. In contrast it can only be valid for a specific choice of the zero value for the temperature T . The proposition 3 highlights the close conceptual interdependence between temperature and entropy, in spite of the fact that temperature is a much more known and »understood« concept than entropy. It is important to note that we have introduced temperature and entropy under the condition that the system is in equilibrium. One can in a strict sense not assign a temperature nor a entropy to a non-equilibrium system.

Proposition 4: An isolated macroscopic system in its ground quantum state has the temperature $T=0$ and the entropy $S=0$.

One usually doesn't describe macroscopic systems in terms of its quantum states, but it is clearly conceptually possible and then a ground state exists. It is less clear that such a ground state is non-degenerate, which is implicitly assumed by giving the state $S=0$. There is, to my knowledge, no general proof of the non-degeneracy of the ground state, but it is found valid for all cases it has been tested. Note that only a degeneracy that grows with the size of the system would affect the validity of the proposition. The proposition 5 provides an absolute reference point for the entropy and the zero point of the temperature is fixed. However, the scale factor between entropy and temperature remains undetermined.

The conventional way to present the content of proposition 4 is through the introduction of the third law of thermodynamics, which originally is a contribution due to Nernst. He was active in the early parts of the 20th century and then it came as an unexpected finding that the entropy S had a value of zero for all substances at $T=0$. Later quantum mechanics was established as a microscopic theory and it became more natural to associate $T=0$ with the ground state. The result that $S=0$ at under such conditions follow from the fundamental work by Boltzmann on statistical mechanics. The proposition 5 provides an example of how thermodynamics can be adapted to progress made in other physical theories.

It is a virtue of the proposition 4 that it provides a basis for a qualitative interpretation of the concepts temperature and entropy. The temperature becomes a measure of the degree of excitation in a quantum mechanical perspective. The higher the temperature the more excited is the system. Below we will return to the question of how to compare the degree of excitation between two different systems. The entropy S can similarly be seen as a measure of the density of states, that can encompass a certain energy increase TdS in an isolated system with $w=0$. As temperature and entropy have been introduced we can now state two basic laws of thermodynamics:

Law 2 (Gibb's law) The number of variables in the equation of state is three plus the number of components.

This law describes a property of reality that is in typical textbooks introduced as self-evident without any specific comments. Even when one has established the ideal gas law, $pV=nRT$, with four variables it is far from evident that a more general description of a real gas with interactions between molecules the equation of state has the same number of variables as, for example, in the van der Waals' gas law. Law 1 provides the basis for many important applications of thermodynamics. It leads to both so called Maxwell relations, Gibb's phase rule as well as other thermodynamic relations that result in concrete predictions that can be tested against experimental observations.

Law 3 (Carnot's law) For a total system with given energy and volume, which is composed of two or more subsystems initially in internal equilibrium the entropy of the total system at final equilibrium is larger (or equal to) the sum of the entropies of the subsystems so that $S(\text{final}) \geq S(\text{initial})$.

The equality sign applies when the subsystems were in equilibrium also initially so that the final and initial states are the same. This Law 2 can be considered as one of many variations of the conventional «Second Law» of thermodynamics. It specifies a central property of the equilibrium state. In many textbooks the second law is said to state that the entropy increases in irreversible processes. One then avoids to mention the complication that the entropy is only defined for equilibrium states. This is the reason why it is more precise to formulate the law in terms of the relation between two different equilibrium states. Important applications of Law 2 are found in the description of chemical equilibria and of heat engines. The latter application led Carnot to the first version of the Law. However, to make an explicit statement about heat engines it is necessary to formulate an additional proposition.

Proposition 5: For a non-isolated system the heat, q , taken up by the system is the difference between the change in internal energy, ΔU , and the work, w , done on the system; $q = \Delta U - w$.

This relation is normally presented as the first law of thermodynamics, while in this text it is seen as basically a definition of heat. The energy concept is central to mechanics, quantum mechanics and theory of relativity. In these theories one makes use of explicit coordinate systems. If one requires that the predictions of the theories should be independent of the choice of the coordinate systems it follows that there exists an invariant scalar and this is called the energy. The constancy of the total energy is in the theories with explicit coordinate systems a consequence of a basically mathematical invariance property. There are no explicit coordinate systems in thermodynamics. To make the theory compatible with the other physical theories one has to explicitly require the total energy to be constant. This is the role of the proposition 5. The new concept of heat is, in the language of theory of science, introduced «ad hoc» to ensure agreement with other theories. The proposition 6 divides an energy change into two categories. Work is well-defined in mechanics (or in electromagnetism), while heat is a quantity specific to thermodynamics. It is possible to provide a quantum statistical mechanical illustration of the division into work and heat for small energy changes at equilibrium. In the expression $dU = \partial w + \partial q$ the work represents energy changes due to changes in the energy of the states, while ∂q is the energy change from changes in population of states at given value of the energies of the states:

$$U = \sum_i p_i^{eq} E_i; dU = \sum_i p_i^{eq} dE_i + \sum_i E_i dp_i^{eq} = \partial w + \partial q \quad (1).$$

(The symbol ∂ is used to denote a small quantity in general while d as a symbol denotes a proper differential.)

In mechanics and related theories the energy is constant in isolated systems and there is no reference to equilibrium conditions. Based on this observation it is then possible to widen the concept of heat within thermodynamics to be valid for all changes so that $\Delta E = w + q$, where E denotes the energy of the system irrespective of possible equilibrium conditions. We reserve the notation U for the energy of equilibrium states.

In teaching thermodynamics it is a challenge to reconcile the fact that real processes occur under non-equilibrium conditions while the theory is focused on equilibrium conditions. One basis for using the theory is that it is possible to identify initial and final states that are both at equilibrium. The discussion of processes is in typical text-books based on three concepts; *reversible*, *irreversible* and *quasi-static* processes. Normally these terms are described within the conceptual framework of operationalism. It is thus stated that a reversible process can proceed in either direction, an irreversible one only goes in one direction and a quasi-static can be made to reverse by a small change in external conditions. It is an ambition of the present text to reveal that operationalism creates more problems than it solves in thermodynamics. The division of these three classes of processes provides an illustration of this opinion. Here we give the following alternative interpretations of the concepts. A *reversible* process is characterized by the fact that the equation of state is satisfied throughout the change. This is a theoretical concept and it is not coupled to any specific real operation. An *irreversible* process is a real process where the properties of the system are changing in time. The irreversible process ultimately ends in an equilibrium state according to proposition 1. The quasi-static process is introduced to handle the transition between the theoretical (ideal) reversible to the real irreversible process. If one ignores the program of operationalism there is no need to specify a real operation that leads from the initial state to the final one and the concept of a quasi-static process becomes superfluous.

In thermodynamics we describe intrinsically very complex systems using only a few variables. One price paid for such a simplification is that one refrains from explicitly describe the processes that lead from one equilibrium state to another. It is solely based

on the description of equilibrium states. The area of “irreversible thermodynamics” provides an approach to enlarge the applicability of the thermodynamic concepts also to the explicit description of dynamic events. The use of the terms “reversible” versus “irreversible” poses pedagogical difficulties. They can be seen as inherited from operationalism, but it is probably difficult to implement a change of terminology. It would be more distinct to replace “irreversible process” with “real process” and “reversible process” with “process at equilibrium” stressing that this is a theoretical construction. Using such a terminology one avoids the (now irrelevant) question whether or not an irreversible process can be made to reverse. This question has usually not a simple answer.

Some basic results.

Above we have presented an abstract theory by introducing a number of concepts, stated five propositions and three laws. To connect to reality we have to relate empirical observation to variables in the theory. This is in general a profound epistemological problem, but here we take the approach to consider this problem solved for mechanics and other physical theories based on a similar framework. To relate the thermodynamic theory to reality we simply adopt the observation criteria from these other theories. This places us in the position to apply the thermodynamic theory to a concrete description of reality.

1.Heat transfer

Consider an isolated system consisting of two parts. These are initially isolated from each other and they are in internal equilibrium with temperatures T_1 and T_2 , respectively. What happens when the two parts are brought in contact so that a transfer of energy in the form of heat can occur, but there is no work involved and no change in volume in the process. We have

$$U_1 + U_2 = U_{tot} = constant$$

since the total system is isolated. Thus the energy change ΔU_1 in one part of the total system has to be balanced by the energy change ΔU_2 in the other part and $\Delta U_1 = -\Delta U_2$.

From proposition 5 we have that the heat transferred between the two subsystems match so that $q_1 = -q_2$. The question we now ask what determines the sign of the heat q or energy ΔU transferred between the subsystems. Consider first the onset of the process

where the heat ∂q is so small that there is a negligible temperature change in the respective subsystems. Since no work is involved in the process it follows from propositions 3 and 5 that the entropy change is

$$dS_i = \partial q_i / T_i$$

The entropy is an extensive quantity so that the change in total entropy is

$$dS_{\text{tot}} = dS_1 + dS_2 = \partial q_1 / T_1 + \partial q_2 / T_2 = \partial q_1 (1/T_1 - 1/T_2)$$

According to Carnot's law $dS_{\text{tot}} \geq 0$. The equality is satisfied when $T_1 = T_2$ but for $T_1 < T_2$ it follows that $\partial q_1 > 0$ while when $T_1 > T_2$ we have $\partial q_1 < 0$. Thus we conclude that heat goes from a system of higher temperature to one of lower, as observed.

So far we have focused on what is valid initially. How should we describe the complete process that leads to full equilibrium within the system? It is necessary to account for the fact that the temperature changes during the equilibration process. In a real system there will be temperature gradients within the subsystems during the process. As was stressed above thermodynamics doesn't deal explicitly with such dynamic effects.

Instead the change from the initial state to the final one is treated for a path where the equation of state is always satisfied. For the specific example there is no work involved and material variables are also assumed constant. Then the energy is only dependent on the temperature and one can write an equation of state as

$$U_i(T) = U_i(T_0) + \int_{T_0}^T C_V^i dT$$

Here C_V is the heat capacity at constant volume. The condition $q_1 = -q_2$ then gives a criterion for the final, common, temperature T_f

$$\int_{T_1}^{T_f} C_V^1 dT = - \int_{T_2}^{T_f} C_V^2 dT$$

Since $w_{\text{eq}} = 0$ we have $dS = dU/T = (C_V/T)dT$. The entropy change is then obtained by integration along a path defined by the equation of state for the two subsystems separately so that

$$\Delta S_i = S_i(T_f) - S_i(T_i) = \int_{T_i}^{T_f} (C_V^i/T) dT$$

$$\Delta S_{\text{tot}} = \Delta S_1 + \Delta S_2$$

For the initially colder system one can obtain lower limit of the entropy change by replacing T with the final temperature T_f in the integral. A similar replacement for the initially warmer system gives, using the energy balance, the same estimate as the lower

limit for the negative entropy change. Whence $\Delta S_{\text{tot}} \geq 0$ for the change, with equality only valid for the case $T_1 = T_2$. Note that all changes in the system are described taking the equation of state to be valid. In more concrete terms this implies that at each stage heat is transferred to system 1 under the condition that the system 1 has the equilibrium temperature corresponding to the amount of heat already transferred to the system. This is a theoretical construction that isn't experimentally realizable. Often textbooks in this case instead introduce the concept of a quasi-static process in an attempt to visualize a process that can be realized experimentally. There are two pedagogical disadvantages with such an argument. The first is that one introduces an unnecessary concept. The second, more severe, is that one gives the impression that thermodynamics can be applied to real dynamical changes in a system, rather than only the equilibrium state.

This example shows that it is a prediction based on Carnot's Law that at thermal contact heat is transferred from a body of higher to one of lower temperature. How should we understand this when we start from a quantum mechanical description of matter? We have two subsystems at energies E_1 and E_2 . Assume that at thermal contact there is only a weak interaction between the subsystems so that energy can be transferred but that the properties remain unchanged in all other respects. There are three possibilities; energy can go from system 1 to 2, energy goes from 2 to 1 or there is no transfer of energy. The transition probability from microscopic states i to j is the same as from j to i , which is called microscopic reversibility. The quantum theory doesn't provide a simple answer to the question on the direction of energy transfer. There is, in fact, a profound problem in reconciling the time reversibility of (quantum) mechanics with the time irreversibility implied in thermodynamics. The result that energy exchanged between subsystems resulting in the increase of the total entropy can possibly be described, using concepts of quantum mechanics, as energy goes from systems of higher degree of excitation to ones of lower. Strictly speaking such a statement is basically an explanation of the concept "degree of excitation". One illustration of the concept is obtained by considering that the two subsystems are microscopically the same except for the fact that one is twice as large as the other. If the latter also have twice as large an energy as the former it is natural to conclude that they have the same degree of excitation. There is then no net energy transfer between the subsystems and they in the language of

thermodynamics have the same temperature. The larger system not only has twice as large energy as the smaller, but it also has twice as large density of states.

In certain presentations of thermodynamics, where one has the ambition to be more rigorous, one introduces as zeroth law. The statement is typically that if subsystems A and B are in equilibrium and this is also true for subsystems B and C the law states that A and C are also in equilibrium. Note that if one in the example above on heat transfer introduces a third subsystem the statement of the zeroth law actually follows from Carnot's Law. The reason for introducing the zeroth law is found in the measurability criterion required in operationalism, since the temperature concept obtains a meaning first in relation to specified measuring process. When one, as in the present text discard "operationalism" and its definitions through measuring processes, there is no longer a reason to introduce the zeroth law.

2 Isothermal expansion/compression of an ideal gas

The equation of state for an ideal gas is $pV=nRT$. One can show that this also implies that the energy U is only dependent on T so that $U(T,V)=U(T,p)=U(T)$.

Thus the energy U is unchanged in an isothermal change. However, there is in general a heat transfer between system and surrounding to compensate the work done on the system. Combining proposition 3 and the equation of state we have

$$dS=(p/T)dV=nR\ln V$$

For a change between initial state i and final state f the entropy change is

$$\Delta S=S_f-S_i=n\ln(V_f/V_i).$$

It is less straightforward to determine the amount of heat transferred to the system.

There is no unique answer since there is a dependence on how the process is actually done. In one limit the external pressure has throughout matched the pressure of the system, which corresponds to a reversible process. Then

$$w = w_{rev} = - \int_{V_i}^{V_f} p dV = -nRT \int_{V_i}^{V_f} d\ln V = -nRT \ln(V_f/V_i)$$

From mechanics we know that to have a compression, $dV<0$, the external pressure p_{ext} needs to be larger than the pressure of the system and conversely $dV>0$ when $p_{ext}<p$.

Thus for an expansion the work has a negative sign and the work performed by the system is less negative for a real process such that $w>w_{rev}$

This implies that for an isothermal expansion $q\leq T\Delta S$,

where the equality sign is for reversible process. For an expansion the work has a positive sign but the inequalities remain the same. For a real gas the equation of state is more complex, but the inequalities remain valid. This also goes for other types of work. The important conclusion is that to maximize (expansion) or minimize (compression) the work and the corresponding transfer of heat it is desirable to have the real process occur as close as possible to the equilibrium path.

3 Adiabatic expansion of an ideal gas

In an adiabatic process there is no heat exchange with the surrounding. The initial and final states differ in volume, pressure and temperature. Since $q=0$ it follows that $\Delta U=w$. Even when we know V, T and p for the initial and V for the final state the work performed is unspecified and thus ΔU . It follows that also T and p are unknown. In one limit the change follows the path given by the equation of state

$$-pdV=C_VdT ; dV/V=-(C_V/nR)(dT)/T$$

$$w = w_{rev} = - \int_{V_i}^{V_f} p dV = C_V(T_f - T_i) ; \ln(V_f/V_i) = -(C_V/nR)\ln(T_f/T_i)$$

In an expansion the temperature of the system decreases. When in reality the expansion occurs relative to a pressure that is lower than the equilibrium pressure of the work performed by the system is smaller and final temperature is higher. This is in qualitative analogy with the relation valid for isothermal processes. In the extreme limit of zero external pressure no work is performed and there is no change in temperature for an ideal gas.

One can construct a cycle for the system based on two isothermal and two adiabatic processes. This is the so called Carnot cycle and the expressions above can be used to calculate the total work, the total amount of heat transferred at given values of the temperatures of the thermal baths for the two isothermal processes. Such an analysis provides the basis for applying thermodynamics to the performance of heat engines.

4 Chemical isomerization equilibrium

The description of chemical equilibria is an important application of thermodynamics.

Let us consider the simple example of an isomerization process $A \leftrightarrow B$ in the gas phase. Assume also that the components can be described as ideal gases so that Dalton's law applies. For an isolated system the differential of the entropy is (proposition 3)

$$dS = \frac{dU}{T} - pdV = C(T) \ln T - nR \ln(p)$$

where $C(T)$ is the heat capacity. In the second equality we have used the ideal gas law and its consequence that U is only a function of T . The two terms on the right hand side are independent and they can thus be integrated separately to yield an expression for the entropy

$$S(T, p)_{ideal\ gas} = \int_0^T C d \ln(T) - nR \ln(p) + constant$$

$$= n \left\{ \int_0^T C^M d \ln(T) + R \ln(p) + constant \right\} = nS^M(T, p)$$

Here the expression between curly brackets is the entropy per mole of the substance S^M . When this expression is applied to a mixture of ideal gases there is a hidden subtlety. There is a question of what pressure to use. According to Dalton's law the total pressure p is the sum of the partial pressures p_i and $p = p_A + p_B$. The entropy of the total system of A and B mixed is

$$S_{tot} = n_A S^M_A + n_B S^M_B$$

provided one uses the partial pressure for S^M_i . However if we consider A and B to be identical such a choice is improper ($\ln p \neq \ln p_A + \ln p_B$). This is called Gibb's paradox and the problem will be discussed further in example 6.

According to Carnot's law the entropy has a maximum with respect to variations in the amount of A and B. For an isomerization reaction $dn_B = -dn_A$ so that

$$0 = \frac{dS_{tot}}{dn_A} = \frac{\partial S_{tot}}{\partial n_A} + \frac{\partial S_{tot}}{\partial n_B} \frac{dn_B}{dn_A} + \frac{\partial S_{tot}}{\partial p_A} \frac{dp_A}{dn_A} + \frac{\partial S_{tot}}{\partial p_B} \frac{dp_B}{dn_A} + \frac{\partial S_{tot}}{\partial T} \frac{dT}{dn_A}$$

Now we make the further simplifying assumption that the two isomers have the same ground state energy and also the same molar heat capacity. In such a case there are no energy changes involved in the isomerization and the temperature of the system is independent of the degree of transformation between A and B. Thus the fifth term on the right hand side is zero. An explicit evaluation reveals that the third and the fourth term cancel and the resulting equilibrium condition is that

$$S^M_A - S^M_B = 0$$

Which in turn implies

$$p_A = p_B$$

so that the two forms occur in equal amounts at equilibrium as intuitively expected.

For the more realistic case when both heat capacities and ground state energies differ between the two isomers the fifth term in the equation becomes important. It is also clear that the final equilibrium state depends on the initial values of T and n_A . To simplify the discussion we ask the question; given the final value of T what is the equilibrium value of n_A ? At equilibrium the differential dS_{tot} should be zero, which implies that

$$S_A^M - S_B^M + \frac{\partial S_{tot}}{\partial T} \frac{dT}{dn_A} = 0.$$

For an isolated system $dU=0$ so that energy changes in the isomerization result in temperature changes. Thus

$$n_A C_A^M dT + n_B C_B^M dT + U_A^M(T) dn_A + U_B^M dn_B = 0$$

so that

$$\frac{dT}{dn_A} = \frac{U_A^M - U_B^M}{(n_A C_A^M + n_B C_B^M)}$$

In addition

$$\frac{\partial S_{tot}}{\partial T} = \frac{1}{T} (n_A C_A^M + n_B C_B^M) \text{ and}$$

$$S_A^M - S_B^M = \int_0^T (C_A^M - C_B^M) d \ln(T) - nR \ln(p_A/p_B)$$

This leads to the final expression for equilibrium

$$\frac{p_A}{p_B} = \exp \left\{ -\frac{U_A^M - U_B^M}{RT} + \frac{1}{R} \int_0^T (C_A^M - C_B^M) d \ln T \right\} \stackrel{\text{def}}{=} K_V$$

For the case when the heat capacities of the two isomers are the same the equilibrium constant is solely determined by the ground state energy difference between the isomers. In the more general case there is also an entropy factor contributing to K_V . It is important to realize that this expression for the chemical equilibrium relies on the use of Dalton's law.

5 Enthalpy and free energy

In the previous section we arrived at an explicit expression for an equilibrium constant K_V . At this stage it is convenient to introduce three more thermodynamic quantities.

These are the enthalpy H, Helmholtz' free energy A, and Gibbs' free energy G. It follows from proposition 3 that

$$dU = TdS - pdV$$

for the case where one only has pressure-volume work. Introducing the definitions $H=U+pV$; $A=U-TS$; $G=H-TS$ one has the relations

$$dH=TdS+Vdp$$

$$dA=-SdT-pdV$$

$$dG=-SdT+VdP$$

In connection with the discussion of the requirement 6 it was pointed out that the energy has a value also for non-equilibrium conditions. The definitions of H,A and G contain the variables p,T and S , which only have values at equilibrium, which implies that H,A and G are only defined at equilibrium. The usefulness of these generalized energies can be illustrated by considering a total isolated system at constant volume consisting of a small part of direct interest, at constant volume, in thermal contact with a large system acting as a thermal bath. There is only heat exchange between the two subsystems so that the entropy change of the bath dS_B can be written as

$$dS_B=dU_B/T=-dU_S/T$$

and we have,

$$dS_{tot}=dS_S+dS_B=dS_S-dU_S/T$$

since the temperature of the system is constant

$$TdS_{tot}=TdS_S-dU_S=-dA_S$$

so that the criterion for equilibrium can be formulated in terms of variables for the system only. At constant temperature and volume

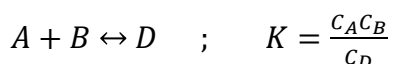
$$\frac{dS_{tot}}{d\alpha} = 0 \text{ (maximum)} \rightarrow \frac{dA_S}{d\alpha} = 0 \text{ (minimum)}$$

Thus Helmholtz' free energy has a minimum for isothermal processes at constant volume. We can now rephrase the result for the chemical equilibrium constant K_V as $\ln(K_V)=-\Delta A_{AB}(T,V)$.

A similar argument gives that for a process at given temperature and pressure it is the Gibbs' free energy that has a minimum.

6 Chemical equilibrium in general

In the previous example we have in some detail discussed chemical equilibria in the gas phase. Even though this is a relevant case the majority of applications concern chemical equilibria in solution. In the simplest form one writes for a reaction like



where C_i denotes a concentration measured as moles per volume or equally well as mole fraction. This form of the equilibrium condition was originally derived by Guldberg and Waage on the basis of an intuitive kinetic argument. Such an argument is easier to accept for a reaction in the gas phase, but it is not generally valid. In the late nineteenth century van't Hoff realized that for solutes in a dilute solution the concentration dependence of the chemical potential, $\mu = \frac{\partial G}{\partial n}$, can be approximately described as $\ln(C_i)$. This relation can be seen as an approximate equation of state based on empirical considerations. To arrive at a theoretically more satisfactory argument it is necessary to go beyond the thermodynamic theory and use an argument from statistical mechanics. Boltzmann's expression for the entropy $S = k \ln(\text{number of possibilities})$ one finds that the entropy of mixing objects A and B is $S = -\{n_A \ln(X_A) + n_B \ln(X_B)\}$ for the case when the probability for occupying a certain position is equal for A and B. This is called ideal mixing. For the case in example 5 such ideal mixing conditions are ensured by Dalton's law. In solution there is typically a non-random mixing due to selective intermolecular interactions. However, these have lesser effects the higher the degree of dilution so the ideal mixing expression can be used as an equation of state for sufficiently highly dilute systems. In this limit one obtains the Guldberg-Waage expression for the equilibrium in solution also. The conventional way to correct for the interactions manifested at higher concentrations is to introduce "activity coefficients" in the expression for the equilibrium.

7 Phase transitions

It is an empirical observation that systems can show abrupt changes in their properties even at very small changes in the surrounding. This implies that the corresponding equations of state contain discontinuities or divergences. The phenomenon is called a phase transition and it is not predicted by the thermodynamic theory. The basic assumption that the equation of state is continuous and differentiable has to be modified. It is not valid for a part of the region of definition. However, assuming the existence of phase transitions leads to a very useful relation called the "Gibbs' phase rule".

For an equation of state with N variables we can choose $N-1$ as independent. At least one of these has to be extensive. Choose such a representation with one extensive, v_e , and $N-2$ intensive independent variables. Then the equation of state can be written as

$$Y = v_e^k f_Y(\{v_i\})$$

Here $k=1$ if Y is extensive and $k=0$ if it is intensive. There are $N-2$ independent intensive variables v_i so the function f_Y is defined on a $N-2$ dimensional space. In thermodynamics one uses the terminology that there are $f=N-2$ degrees of freedom. The number of degrees of freedom can be reduced by imposing additional constraints on the intensive variables. One such condition is that there is coexistence between two or more phases. For two coexisting phases the variables in the equation of state are confined to a surface of dimensionality $N-3$. Then the number of degrees of freedom is reduced to $f=N-3$. If $f \geq 1$ one can have two coexisting phases and $f=N-4$. This can continue until one reaches $f=0$. Combining Gibbs' law with the constraints implied by phase coexistence results in Gibbs' phase rule

$$f = 2 + c - p$$

where c is the number of components and p the number of phases. For a one component system, $c=1$, the maximum number of three phases that can coexist at equilibrium. Zero degrees of freedom implies a point in the variable space and the conditions of three phases at equilibrium is called a triple point. For water, the vapor, the liquid and the solid ice coexist at equilibrium at $T=273.16^\circ\text{K}$ and $p=610\text{Pa}$. It is a very clear prediction of the theory that for a pure substance like water three phases can coexist only at a specific combination of temperature and pressure. This is far from intuitively obvious and it demonstrates a strong point of the theory. The Gibbs' phase rule emerges clearly from Law 1 (Gibbs' law) in the formulation of the theory presented above. If one instead tries to derive the result from a conventional thermodynamic theory containing the zeroth, the first, the second and the third laws it is difficult to see how Gibbs' phase rule could emerge in a logical way.

8 Concluding remarks

The presentation above of the thermodynamic theory has two parts. In the first half the formal theory was laid down and the ambition was to be logically consistent and present all essential ingredients. Whether or not this ambition is met by the text is open to debate. In the second half seven examples were given that strive to illustrate the relation between the abstract theory and some basic applications of the theory to problems of practical interest. Once this level has been reached textbooks on thermodynamics are typically using the tools in a consistent way.

The way the theory is presented above has clear similarities with the way Callen describes thermodynamics in his book. The essential features of the formulation of the theory made above are:

The epistemological point of view is clearly declared.

Thermodynamics is explicitly related to other physical theories.

It is made very clear that the thermodynamic theory is describing (conditional) equilibrium states.

The concept of an equation of state is given a more central role than is customarily done.

The number of variables in an equation of state is seen as emerging from a fundamental property of reality.

“The first law of thermodynamics” is primarily seen as a way to introduce the concept of heat in an *ad hoc* way to achieve agreement with other physical theories based on the explicit use of coordinate systems.

“The third law” is introduced as a result from quantum mechanics and statistical mechanics.

Several features in text-book presentations of the theory result from the use of “operationalism” as a basis for formulating thermodynamics. “Operationalism” is in general untenable and the programme has little value for understanding thermodynamics and it should be abandoned. Thus the “zeroth law” is superfluous and so is the concept of a quasistatic processes.

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