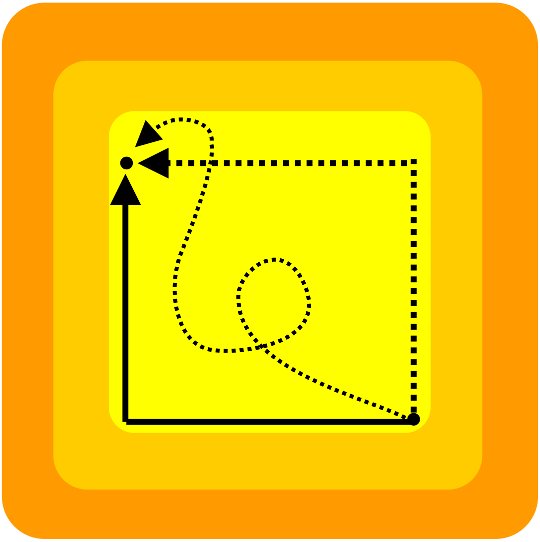
Georg Job

A New Concept of Thermodynamics

Entropy as Heat



Eduard-Job-Foundation for Thermal and Chemical Dynamics

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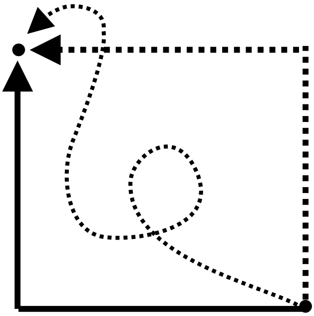

Eduard-Job-Foundation for Thermal and Chemical Dynamics

English Translation of

G. Job: “Neudarstellung der Wärmelehre”,

Akademische Verlagsgesellschaft
Frankfurt am Main, 1972

Translated by
Harry Schmeichel, Timm Lankau, Hans Fuchs, Joel Rosenberg
Hamburg, July 2007

Preface

The presented book originated from a series of lectures presented during the 1970 summer semester in Hamburg with the title "Trial of a New Concept of Thermodynamics". The impetus for this series was a talk, which I gave in 1967, in the context of a seminar about physical metallurgy at the Institute of Physical Chemistry. My task was to give a short, two-hour overview of thermodynamics and the thermal properties of substances. Because of the shortness of time it was not possible to do it in a traditional way, starting with temperature and heat, continuing with the main laws of thermodynamics, thermodynamic potentials, etc., and make it comprehensible for younger students on the one hand, and also interesting enough for my colleagues in the Institute. As a way out, it was not far-fetched to try as directly as possible to reach the most important core of thermodynamic concepts, and grab the devil by its horns, starting with a wanted poster of entropy. Surprisingly, it was shown that it is possible to build the complete theory easily and logically, without recourse to the results of the conventional theory. The resonance of the talk with the audience encouraged me to complete my approach, removing unnecessary additives and improving the foundation, and developing a mathematical apparatus, which fits to the new requirements. This consideration formed the basis of the lecture series mentioned above.

Here I want to thank Mr. *F. Bruhn*, *M. Bühring*, *M. Deneke*, *J. Heesemann* and *W. Stränz* who offered to rewrite my incomplete notes in a readable form. They have contributed to the quicker publication of the book; without their help I would barely have found the time for it. I must also not forget Mr. *M. Melcher*, who prepared many of the experiments in the lecture series, and my sister-in-law Mrs. *Gd. Job*, who with patience and accuracy did the typing. By Christmas 1970 the first draft was completed, then after a thorough revision in 1971, the book was produced first as a lecture script by the chemistry student association in Hamburg. In order to facilitate the transition to conventional textbook form, the usual terms and mathematical procedures were added, along with additional sections, to produce the version presented here.

Hamburg, May 1972 Georg Job

Preface to the English Edition

An English version of the German edition was planned long before, but I never found the time to start with this work. It was my brother, *Eduard Job*, who got the whole work going. It was his idea, to make this approach accessible for a broader readership. A strong motive was the possibility to protect others from the numerous severe obstacles he had met during his studies of this subject in Hamburg and Chicago.

I have to mention *Harry Schmeichel (California)*, *Timm Lankau (Taiwan)*, *Hans Fuchs (Switzerland)* and *Joel Rosenberg (Massachusetts)*. They helped to translate, proofread, correct and modify the given text, in order to express the basic ideas in a better comprehensible form. Since the new approach requires a number of new technical terms for which no standard translation exists it was rather hard to do this work.

Now the IUAPC Conference 2007 in Turin is a good reason for me to prepare at least a provisional version. I want to apologize for eventually incompleteness due to the short time for preparation. I am thankful for any suggestion for improvement. Criticism of the readers are quite welcome.°)

Hamburg, July 2007 Georg Job

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CONTENTS

1. INTRODUCTION

Thermodynamics is generally considered a difficult and abstract subject, particularly by beginners. Its development appears arbitrary and unrelated to such topics, as mechanics and electricity and its concepts are not easily clarified by making use of analogies to other areas of physics. If we attempt to apply intuition based on everyday experience, our understanding of thermodynamics becomes even more obscure. In thermodynamics, the variety of abstract concepts such as entropy, enthalpy, state function, cycles, free energy, reversibility, latent heat, etc. make it hard for the student to attain a comprehensive overview of the subject.

For example, the concept of "heat" already shows a noticeable contradiction between theory and intuition. Whereas in everyday experience heat is considered to be something that may be produced in an oven, contained in a heated room and escapes along with air through an open window, in physics heat is *not* something that is produced in an oven, contained in a room or escapes through an open window. In theoretical physics heat refers strictly to the energy that is transferred to a body through random molecular motion or radiation rather than as something that is contained or created within matter. In physics, heat, similar to work, represents a form of energy that is *transferred* from one body to another and is not *an inherent property* of a body.[1] Expressed mathematically, the quantity of heat Q, just like work, is not a function of state and its differential dQ is therefore incomplete. This conflict between theory and intuition is particularly evident when even scientifically educated people do not clearly understand the relationships. For example, many people insist that a body not only accepts heat but also possesses it. Such an opinion may be intuitively correct but is incorrect from a theoretical standpoint except under some very special conditions.

We successfully deal with our environment using a concept of heat that differs from the one taught in physics. Even years of high school and university teaching have not changed this. Nevertheless, it was deemed worthwhile, even if only as an academic exercise, to try to construct a theory based on the intuitive

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[1] Even this description of heat is not uniform in different physics textbooks!

concepts of heat. This attempt turned out to be successful and the familiar theory of thermodynamics has been developed from a completely different starting point. The resulting educational framework is built on a new foundation, conceptually rearranged and stripped of all unnecessary mathematical terms.

This new approach has the advantage of mathematical rigor, consistency of concepts and compatibility with intuitive understanding. On the other hand, deviation from common ways of thinking developed over more than a century is a definite disadvantage. One can ameliorate resistance to this new interpretation of heat by avoiding the ambiguous word heat altogether. Although we cannot avoid its use in earlier chapters, later, for clarity, reference to the word heat is omitted despite certain statements becoming less intuitive as a result.

2. PURE THERMODYNAMICS

This chapter is addressed to thermodynamics in the narrow sense of heat phenomena. It describes measuring methods of the amount of heat, the flow and generation of heat, energy turnover during heat transfer and clarifies basic concepts such as temperature, heat capacity and heat engines. Later chapters cover the laws describing the relationship between thermal and other physical phenomena such as thermal expansion, adiabatic cooling, heat of transition and thermoelectricity.

2.1. Heat

In physics, natural laws are usually presented as mathematical relationships between observed quantities defined by rules for their direct measurement or by an instruction for an indirect calculation from other measurable quantities. In order to make these definitions sensible, we first need a qualitative overview of the subject. Our objective is to choose a measurement process, which preserves those properties familiar to us through everyday experience or common use of language, assuming, of course, that nature allows us to do this successfully.

2.1.1. The Intuitive Interpretation of Heat

What are the everyday perceptions about heat? One can observe different conceptual levels, which may be characterized roughly as follows:

1st Level: Heat, like cold, is a property of a body. It can be caused by friction or fire. When the cause stops, the heated state gradually fades away. A hot body cools down slowly by itself whereas a cold body warms up slowly by itself.

2nd Level: Heat and cold exist in bodies in different amounts. The more heat contained in a body, the warmer it appears. In order to heat a large body, more heat is required than for a small one. When a body cools down, heat is not destroyed but flows into its surroundings. For example, by placing a hot pot in cold water, the surrounding water becomes warm. Heat and cold can be generated, e.g., heat is produced by an electric hotplate and cold is produced by a refrigerator.

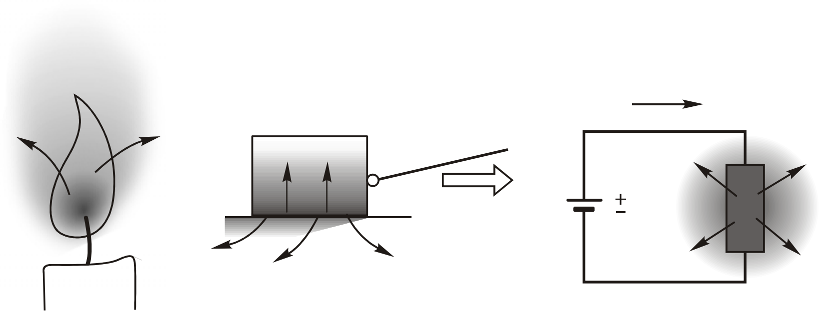
3rd Level: A body feels hot because it contains heat. Cold reflects an absence of heat. Rather than cold being produced in a refrigerator, heat is extracted and passed to the outside environment. The extracted heat is not destroyed but spreads throughout the room, just as ripples on a lake after a stone is thrown or as sound waves within a room.

At Level 1 heat is only perceived as a kind of intensity, as *hotness* to be more precise. Level 2 introduces the concept of an *amount* of heat. On a first impression, both heat and cold can be produced but not destroyed. At Level 3 this view is simplified by treating *cold as the absence of heat* while preserving the remaining content of Level 2.

Let us pursue these ideas further and consider the last and most advanced conceptual level. In summary, heat exists in every body in a greater or lesser amount it can be transferred to or extracted from a body, but the total amount of heat can be increased but never decreased. In order to complete this picture, we shall interpret the results of a few simple additional observations.

a) Heat production:

Figure 2.1 shows examples of processes in which heat appears to be generated. From experience we know that heat is only produced by consumption of an equivalent, "consuming a certain amount of fuel (fire) , force (friction) , electricity (electric heating), etc.", as we used to say in everyday language.



by combustion by friction by electric current

Fig.2.1: Heat production

b) Heat distribution:

The added heat distributes itself more or less uniformly throughout a homogeneous body (Fig. 2.2) such that the inner and outer parts of the body become equally warm. In contrast, an electrically charged conductor carries its charge only on its outer surface, the interior parts possessing no electric charge.

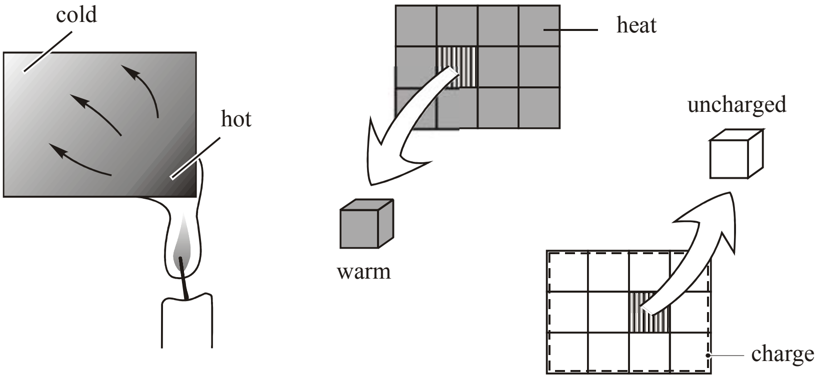


Fig. 2.2: Distribution of heat compared with that of electric charge

c) Heat transfer:

Heat flows from a hot to a cold body until both become equally warm (Fig. 2.3). Some substances conduct heat well (metals) and some poorly (foamed materials). Good conductors are used for heat transfer and poor ones for insulation.

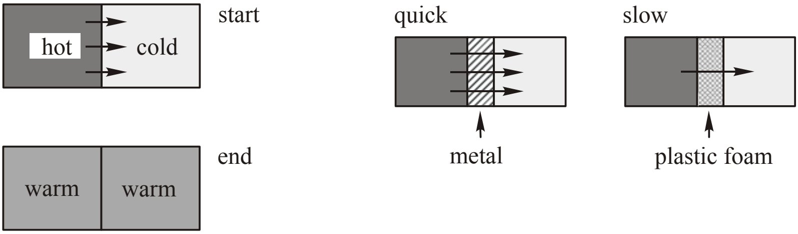


Fig. 2.3: Heat transfer from hot to cold

d) Weight of heat:

As a hot body cools down, it does not become noticeably lighter (Fig 2.4). For that reason we consider heat to be weightless. We do not want to discuss the nature of heat; we only try to characterize it through its properties.

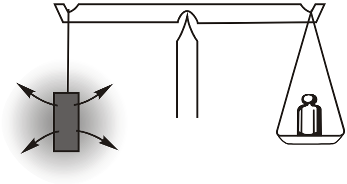


Fig. 2.4: Equilibrium untouched by cooling (or heating) of a body

e) Expansion and heat exchange:

The hotness of a rubber band depends on its extension. When it is extended the rubber band warms up, even though no additional heat is added, and heat flows out to the surroundings so that it cools down slowly (Fig 2.5). When the rubber band is released it becomes cooler, even though no additional heat is removed, and now heat slowly returns from the surroundings. The rubber band ends up no hotter or colder than its environment.

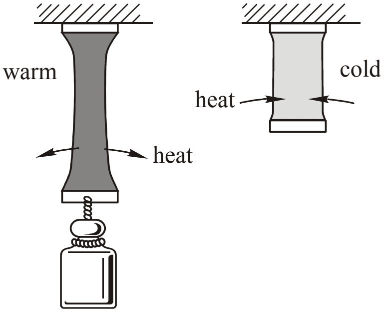
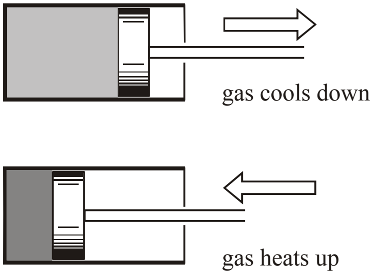


Fig. 2.5: Elongation of a rubber band

We find similar behavior when we compress or expand a gas. The hotness of a gas drops when the pressure is reduced and rises when the pressure is increased (Fig 2.6) . This can be seen when the gas is trapped in a cylinder, and moving a piston can easily change the pressure. When the cylinder is not "heat-tight", it means that heat can enter or leave the gas through the walls. Then just like in the rubber band experiment, the hotness of the gas will increase and decrease, but will end up no hotter or colder than its surroundings.



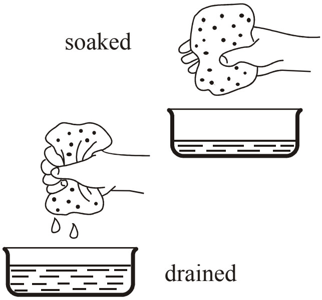


Fig. 2.6: Gas in a cylinder

Fig. 2.7: The sponge model

Solid and liquid bodies behave in a similar manner to gases, but the observed effects are less pronounced. The analogy with a sponge (Fig. 2.7) demonstrates visually how to understand the "absorption" or "expulsion" of heat in the gas or any other body. We will examine this behavior more closely later.

f) Side effects of heat:

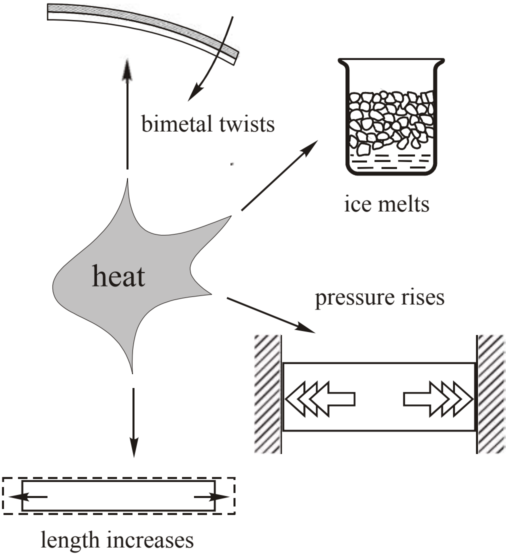


Fig. 2.8: Heat causes different side effects

> The most important effect of supplying heat to a body is that it gets hotter. However, numerous other side effects may be observed (Fig 2.8). For example, a metal rod expands, a bimetallic strip bends, iron loses magnetism, the voltage of a battery changes, ice melts and water evaporates. Note that the melting ice and the boiling water do not become warmer but the amounts of liquid water and steam increase, respectively. In these transformations, the main effect of heat, an increase in hotness, does not occur. When heat is removed, the effects disappear: the metal rod contracts, the bimetallic strip straightens, iron becomes magnetic again, water freezes, etc.

By now some readers will have noticed that what we call heat is fundamentally different from the interpretation of heat in traditional thermodynamics, where the word "heat" denotes a specific form of energy. By contrast, our description of heat is analogous to that of electric charge, mass or volume. The term "thermal charge", for example, is meaningful in our context. In order to avoid confusion with traditional physics, we will denote the word "heat" and its combinations with an asterisk (*) when the new interpretation is used, and with a dot (•) when the traditional interpretation is used.

2.1.2. Measure of Heat*

So far we have considered the properties and effects of heat* in a purely qualitative manner. Based on these observations, in order to develop a theory which can be experimentally tested, we need to define a measure for the amount of heat* and of the magnitude of its effects, for example a measure of hotness. Before defining such measures, we make some preliminary considerations.

The primary consequence of the assumed indestructibility of heat* is that a heat-producing process can never be rolled back like a film. Reversing the process would destroy the heat* produced which violates our indestructibility assumption. Thus, a reversible process in which all steps can be reversed does not produce heat*. In order to avoid an uncontrollable increase in heat*, we stipulate that a reversible process must be used for our measurement process. Although this makes the measurement more difficult, we have no alternative.

Which processes are reversible? Those described in paragraphs a) through c) above are definitely not reversible. Nobody has yet observed a burning candle to restore itself to its original length by recapturing the heat and gases from its environment. Nor does heat* naturally concentrate in one place or flow from a cold to a warm body. In general, reversibility cannot be expected in a spontaneous process because it should then flow freely in either direction.

By contrast, the processes described in paragraphs e) and f) above could be reversed under ideal conditions. For example, a well-insulated rubber band extended in a number of steps would warm up in a stepwise manner and then cool down to its original state when these steps are reversed. Even the exchange of heat* with its surroundings is exactly reversible in principle. If the tension is increased so slowly that the rubber band does not become noticeably warmer than its environment, or become colder when the tension is lowered, then the temperature difference between the forward and reverse paths vanishes (Fig. 2.9). Moreover, other temperature-induced changes in length, volume, state of aggregation, etc. are in general also reversible.

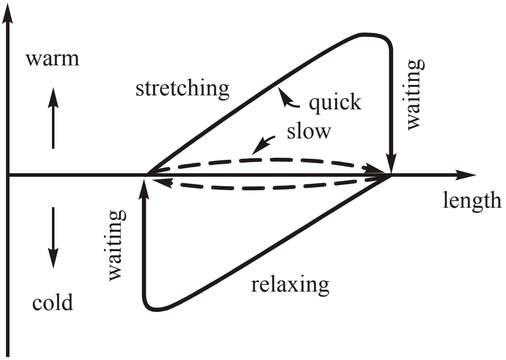


Fig. 2.9: Stretching and relaxing of a rubber band

In order to quantify an amount of heat*, we can consider the following method as an example. When we add heat* to a one-meter rod — ignoring the details of this procedure at this time — the rod expands. When the length increases to 1.001 m, we stop adding heat. We then repeat the procedure with a new rod of the same length. Subsequently, we use a third and fourth rod, etc. until all the heat* is stored. Instead of using a new rod each time, we could use the same rod again after cooling it down to a one-meter length. The assumption that it requires the same amount of heat* each time is valid. Therefore, we only need to count the number of heated rods to obtain a measure of the total amount of heat* used. This procedure is analogous to measuring the amount of water in a container by emptying it with equal measuring cups (Fig. 2.10).

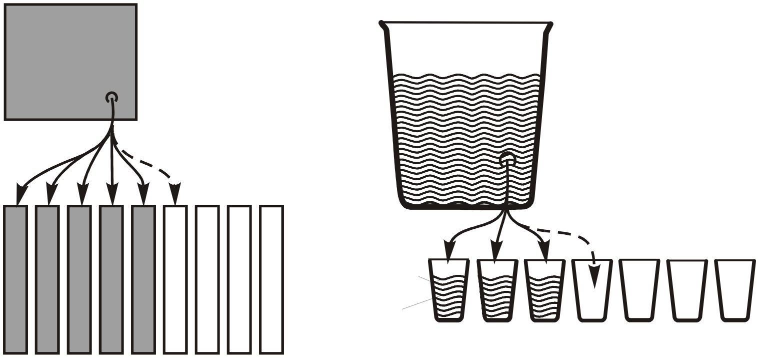


Fig. 2.10: Portioning of heat (left) like water (right)

Another method is to melt ice cubes of equal size. The amount of heat* required to melt a precisely defined ice cube under controlled conditions could be used as a unit of heat*. We know from experience that it does not matter whether we use two separate or two adjacent ice cubes or even one large ice cube weighing as much as two smaller ones. This argument can be extended to *n* pieces of ice. Rather than count ice cubes, it is simpler to use the amount of

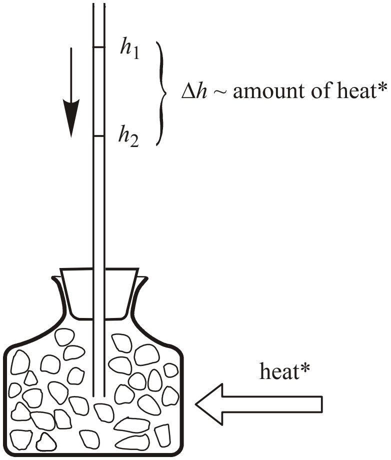


Fig. 2.11: A simple type of an ice calorimeter

melted ice as measure of heat*. This allows us to construct a practical measurement procedure. Liquid water requires less volume than solid ice. The change in volume reflects the heat input. For example, we can use an ice water bottle with a capillary tube (Bunsen ice calorimeter) where we can monitor the water level, i.e., the change in volume of the water (Fig 2.11). With input of heat* the water level drops and with loss of heat* (formation of ice) it rises. This corresponds to a procedure to measure volume whereby water is poured from a given container into a calibrated cylinder.

2.1.3. Heat* Measurement Procedure

We now have to consider how we can transfer heat* from an object to an ice water bottle or any other "calorimeter" (e.g., a set of equal one-meter rods). We know that a body expands with input of heat* and contracts with loss of heat*. Conversely, a compressed body gives off heat* while a relaxed body allows the heat* to return. This phenomenon can be utilized for heat* transfer. We can take the gas in a cylinder (Fig. 2.6) and make the cylinder walls "heat-tight". If one of the walls can be added and removed, we can think of this device as a "heat syringe", and the removable wall as a "heat valve". This device can transfer heat* just like a water syringe can transfer water (Fig. 2.12). The heat syringe can be brought into contact with various objects under investigation. In principle, other objects can also be used e.g. the rubber band.

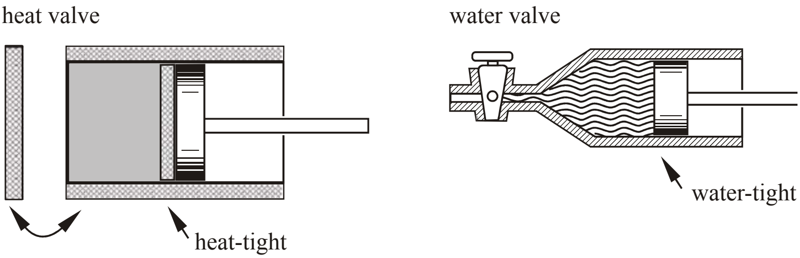


Fig. 2.12: A heat syringe works like a water syringe

To determine the amount of heat* required to expand a rod from 1 m to 1.001 m, we could use the following procedure (Fig. 2.13):

a) A heat syringe in its initial state is brought into contact with our ice water bottle. The heat valve is opened, we extract some heat* and the water level in the capillary tube rises.

b) We remove the heat syringe from the bottle and bring it into contact with the rod. During the transport from bottle to rod we keep the heat valve closed to avoid heat* losses.

c) We force heat* into the rod until it expands to the desired length.

d) We deliver the remaining heat* to the ice water bottle. During the transport from rod to bottle the heat valve is again closed.

e) The surplus heat* is returned to the calorimeter. As a result, the water level in the capillary tube drops and the heat syringe returns to its initial position.

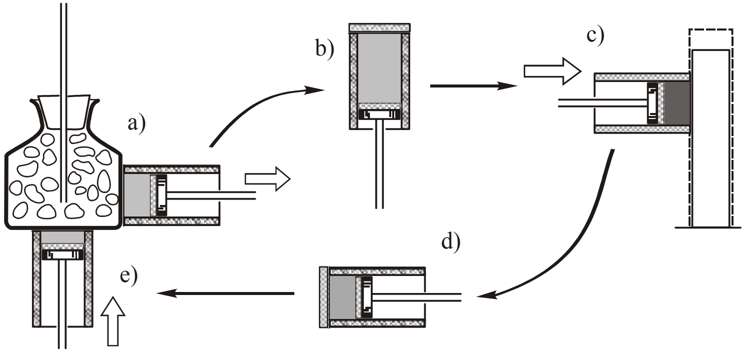


Fig. 2.13: Measuring the amount of heat* for extending a rod

The difference in water levels in the capillary tube between the initial and final stages should be proportional to the amount of heat* delivered to the rod. It is assumed that during this entire process heat* is neither lost nor gained nor produced internally. Unwanted transfer of heat* to or from the environment can be prevented through good insulation and internal heat* production can be avoided by strictly enforcing reversibility in each step.

How much success will we have in achieving the last condition in our procedure? We have shown that steps a), c) and e) can be made reversible if they are performed slowly enough. In addition, all friction between the piston and cylinder has to be eliminated in order to avoid producing heat*. However, steps b) and d) pose some difficulties. If we bring the heat syringe into contact with a warmer body, the piston moves; if we hold the piston in a fixed position, the gas pressure in the cylinder rises. This occurs because heat* flows from the warm body to the colder heat syringe causing the gas to expand. As mentioned above, we cannot allow spontaneous changes to occur in the measurement procedure. Before we bring the heat syringe into contact with a body, the gas in the cylinder has to be compressed and therefore made warmer, so that the piston remains at rest during the brief contact. We can then extract heat* from the hot body. A corresponding procedure applies when the body is colder than the heat syringe. With these precautions, steps b) and d) become reversible.

Thus we have determined a useful measurement procedure that follows logically from our previous assumptions. In summary, these are:

a) Every body contains a definite amount of heat* under specified conditions.

b) Heat* can be produced but not destroyed.

We are now in a position to examine these statements quantitatively. For assumption a) to be valid, the amount of heat* in a body, measured by the above procedure (or a similar one) relative to a standard state, must always be the same, independently of whether we use a heat syringe or a rubber band for the transfer of heat, or whether we count pieces of ice or one-meter rods, as long as the calibration is correct. In order to test assumption b), we could extract heat* from a calorimeter and deliver it to a thermally insulated test device. For example, we could transfer the heat* to the boiler of a steam engine, to an incandescent bulb or to a thermocouple and then "collect" this scattered heat* with a heat syringe and return it to the calorimeter. When all bodies return to their initial state, then we know from assumption a) that they contain no more heat* than they had initially. Any additional heat* created in the process must now be in the calorimeter and can be measured directly. Statement b) is false if in any test the calorimeter indicates less heat* at the end than was recorded initially.

Experience shows us *indirectly* that our assumptions are valid. By the above measurement procedure, heat* is explained as a physical quantity. We will denote it by the symbol *S*. We used the word "indirectly" because later (section 2.5.1) it will transpire that heat* can be equated to entropy in traditional thermodynamics.

Thus the properties of heat* can be deduced by comparison with those of entropy. We can rely on experience without actually having performed the measurements because the results, which the tests would deliver, are easily predictable.

2.2. Work and Temperature

Work is required for or may be gained by transferring heat*, because pushing a piston or stretching a rubber band demands work, for example. In the following sections we shall consider the energy exchanges in such processes.

2.2.1. Potential Energy and Energy Conservation

When a mass of water d*m* is moved from one container (I) to another (II) where the second container is higher by Δh than the first one, the work performed is given by

$$\mathrm{d}W = \Delta h\, g\, \mathrm{d}m,$$

where g is the acceleration of free fall. The work performed in lifting the water is stored and is retrievable by reversing the process. We assume here that the process is carried out in a reversible manner. The stored work is called potential energy E. The mass of water d*m* in container II is said to have a potential energy greater by d*W* compared with container I:

$$\mathrm{d}E_{\mathrm{II}} - \mathrm{d}E_{\mathrm{I}} = \mathrm{d}W.$$

Note that the mass of water d*m* in container I, compared with another container at a lower level, already possesses potential energy. The absolute value of energy cannot be determined but rather the difference compared with a conveniently chosen reference point.

Let us now consider the corresponding heat* transfer process. For example, it takes work to "lift" the amount of heat* d*S* from a cold (I) to a hot (II) body by means of a heat syringe. If carefully done, the associated work d*W* is retrievable because the process is basically reversible. We can assign a potential energy $\mathrm{d}E_{\mathrm{II}}$ to the heat* d*S* in body II that is greater than the corresponding amount $\mathrm{d}E_{\mathrm{I}}$ in body I by

$$\mathrm{d}E_{\mathrm{II}} - \mathrm{d}E_{\mathrm{I}} = \mathrm{d}W.$$

Similarly, it takes work d*W* to move a small amount of electric charge d*q* from one body (I) to another (II) which is more highly charged. Again, d*W* is recoverable if the charge transfer is reversible. As in the previous cases, the difference of the potentially usable, stored work d*E* in body II relative to body I, is given by

$$\mathrm{d}E_{\mathrm{II}} - \mathrm{d}E_{\mathrm{I}} = \mathrm{d}W.$$

Numerous other methods exist for storing work e.g. a compressed steel spring, a flying projectile, a rotating flywheel, a charged capacitor, a current-carrying inductor, etc. They all represent stored work, or in other words, a form of energy (elastic, kinetic, electric, magnetic, etc.). In all observed natural processes, work is converted from one stored form into another form. For example, when a steel ball is dropped on to a rigid floor, the initial potential energy (stored work done in overcoming gravity) is converted to kinetic energy (stored work done by the force of gravity) and then upon impact to elastic energy (stored work done by elastic deformation). The upward motion repeats the process in reverse order.

One of the most remarkable achievements in physics during the nineteenth century was the realization that work could be transformed from one stored form to another but the total amount remains constant. Work cannot be created nor destroyed. Consequently, if energy vanishes in one place, it has to reappear in another form elsewhere and vice versa. This realization is generally referred to as the law of conservation of energy.

Applied to the case of heat* transfer, the law of conservation of energy implies that the expended work d*W* is independent of the path and method used (heat syringe, rubber band, etc.) similar to the case of raising water (Fig. 2.14)

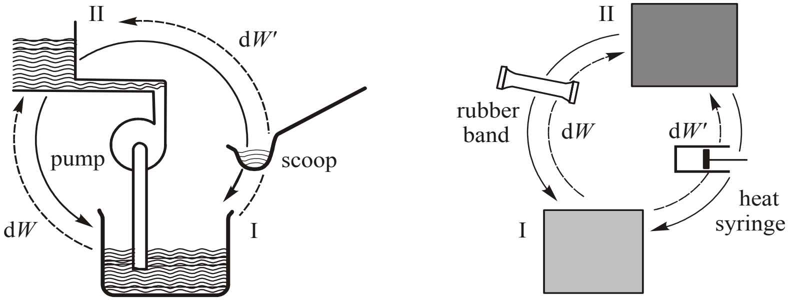


Fig. 2.14: Work for water (left side) and heat* transfer (right side)

or moving an electric charge. Otherwise, in contradiction to this law, it would be possible to create work from nothing or make it disappear by delivering heat* by one path and returning it via another.

2.2.2. Heat* Potential

When we refer to a "potential" ψ at a given location, we generally mean the potential energy dE of a small **a**mount da (of substance, charge, mass, heat*, etc.) at this location, divided by this amount:

$$\psi = \frac{\mathrm{d}E}{\mathrm{d}a} .$$

The change in potential $\Delta\psi$ between two locations is given by the quotient of the work dW — that is the work required to move da from one location to another — divided by da:

$$\Delta\psi = \frac{\mathrm{d}W}{\mathrm{d}a} .$$

Although $\Delta\psi$ can be determined, ψ cannot. While for small da the potential energy is proportional to the amount da, the potential is only a function of its location. Thus, the potential ψ can be interpreted as a "work level" associated with the amount of water, electricity, heat*, etc. Storage of work or potential energy is the product of the level and the quantity located there. In other words, it is the energy required to raise the quantity to that level.

Examples:

a) Gravity: $\mathrm{d}W = \mathrm{d}m \cdot g \cdot \Delta h$ work to raise the mass dm in a gravitational field

$$\frac{\mathrm{d}W}{\mathrm{d}m} = \Delta(g \cdot h) ,$$ $g \cdot h$ “gravitational” potential.

b) Static Electricity: dW work to move the charge dq in an electric field

$$\frac{\mathrm{d}W}{\mathrm{d}q} = \Delta\varphi ,$$ φ electric potential.

c) Thermodynamics: dW work to transfer an amount of heat* dS

$$\frac{\mathrm{d}W}{\mathrm{d}S} = \Delta T ,$$ T thermal potential.

The last equation defines a potential for heat* denoted by T. The value of this potential can only be determined in respect to a reference body (e.g., an ice water bottle). The potential energy dE of an amount of heat* dS in a body with heat* potential T is given by

$$\mathrm{d}E = T \cdot \mathrm{d}S.$$

By partitioning a hot body into parts and then transferring a small amount of heat* from a reference body to one of these parts, the work required is the same as that needed for the composite body. The thermal potential T is unaffected by the partitioning. For comparison, this is not the case for the electric potential. Since electric charge is distributed on the surface of the conducting body (Fig. 2.2), partitioning an electrically charged body usually changes the distribution of the charge, and therefore the field strength. Since the potential of an electrically charged body is determined by measuring the work performed in bringing a test charge dq up to it from infinity (Fig. 2.15), partitioning usually affects the electric potential.

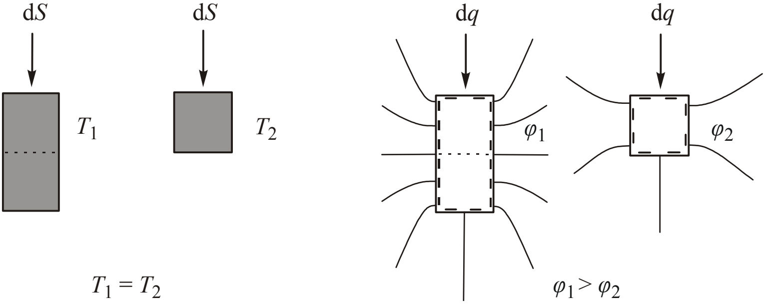


Fig. 2.15: Comparison of thermal and electric potential

2.2.3. Thermal Tension

Let us consider a body that is heated successively by small portions of heat* dS, for instance, by means of a heat syringe (Fig. 2.16, left side). At each step the gas must be compressed more strongly, requiring more work to force the heat* into the body. It appears as if the heat* in the body is under pressure or tension which rises with the thermal level. Let us denote this "thermal tension" by t. This phenomenon is well understood for the transfer of water from one container at a

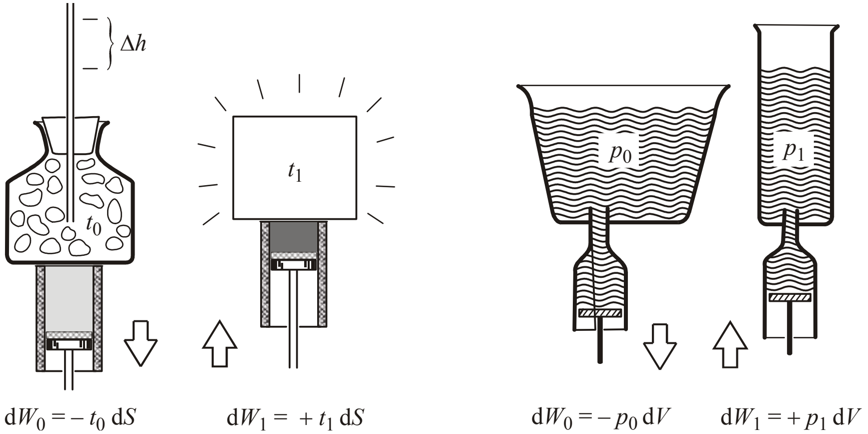


Fig. 2.16: Comparison of thermal tension and hydraulic pressure

hydrostatic pressure p_0 to another with pressure p_1, since the water level rises steadily (Fig. 2.16, right side). In transferring a volume dV of water in the first step, we apply work $dW_0 = -p_0 \cdot dV$. The sign is negative because work is gained and not expended. (The accepted sign convention is to treat an input to a system as positive and an output as negative.) In the second step the work $dW_1 = +p_1 \cdot dV$ is performed. The total work is therefore given by

$$dW = (p_1 - p_0)\,dV\,.$$

Similarly, the work for the transfer of heat* (Fig. 2.16, left side) consists of the two parts $dW_0 = -t_0 \cdot dS$ and $dW_1 = +t_1 \cdot dS$ that overcome the supposed thermal tensions t_0 and t_1:

$$dW = (t_1 - t_0)\,dS\,.$$

If, on the other hand, the transfer work is calculated based on the heat* potential, we get:

$$dW = (T_1 - T_0)\,dS\,.$$

That means, that the heat* potential T indeed can be interpreted as a kind of thermal tension t:

$$T \equiv t.$$

2.2.4. Temperature

We know from experience that the thermal tension parallels our perception of hot and cold, or in other words, our sensation of temperature. The hotter a body feels, the higher its thermal potential. The thermal potential of a body is a measure of temperature and can be used to define temperature as a physical quantity. The equilibration of temperature of bodies in thermal contact is analogous to the equilibration of pressure of connected vessels and of the electric potential of conductors in contact.

The change in potential between ice water and boiling water at a pressure 1.013 bar (1 atmosphere) remains the same regardless of the size and shape of the container. By selecting a heat* unit that divides this change in potential into 100 equal parts, we generate a temperature scale comparable to that currently accepted (Fig. 2.17).

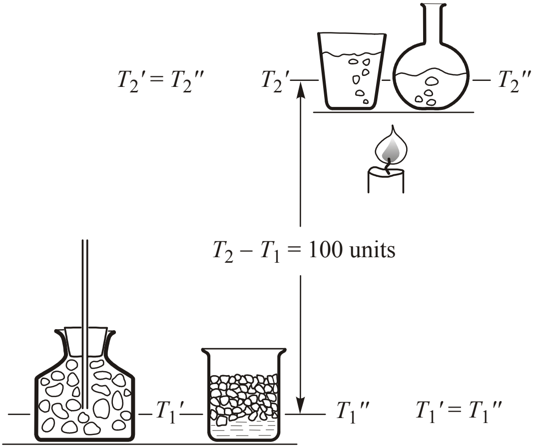


Fig. 2.17: Defining a temperature scale

2.2.5. Heat Engines

Consider an experiment, which heats up a body through small increments. If we reverse this process, the required work has to be released. A heat* engine is based on this principle. It removes an amount of heat* S from a heat* reservoir at nearly constant temperature T_1 and transfers it to another reservoir at a temperature T_0. The amount of heat* S is transferred from a potential T_1 to a lower one T_0. For a machine working without loss, the following work is delivered (note negative sign for work delivered!):

$$W = -(T_1 - T_0)\cdot S.$$

A water wheel and a turbine work in a similar fashion if placed between two water containers at different hydrostatic pressures. An electromotor represents an equivalent electric example for such a power machine (Fig. 2.18).

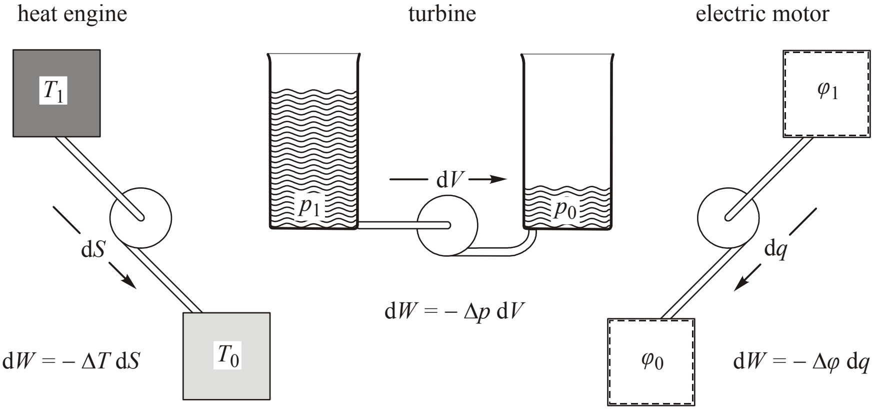


Fig. 2.18: Heat* engine, water turbine, and electric motor

2.2.6. Thermal Work

When heat* is forced into a body, work must be performed to overcome the thermal tension T in a similar way to the charging of a body against its electric potential φ or the filling of a rubber balloon with water against its internal pressure p. For the addition of heat* $\mathrm{d}S$, charge $\mathrm{d}q$ and water volume $\mathrm{d}V$, the required work is:

$\mathrm{d}W = T\cdot\mathrm{d}S$ thermal work,

$\mathrm{d}W = \varphi\cdot\mathrm{d}q$ electric work,

$\mathrm{d}W = +p\cdot\mathrm{d}V$ mechanical work (note the positive sign).

Thermal work should not be confused with the work required for "lifting" heat* (for example with a heat syringe to a higher level of temperature. When the body supplying the heat* is at the same temperature as that which receives it, the work required for "lifting" vanishes whereas the thermal work remains.

2.2.7. Heat* Capacity

In general, temperature T is not proportional to the heat* content S of a body (Fig. 2.19). The ice water bottle provides an extreme example: On heating, its temperature remains constant as long as ice is present.

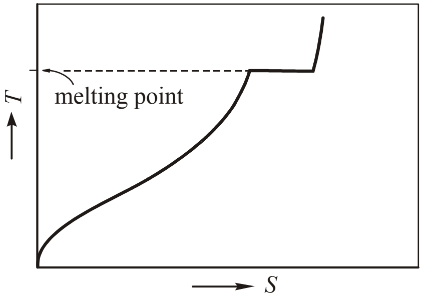


Fig. 2.19: Temperature T as a function of the heat* content S

In order to describe the thermal behavior of a body, T is usually not discussed as a function of S. Instead, the heat* capacity $Ç$ is considered, i.e., the amount of heat* required to raise the thermal tension by one unit:

$$Ç = \frac{\mathrm{d}S}{\mathrm{d}T} .$$

The capacitance C of a conducting body is defined analogously as the amount of charge required to raise the electric potential by one unit:

$$C = \frac{\mathrm{d}q}{\mathrm{d}\varphi} .$$

The heat* capacity $Ç$ of a body depends not only on its state, meaning, for example, upon its temperature and pressure, but also on the conditions under which the heat* is transferred. For example, for the same change in temperature, a body that is free to expand can receive more heat* than one that is constrained

2.3. Heat* Production

This section deals with conditions under which heat* is produced, and the consequences of this production which were excluded previously as bothersome side effects.

2.3.1. Absolute Temperature

Let us compare two simple experiments. In order to avoid corrupting the results with an undesirable loss of heat to the surroundings, we must insulate the test body well or work sufficiently quickly.

a) If we stretch a rubber band: this requires work and T increases. If we then allow the rubber band to return to its original length slowly (it should not snap back!), the work is regained and T returns to its initial value (Fig. 2.20). This process is reversible. No heat* is produced because the rubber band remains as cold or warm at the end as it was at the beginning.

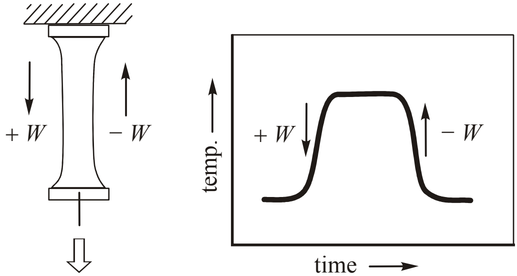


Fig. 2.20: Work for stretching of a rubber band

b) If we bend a malleable piece of flat iron: this requires work and T increases. If we then bend the iron back to its initial shape, this again takes work and T increases further (Fig. 2.21). This process is not reversible. The iron has returned to its initial shape but it is now warmer. Only after we extract some heat* from it does it return to its original state, except for a negligible amount of embrittlement. In this case, heat* is produced, and the expended work is used up.

We now want to generalize these results and express them quantitatively. If a small amount of heat* is to be produced in a body, denoted by S_p, this can only happen by using up energy to overcome its thermal tension T. To justify this

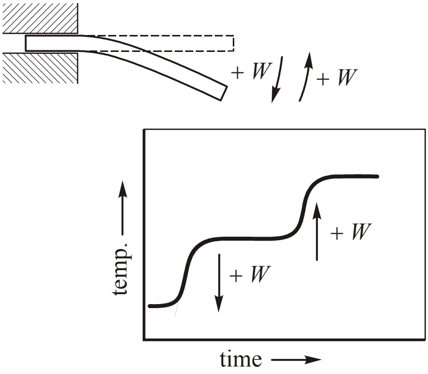


Fig. **2.21**: Work for bending a flat iron

statement, we can argue that when we release the produced heat* and return the body to its initial state, the amount of thermal work released, $|W| = T \cdot S_p$, must equal the work expended on heat production, W_p, in accordance with energy conservation:

$$T \cdot S_p = W_p \,.$$

This equation leads to an important result: There must be an absolute zero point of the thermal potential, in contrast to that for electric potential. Furthermore, this temperature T must be positive. Since work must be expended to produce heat*, $W_p > 0$, and we know of no counterexamples where heat* is produced, $S_p > 0$, *and* work is gained, $W_p < 0$, it follows as a consequence that $T > 0$.

One additional observation is necessary: The heat* content S of a body can increase both by an amount imported from an **e**xternal source, S_e, and by an amount **p**roduced inside the body, S_p:

$$\Delta S = S_e + S_p.$$

2.3.2. Prerequisites for Heat* Production

We have seen that energy is required for heat* production and this seems to be the only prerequisite. Other bodies participate in and support this process but remain unaffected. For example, work is expended on bending the iron strip while nothing else important changes. The same conclusion applies when heat* is produced in an electric resistor, by stirring a liquid or by friction in a bearing. Conversely, one can suspect that heat* is always produced when the required energy is available. The following examples provide some justification for this statement.

a) When a rolling vehicle slows down, its kinetic energy is released. This energy can be stored as potential energy if the vehicle rolls uphill. There is no, or more accurately, only little heat* produced. This possibility is eliminated when the vehicle rolls on level ground and all of the released energy is used for heat* production.

b) Part of the energy stored in a galvanic cell is transferred to the outside by electric current. If all of this energy is used to lift a weight by an electric motor, no heat* is produced (Fig. 2.22). If we replace the motor with a purely resistive load in the circuit, the total electric work is used up for producing heat* and none is stored as potential energy in contrast to the first case.

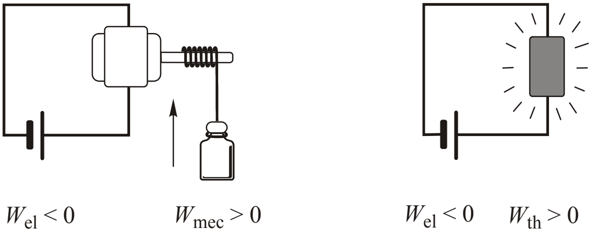


Fig. 2.22: Released energy used for lifting a weight or producing heat*

c) Work stored on compression of a gas is released when the gas is allowed to expand. From the earlier discussion, we expect that the gas will cool down when expanding (Fig. 2.6), but that is true only if no heat* is produced. If it is produced, it will more or less compensate the temperature drop and the gas will maintain its temperature. We can use a small motor for demonstration. If the work from an expanding gas is used to drive this motor and little heat* is produced, the gas, as expected, will cool down, but when the motor idles, the temperature of the vented air changes very little.

In summary we can state that heat* is produced in a process where excess energy is neither used for work nor stored. This applies in particular to processes involving friction. Work used to overcome friction or some other resistance cannot be stored or captured in such a way that it can be reused.

2.3.3. Feasible and Unfeasible Processes

The insights gained above allow us to determine, on the basis of energy balances, whether or not a process is feasible. A process whereby energy is released, i.e., where stored work is not fully converted from one form of storage into another, can run by itself. A process, which requires extra energy, cannot run by itself. It is assumed in both cases that these processes do not violate any laws of nature. The work released in the first case can be consumed by heat* production and hence complies with energy conservation. In the second case, by contrast, the missing energy has to be supplied externally.

Not every process that is capable of releasing energy will actually run its course. For example, a gaseous mixture of oxygen and hydrogen is stable at room temperature even though energy could be released in a chemical reaction. Similarly, the Alps are preserved although work could be gained by leveling them. The above processes are possible but inhibited. These natural inhibitions are extremely important for the world, as we know it. Without them, mountains would disappear and the oxygen in the air would destroy all organic matter and, with it, all living beings. Since the process of oxidation is too slow under normal circumstances, life can survive on earth

2.3.4. Lost Work

If work W_p is used up in a heat-producing process, then it is not possible to regain the full amount. This occurs because heat* cannot be destroyed and those places and reservoirs where heat* can be stored are at a positive temperature. Therefore, at least the potential energy, $T{\cdot}S$ that exists at the coldest accessible place is lost. We describe W_p as "lost", "wasted" or "devalued" work because it can only be partially restored through cumbersome procedures. The rate at which work is lost is called loss power.

One of the most convenient ways to introduce heat* in a specified place is to utilize lost work. In order to heat up a room or a body, we produce heat* locally via a chemical reaction (fire, gas burner) or with an electric heater. In general, we do not transfer heat* from a reservoir or some distant source. After measuring the lost work and the temperature of the body that is being heated, we can easily calculate the amount of heat* produced, provided an appropriate thermometer is available.

One can use this simple method to calibrate a calorimeter or to determine heat* capacities. In the latter case, we can heat an insulated test body via an electric heater and monitor the rise in temperature (Fig. 2.23). The electric work expended, $\mathrm{d}W_\mathrm{p}$, divided by the measured temperature T, yields the increase $\mathrm{d}S$ in the heat* content S. The ratio of $\mathrm{d}S$ to the observed temperature rise $\mathrm{d}T$ represents the heat* capacity $Ç$ and we obtain S by integrating the heat* capacity.

$$Ç = \frac{\mathrm{d}S}{\mathrm{d}T} = \frac{1}{T} \cdot \frac{\mathrm{d}W_\mathrm{p}}{\mathrm{d}T}, \qquad S = S_0 + \int_{T_0}^{T} Ç \cdot dT$$

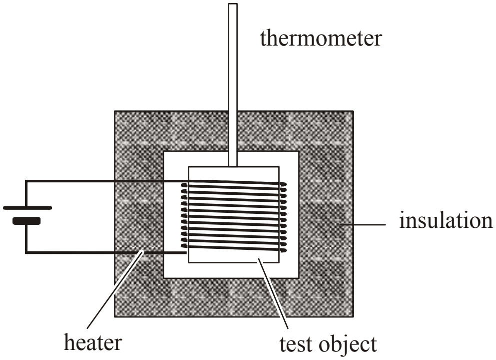


Fig. 2.23: Measuring heat* capacities

2.3.5. Heat* Conduction

If heat* S flows through a conductive link (referred to as a "conduction path") from a body at temperature T_1 to another at T_0, then potential energy $(T_1 - T_0) \cdot S$

is released (Fig. 2.24). Where does the energy go? Since it cannot be stored anywhere, it must be used for heat* production. This heat* S_p, produced in the conduction path, must flow in the direction of decreasing temperature and thus will end up in the colder body with thermal potential T_0. S_p can be computed from the energy W_p released i.e., the work released by heat* S "falling" across the temperature drop:

$$W_p = (T_1 - T_0) \cdot S, \qquad S_p = \frac{W_p}{T_0}.$$

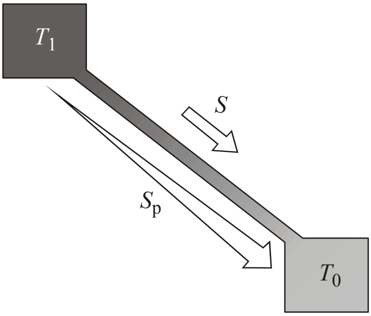


Fig. 2.24: Heat* production during heat* conduction

Conduction across a temperature gradient increases the heat* flow. This is a surprising but inevitable consequence of our considerations. For that reason we have to be careful when applying conduction during calorimetric measurements. Earlier we transferred heat using a heat syringe instead of by conduction (Fig. 2.13) because conduction is not reversible and we were not sure if heat* is produced or not. We have now shown that this exclusion was justified.

The thermal work performed on the colder body, W_0, is given by

$$\underbrace{T_0(S + S_p)}_{W_0} = T_0 S + T_0 \cdot \left[\underbrace{\frac{(T_1 - T_0)S}{T_0}}_{S_p}\right] = \underbrace{T_1 \cdot S}_{-W_1}.$$

This work is equivalent to the amount released by the warmer body, $-W_1 = T_1 \cdot S$. While the amount of heat* increases by conduction, the energy current remains constant. This process is commonly described as energy transfer rather than as heat* transfer because it is simpler in this special case.

The energy W_p is the work wasted along the conduction path. If the conduction path would have been replaced by a heat* engine, then this amount of energy would be the gained useful work from the engine. Here this energy is *not used* but, as we said before, it is lost, wasted, or devalued. These words don't convey what causes the loss, so we might instead say that the energy is "*burned up*" to connect the idea of "waste" to the production of heat*. When energy is burned up, the amount of "thermal charge" is increased.

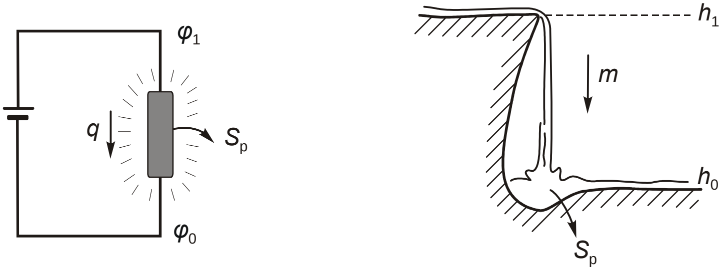


Fig. 2.25: Other cases of potential drop and heat* production

Heat* conduction can be compared either with electric conduction or — more intuitively — with a waterfall (Fig. 2.25) . The lost, or better, burned up work W_p is represented by the potential drop of each quantity (charge q, water mass m) through the "conduction path". The produced heat* is given by the ratio W_p/T_0 where T_0 is the temperature of the "conduction path:"

$$W_p = (\varphi_1 - \varphi_0) \cdot q, \qquad S_p = \frac{W_p}{T_0} \qquad \text{(electric resistor);}$$

$$W_p = (g \cdot h_1 - g \cdot h_0) \cdot m, \qquad S_p = \frac{W_p}{T_0} \qquad \text{(waterfall).}$$

In all these processes, two steps can be distinguished:

potential drop and heat* production.

In the case of heat* conduction this distinction is obscured because the quantities which flow and which are produced are of the same kind.

2.4. Heat* Content at the Absolute Zero of Temperature

If we remove all heat* S from a substance, we expect its temperature T to drop to zero. Actually we can make the temperature T approach zero as closely as desired by continuously extracting heat*. Since T can be measured, it is easy to observe this behavior. Expressed mathematically, we have:

$T \to 0$ as $S \to 0$ (more precisely: $T \to 0$ for S sufficiently small).

It is more difficult to determine the amount of heat* remaining in a body. One could destroy the body chemically and thus release and measure the heat* which remains, since heat* cannot be destroyed. However, both the reactants *and* products of the chemical reaction contain some heat*. Therefore, this method can only determine the difference ΔS of the heat* released by the initial materials and absorbed by the final materials. Such investigations show that ΔS vanishes at very low temperatures (the procedures are described in chapter 4). This result and other empirical facts support the obvious assumption that bodies at zero absolute temperature contain no heat*:

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

These two relations formulated here have some peculiar exceptions. If a drop of water evaporates completely, then its heat* content goes to zero without a change in temperature. This is in violation of the first relation. If we allow a thermally insulated gas to expand continuously, then its temperature drops and approaches zero although its heat* content remains constant. This is a violation of the second relation. We will apply the above relations to non-degenerate cases only, such that the volume of a body cannot vanish or become arbitrarily large. Furthermore, the amount of the substance used may approach zero — a vacuum is permissible in our considerations — but it may never approach infinity. The above discussion can be summarized as follows:

$T \to 0$ if and only if $S \to 0$ for finite systems.

Some materials, such as liquid glass for example, are observed to give off less heat* if they are cooled down quickly, than they would if they were cooled down slowly, although the initial and final temperatures are equal in the two cases. It is as if heat* is trapped or frozen into the body if it is cooled too quickly. In the case of glass, it is the heat* required to melt it (the heat* of fusion) which is frozen in.

Melted glass crystallizes very slowly, and rapid cooling delays the process to the point that it stops and the heat* of fusion cannot be released. A further temperature drop would slow down the crystallization even more, so this method cannot be used to extract the frozen heat*. These amounts of heat* are literally trapped in, as in a thermos flask. Since they cannot be released, they do not influence a thermometer and contribute nothing to the measured temperature of a body.

Some materials trap heat* even in an absolutely cold environment. By excluding these exceptions, the above theorems remain valid for finite systems. Their consequences agree with our experience.

2.5. Comparison with other Theories of Heat

People familiar with other approaches to thermodynamics need to know how this new approach is related to traditional conceptual approaches. This knowledge is also necessary in order to use intelligently the tabulated data and knowledge available in the literature. Even for those not well versed in historical terminology, it should not be too difficult to understand the essential ideas.

2.5.1. Comparison with Traditional Thermodynamics

So far we have formulated several concepts to describe the observed thermal phenomena. The same processes can be described using the standard language of conventional thermodynamics. A comparison will yield the corresponding concepts of each approach. In this section only we will mark all variables as they are used in the new approach with an asterisk (*) as we have been doing with heat*. Variables from traditional thermodynamics will not be marked.

We mentioned earlier that heat* can be equated with entropy (see the end of section 2.1.3). Both quantities can be identified strictly from the following comparison. Our procedure for heat* transfer from one body to another is very similar to a reversible CARNOT process. Section 2.1.3 gives the example of expanding a rod from 1.000 to 1.0001 m with a heat* input via a heat syringe from an ice water bottle. During this process the entropy decrease $-\Delta S_1$ of the first body (ice calorimeter) equals the entropy increase ΔS_2 of the second body (rod) because the entropy of the total system (ice calorimeter and rod) remains constant due to reversibility:

$$-\Delta S_1 = \Delta S_2 \, .$$

According to traditional theory, the mass *m* of freezing water in our heat* measurement process is proportional to the entropy loss of the calorimeter, $-\Delta S_1$ In addition, *m* is by our definition a measure of the increase in heat* of the body under investigation:

$$\Delta S_2{}^* \sim m \sim -\Delta S_1 = \Delta S_2 \, .$$

If we set the proportionality constant between $\Delta S_2{}^*$ and ΔS_2 to unity by an appropriate choice of units and select the zero of entropy properly, then the entropy *S* and the heat* content S^* of a body are equal:

$$S = S^* \, .$$

In traditional thermodynamics, "heat" is treated as a form of energy, represented by *Q*. Entropy, *S*, is introduced as the integral $\int \mathrm{d}Q_{\mathrm{rev}}/T$. Those who are familiar with this abstract introduction might wish a more detailed justification of the last equation in order to see how it fits in with previous concepts. The following comments might help: Entropy is a state function, which always increases for real processes in isolated systems. Since it is an extensive or substance-like quantity, one can assign a density to it for every region of space. It follows that entropy can be viewed as an entity distributed in space that may be added to or extracted from a body, and whose total amount always increases. Since $\mathrm{d}S = \mathrm{d}Q_{\mathrm{rev}}/T$, the qualitative effects of an entropy increase are the same as a heat$^\bullet$ input, *Q*. You can think of each increase d*S*, for either reversible or irreversible processes, to be caused by a reversible heat$^\bullet$ input, $\mathrm{d}Q_{\mathrm{rev}}$, even if it is actually caused by an irreversible process. Since we cannot tell whether the heat effects are due to entropy or the energy $\mathrm{d}Q_{\mathrm{rev}}$ received by a body, we are free to interpret the quantity *S* as heat, rather than *Q*.

Now let us consider the determination of the absolute thermal potential T^* of a piece of matter by producing a small amount of heat* $S_p{}^*$ inside it as described in section 2.3.1. The energy W_p expended for this purpose is supplied to the piece and then completely emitted as thermal work, W^*. Conservation of energy requires that

$$W_p = -W^* = T^* \cdot S_p{}^* .$$

Expressed in traditional terminology, the performed work W_p is expended in the first irreversible step and as a result, the entropy must increase by some — as yet undetermined — amount. In the subsequent reversible step, the heat$^\bullet$ Q is released and simultaneously the entropy is decreased by Q/T, where T is the thermodynamic temperature of the material. Since the body returns to its initial state at the end, the total change in energy and entropy are zero. Expressed mathematically, we have $W_\mathrm{p} + Q = 0$ and $S_\mathrm{p} + Q/T = 0$, or

$$W_\mathrm{p} = -Q = T \cdot S_\mathrm{p}.$$

Comparing both equations for W_p, we see that heat$^\bullet$ in its traditional sense, Q, is equal to thermal work, W^*, and since $S = S^*$, the thermodynamic temperature, T, must be equal to heat* potential, T^*:

$$Q = W^*, \qquad T = T^*.$$

As a result, our heat* capacity $\text{Ç}^* = \mathrm{d}S^*/\mathrm{d}T^* = \mathrm{d}S/\mathrm{d}T = \text{Ç}$. Usually the quantity $\text{Ç} = \mathrm{d}S/\mathrm{d}T$ is not used in traditional thermodynamics, but it could be called "entropy capacity". Our heat* capacity Ç^* differs from the commonly used heat$^\bullet$ capacity $C = \mathrm{d}Q/\mathrm{d}T$ by the factor T, because $T \cdot \mathrm{d}S = \mathrm{d}Q$. We can write

$$C = T \cdot \text{Ç}^* = T\,(\mathrm{d}S/\mathrm{d}T).$$

Therefore, in our terminology traditional heat$^\bullet$ capacity C may be referred to as "thermal work capacity". Except for the sake of this comparison, there is no reason to introduce a quantity C in our new interpretation. Similarly, there is no need to introduce a quantity Ç in the traditional view. In all cases, we can state that

$$\overbrace{\text{entropy capacity = heat* capacity}}^{\text{Ç} = \text{Ç}^*} \qquad \overbrace{\text{heat}^\bullet \text{ capacity = thermal work capacity}}^{C = C^*.}$$

Thus, the basic quantities and their derived variables are in one-to-one correspondence without requiring conversion. That has some practical consequences. We can measure the heat* potential with a common mercury thermometer and we can read off the heat* content of many bodies in the "entropy" column of published tables. If the quantities remain the same, what has really changed?

Briefly stated: It has been shown that the central concepts of thermodynamics can be introduced in a simple and intuitive way, although under different names. The discrepancies between the energetic interpretation of heat and our common language have been largely eliminated. Entropy, for most people a hard-to-grasp concept, has been given an adequate interpretation. Finally, we can make comparisons with other areas of physics that facilitate our understanding of the conceptual framework and remove the abstractness of thermodynamics. Those who are uncomfortable that heat conduction is treated as a composite procedure (heat transfer from high to low temperature *combined* with heat production) may consider energy flow instead of entropy flow and, in this way, retain traditional formulae without returning to the traditional interpretation.

In order to clarify these differences, let us contrast some analogous statements, in traditional and new terminology.

a) Energy Law (First Law) :

— Traditional: The internal energy of a system is a state function. Its change is due to the sum of all heat• and work inputs to the system received from its surroundings. The energy of an isolated system remains constant during all internal processes.

— New: Work can be stored in various ways and can be regained. It cannot be created or destroyed.

b) Entropy Law (Second Law):

— Traditional: The entropy of a system is a state function. Its change is due to the integral of all heat• inputs to the system received from its surroundings in a reversible way, dQ_{rev}, divided by the absolute temperature T at which the heat• is introduced. The entropy of an isolated system can increase but never decrease during all internal processes.

— New: Heat* is contained in larger or smaller amounts in a body depending on its state. It can be produced but cannot be destroyed.

c) NERNST Heat Law (Third Law):

— Traditional: The entropy of a system in equilibrium vanishes as its temperature approaches absolute zero.

— New: Absolutely cold bodies contain no heat* unless some of it is trapped in.

d) Heat Engines:

— Traditional: The efficiency of an ideal heat engine, defined as the useful work divided by the expended heat•, Q_{in}, is given by the temperature difference between heat• input and output, $\Delta T = T_{in} - T_{out}$, divided by the absolute temperature of the heat• input: $W/Q_{in} = \Delta T/T_{in}$.

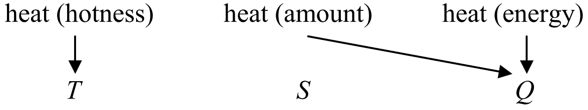
— New: The useful work of a lossless heat* engine is the product of the thermal potential drop, ΔT, and the amount S of the transferred heat*: $W = \Delta T{\cdot}S$.

The new interpretation treats work — or rather work storage — as synonymous with energy, since there is no compelling reason to differentiate between stationary and moving forms of energy or work. On the contrary, one can avoid unnecessary explanations by not making this distinction. A good example is the treatment of electric charge. Certain important statements become almost self-explanatory with the new interpretation. For example, the statement that it is impossible to build a perpetually running heat engine driven by a constant temperature heat reservoir (W. THOMSON's version of the Second Law) is analogous to: "It is impossible to operate a water mill without a drop in elevation". Similarly, the statement that it is impossible to reach the absolute zero of temperature (the frequently used form of the Third Law), in other words to remove all the heat* contained in a body, is analogous to saying: "It is impossible to reach the absolute zero of pressure by removing all the gas from a tank".

We are faced with the curious fact that the choice of a single concept — namely, the "heat" concept — has decisively influenced the structure of an entire theoretical framework. This choice affects not only the immediacy of its statements, but also the conciseness of its computational methods, as we will see later. How is this possible?

In contrast to scientific description, common language is relatively imprecise. A single word can denote different concepts. For example, to an unbiased layman the word "force" conveys ideas and characteristics that correspond to physical quantities like pressure, force, energy, momentum or potential. There exists considerable leeway in establishing a correspondence between scientific and commonly used concepts.

In traditional thermodynamics there are three quantities — temperature T, entropy S and the energetic (work-like) quantity Q — that could be described by the word "heat":



After the name "amount of heat" was assigned to the energetic variable Q, and with it all connotations connected with this name, it became difficult to explain the quantity *S*. This variable was introduced only formally and remained abstract. This can be compared to the crippling effect of the insertion of both feet into a single trouser leg (Fig. 2.26). If you want to take even a few steps you need crutches. Thermodynamics has become fixed in a similarly awkward situation by declaring, as the First Law of the whole theory, the equality of heat and work. There is no longer a variable for describing the heat contained in a body, so crutches like "enthalpy" and "free energy" must be used to overcome this disability. They would otherwise not be necessary.

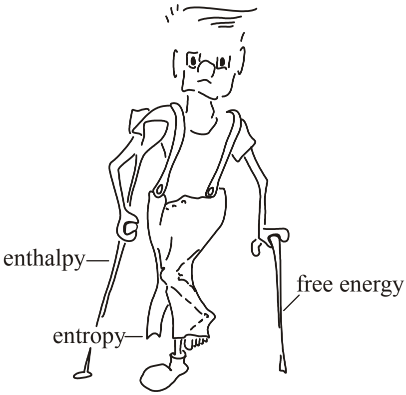


Fig. 2.26: The misfortune of thermodynamics

It is compelling to find the reasons for this misfortune of thermodynamics that led to a contradiction between theory and intuition, and the numerous abstract concepts that make it difficult to understand. In order to uncover these reasons, we have to take a look back to the nineteenth century.

2.5.2. Historical Background [2]

Since long ago, two theories have been known to describe the concept of heat. Heat was first explained in terms of waves or motion, prompted by the observation of phenomena such as heat radiation and heat production through friction. Here heat can be created and can disappear. No distinction was made between intensity

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[2] Detailed discussion in G. Job, Sudhoffs Archiv 53 (1970) 378

(temperature) and quantity (amount of heat), as you find in common language even today.

Later, during the 18th century, under the influence of the evolution of chemistry, scholars tended to interpret heat as a kind of substance called caloric, which could neither be produced nor annihilated like a chemical element. As a result, the first quantitative statements could be made about heat. Transports of heat, as well as the changes of temperature when hot and cold bodies are in contact, were easily explained by making the temperature proportional to the concentration of heat. The processes of fusion and evaporation were viewed as a reaction of this "heat substance" with the heated body. Heat was not produced by friction; the substance was released by the worn down material like oil from pressed seeds. According to this substance theory, heat could not be produced, nor could it be destroyed. In order to explain the temperature balance achieved by bodies with different initial temperatures, J. H. LAMBERT (1779), M. A. PICTET (before 1800) and other contemporaries assumed that heat was subjected to a kind of tension that increases more and more when a body becomes hot. This was assumed to be the cause of the tendency of heat to disperse.

In 1824, S. CARNOT, whose considerations laid the foundation for thermodynamics, compared a heat engine driven by cold and hot heat reservoirs with a water mill. He drew analogies between the temperature difference and the drop in elevation of the water, and between the heat transferred and the water flowing down, and then computed the work gained from such an engine. He did not obtain his results from the analogy but derived them from the well-known impossibility of a perpetual motion machine (*perpetuum mobile*) on the basis of the substance theory of heat. In essence, he used two assumptions:

a) Work cannot be created.

b) Heat is not producible and not destructible.

Building on CARNOT's ideas, E. CLAPEYRON (1834) introduced the relationship between steam pressure and heat of evaporation that became known as the CLAUSIUS-CLAPEYRON Equation because R. CLAUSIUS (1864) expressed it in its final form. In 1848 W. THOMSON suggested a definition of temperature that corresponds to the introduction of T as the potential of the heat substance.

This generally successful interpretation of heat was contradicted by results of different experiments that showed that heat seems to be produced, related to the amount of work expended. This indicated a connection between these two quantities. B. THOMPSON, H. DAVY (about 1800) and especially J. P. JOULE, by his careful experiments after 1840, further refined the idea. JOULE measured the same heating effect when he expended a definite amount of work, regardless of the method he used. R. MAYER, J. P. JOULE and H. v. HELMHOLTZ then assumed that heat and work are interconvertible. Confusion spread when they tried to apply the principle of conservation of energy to all of physics, since formerly it was proven only for mechanical processes. Did heat in a steam engine behave like water in a mill according to CARNOT's explanation, or was it used up as MAYER and JOULE claimed?

In 1850, R. CLAUSIUS suggested a compromise between the conflicting interpretations. Heat was neither arbitrarily convertible into work, nor was its amount conserved in a steam engine during the transition from higher to lower temperature. Both processes had to be considered as interconnected in a determined manner. He showed that one could arrive at the corresponding statements made by CARNOT and CLAPEYRON by changing the assumptions of the substance theory of heat as follows:

a) Work cannot be created *nor destroyed without using up or creating an equivalent amount of heat.*

b) Heat ~~is not producible and not destructible~~ *cannot flow from a lower to a higher temperature by itself.*

Although this theory was further developed by THOMSON in parallel with CLAUSIUS, it was not accepted initially because it lacked the simplicity and elegance of the old interpretation. Later, however, it replaced all other competing theories. It was helped by the fact that the discovery of the energy principle made an overwhelming impression on scientists of that time. They had exaggerated expectations from this law of nature. In some places it was considered as the "only formula required for the true knowledge of nature" (G. HELM, 1898). According to H. HERTZ, many of his contemporaries considered the reduction of all natural phenomena to the laws of energy conversion as the ultimate goal of physical research. It is understandable that in such an environment the CLAUSIUS-THOMSON theory of thermodynamics was treated as a kind of archetype theory because its heat quantity was not a quantity on its own, unlike electric charge, but was simply interpreted as a form of energy. Efforts were made to develop other disciplines according to this ideal, rather than making the framework of thermodynamics similar to that of its related areas. The hope of the "energetic advocates" was not realized, but they left us their version of thermodynamics.

What was overlooked is that a minimal change of CARNOT's basic assumptions is sufficient to eliminate the contradictions between the old theory and experience. In this way the switch to the energy interpretation, which has cost so much effort and controversy, could have been avoided:

a) Work cannot be created *nor destroyed*.

b) Heat is ~~not~~ producible and not destructible.

By striking out the one word "not" in the last sentence, we reject the substance theory just as CLAUSIUS did.

3. GENERAL THERMODYNAMICS

On heating a body one can observe a temperature rise – the primary effect – as well as various secondary effects such as expansion, pressure increase, bending, charge increase (pyroelectric effect), chemical changes, etc. Conversely, mechanical, electrical and magnetic effects can cause thermal side effects like a temperature change or a heat transfer to or from the environment. This chapter deals with the interactions and relationships between thermal and other physical quantities. However, chemical transformations are left until chapter 4.

3.1. Elastic Coupling

This term refers to a conceptual model that applies to many physical processes. It is particularly suitable for describing conditions of thermodynamic equilibrium. First we shall clarify the conceptual and mathematical framework of this model with mechanical examples before applying it to thermal phenomena.

3.1.1. Elastic Behavior

If we stretch a rubber band (at constant temperature) from a length l_0 to a length l, we observe an opposing force F which is uniquely determined by this extension, and which increases with length l:

$$F = F(l).$$

We refer to this behavior as elastic. We observe a steep increase in force at small extension, a somewhat reduced value on further extension and finally another increase at even larger extension. Figure 3.1 depicts the function $F = F(l)$ graphically in exaggerated form.

Let us define the "stiffness" of the rubber band at length l_1 by $\mathrm{d}F/\mathrm{d}l$, which represents the slope of the curve at point P. The term "spring constant", commonly used for a linear relationship between F and l, namely $F = a\cdot(l - l_0)$, is

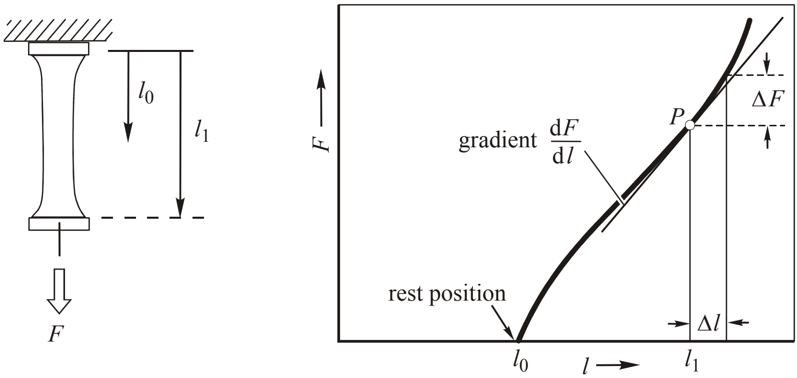

Fig: 3.1 Force as a function of length

inappropriate here. A change of Δl in l causes a change in F of ΔF. For small changes, we have $\Delta F = (\mathrm{d}F/\mathrm{d}l)\cdot\Delta l$, or in differential form,

$$\mathrm{d}F = \frac{\mathrm{d}F}{\mathrm{d}l}\mathrm{d}l.$$

It takes a force F to stretch the rubber band by Δl. The product of force times the increase in length yields the work $W = F\cdot\Delta l$, or in differential form,

$$\mathrm{d}W = F\cdot\mathrm{d}l.$$

This work is stored by the rubber band such that the energy increase is given by

$$\mathrm{d}E = F\cdot\mathrm{d}l.$$

If we allow the rubber band to return to its original length, all the energy stored in its extended state is released.

If we now replace the rubber band by a strip of plastic material (like chewing gum), we also observe an opposing force when stretching the material. However, this force F is not uniquely determined by the length l of the strip. When the stretching ceases, the force disappears and the strip remains extended. The work performed in stretching the strip by dl against the opposing force F is $\mathrm{d}W = F\cdot\mathrm{d}l$. Similarly, the energy content of the system is given by

$$\mathrm{d}E = F\cdot\mathrm{d}l.$$

In contrast to the example of the rubber band, this energy is not retrievable since the process is irreversible. Systems of this type are less easily described than those exhibiting reversible behavior.

3.1.2. Main Quantities

We shall denote those quantities on the right hand side of the energy equation preceded by the differential symbol d as "work coordinates" (for example, l). PLANCK called these variables "work coordinates". We will call changes in these variables "displacements" (for example, $\mathrm{d}l$), and the corresponding factor multiplying the variable as a "force". An external force is considered positive when it tends to increase the work coordinate. The product of the displacement and the corresponding force is the "work" performed on a system, which describes an increase in energy.

– Examples of “positions” or “work coordinates":
  length, volume, area, amount of “something” (charge, substance …), etc.

– Examples of "forces":
  force, pressure, voltage, potential, etc.

– Examples of "work":
  mechanical, magnetic, electric, thermal, chemical, etc.

In the following sections we shall only consider lossless systems, i.e., those capable of releasing all the expended work when the process is reversed. Such systems cannot create entropy internally, $\mathrm{d}S_\mathrm{p} = 0$, and the entropy content can only be changed through an external input, $\mathrm{d}S = \mathrm{d}S_\mathrm{e}$. The selected work coordinates uniquely determine the state of the system, particularly the applicable forces. In this case we refer to the differential equation describing the change in energy of the system as the "main equation", and we call the system "elastic". Expressed mathematically, $\mathrm{d}E$ is a total or complete differential. We will call forces and work coordinates "main quantities". Since we are only interested in the interdependence of forces and positions, we shall choose or define the concepts we need (like stiffness) so as to make them independent of all other details of the selected process, and not use any names that refer to the specific system under consideration, at least in this section.

The energy as a function of the work coordinate, i.e., $E(l)$ in the case of the rubber band, represents the "characteristic function" of an elastic system. Once this function has been determined, all properties of the system described by the main quantities can be determined. Missing forces can be derived from E by taking the derivative. For our rubber band with $\mathrm{d}E = F \cdot \mathrm{d}l$, this yields:

$$F(l) = \frac{\mathrm{d}E(l)}{\mathrm{d}l}.$$

Our description of an elastic system is quite general. It applies to the charging of a capacitor, input of heat to a body or a weight being lifted via a pulley (Fig 3.2). Even a moving body, belongs to this group although this example will not be used later. If we choose the momentum $m \cdot v$ as the work coordinate, then the velocity v becomes the corresponding "force". Since the kinetic energy of a body with constant mass m is $E = \frac{1}{2} m \cdot v^2$, we have:

$$\mathrm{d}E = v\,\mathrm{d}(m \cdot v).$$

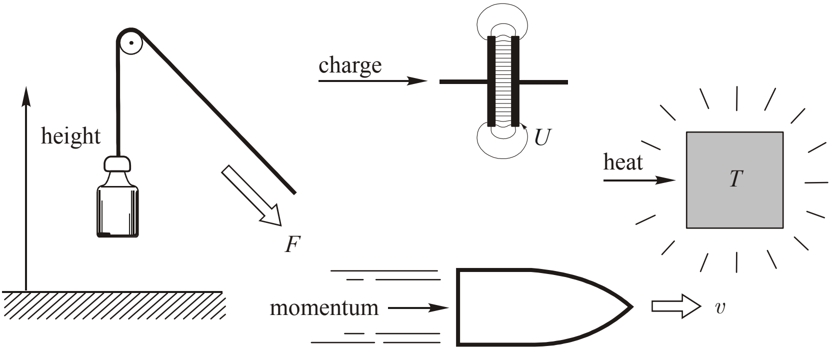

Fig. 3.2: Examples of “elastic” systems

3.1.3. Co- and Counter-Coupling

Consider the following mechanical system: An elastic body of arbitrary shape where two rods are pressing it against a rigid wall with forces F and F' (left side of Figure 3.3). Both rods are free to move and their positions are specified by the coordinates l and l'. However, the two rods are neither totally independent, nor rigidly connected in such a way that the position of one completely determines the position of the other. The connection is "elastic": When one rod is pushed in, the other is pushed out. By holding one rod fixed its motion ceases, but the force, which pushes the rod out increases. We will refer to this kind of interdependence of two processes as counter-coupling, which describes the case where one process hinders the other. We call the opposite behavior, where one process reinforces the other, co-coupling. The right hand side of Figure 3.3 gives an example of the latter.

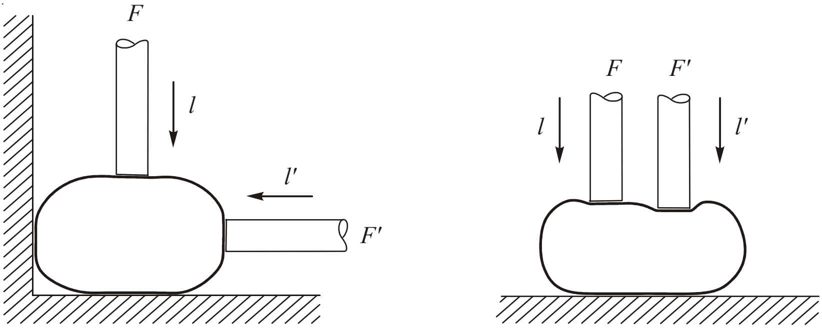

Fig. 3.3: Counter- and Co-coupling of two rods

Instead of focusing on the rods, it is generally more convenient to monitor their work coordinates. Therefore we will introduce the following way of talking: We say that l and l' are elastically coupled, even though they are only mathematical variables. This is either co- or counter-coupling, depending on whether an increase in l results in an increase or decrease in l'.

3.1.4. Energy and Forces

The systems, illustrated in Figure 3.3, have two possibilities for performing and storing work, that is by moving either one rod or the other:

$$\mathrm{d}W = F\cdot\mathrm{d}l \qquad \text{and} \qquad \mathrm{d}W' = F'\cdot\mathrm{d}l'.$$

The energy differential — the increase in the work stored — depends on two possible processes:

$$\mathrm{d}E = F\cdot\mathrm{d}l + F'\cdot\mathrm{d}l'.$$

This is the main equation for our "two-actuator" elastic system (i.e., a system having two independent variables). The variables l and l' are the positions or work coordinates and the factors F and F' represent the corresponding forces. By taking the differential of the characteristic function $E(l, l')$, we obtain:

$$\mathrm{d}E = \left(\frac{\mathrm{d}E}{\mathrm{d}l}\right)_{l'} \cdot \mathrm{d}l + \left(\frac{\mathrm{d}E}{\mathrm{d}l'}\right)_{l} \cdot \mathrm{d}l' .$$

Comparison of the last two equations yields:

$$F = \left(\frac{\mathrm{d}E}{\mathrm{d}l}\right)_{l'}, \quad F' = \left(\frac{\mathrm{d}E}{\mathrm{d}l'}\right)_{l} .$$

This notation for derivatives, commonly used in thermodynamics, indicates the variable held constant during the differentiation by an index outside the brackets. This cumbersome notation shows all the independent variables, here l and l'. The reason why this notation is necessary is that the energy could also be treated as a function of (l, F') or (F, F'), instead of (l, l'). Just writing the derivative as $\mathrm{d}E/\mathrm{d}l$, without mentioning the second variable, would be ambiguous since it could also represent the derivative with respect to l of $E(l, l')$, $E(l, F')$, $E(l, F)$, etc.

The force F depends not only on l, as in the case of the rubber band, but also on the position of the second rod. A similar statement holds for F'. Expressed mathematically:

$$F = F(l, l'), \qquad F' = F'(l, l').$$

Such functions cannot be represented graphically by a single curve; a two-dimensional surface (Fig. 3.4, left side) is now required.

If l increases by $\mathrm{d}l$ while l' is held constant, then F increases by $\mathrm{d}F = (\mathrm{d}F/\mathrm{d}l)_{l'} \cdot \mathrm{d}l$. The notation $(\mathrm{d}F/\mathrm{d}l)_{l'}$ just describes this relationship: an increase in F (numerator) due to an increase in l (denominator) while l' is held constant (index). More intuitively, this coefficient $(\mathrm{d}F/\mathrm{d}l)_{l'}$ represents the "stiffness" of the elastic body in the direction of l: the higher the stiffness, the greater the force needed for a change in the position of the piston while the other piston is fixed. An additional increase in l' by $\mathrm{d}l'$ produces a change of $(\mathrm{d}F/\mathrm{d}l')_{l}\mathrm{d}l'$, and is positive for counter-coupling and negative for co-coupling (Note the sign!). The total change in $\mathrm{d}F$ is now given by:

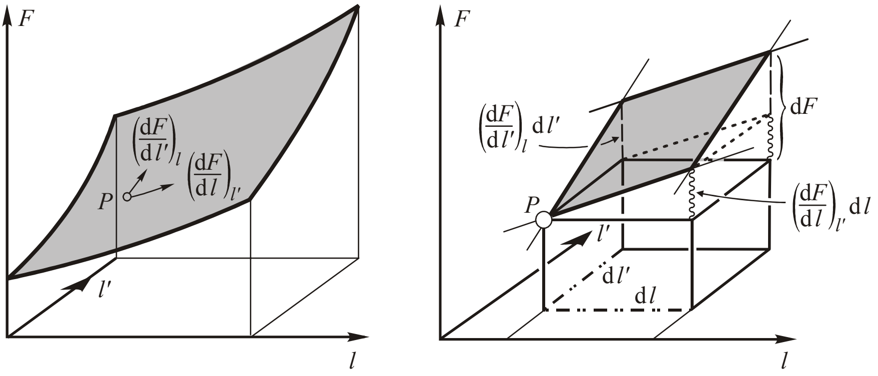

Fig. 3.4: $F(l, l')$-surface (left-hand) and a small section out of it (right-hand)

$$\mathrm{d}F = \underbrace{\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{l'}}_{\text{stiffness}} \mathrm{d}l + \underbrace{\left(\frac{\mathrm{d}F}{\mathrm{d}l'}\right)_{l} \mathrm{d}l'}_{\text{coupling coeff.}},$$

The corresponding equation for F' is:

$$\mathrm{d}F' = \underbrace{\left(\frac{\mathrm{d}F'}{\mathrm{d}l}\right)_{l'}}_{\text{coupling coeff.}'} \mathrm{d}l + \underbrace{\left(\frac{\mathrm{d}F'}{\mathrm{d}l'}\right)_{l}}_{\text{stiffness}'} \mathrm{d}l'.$$

The right side of Figure 3.4 illustrates these relationships by showing a small, almost flat, section of the $F(l, l')$-surface. Since these forces are obtained from the energy derivatives, we can show that the two coefficients resulting from coupling are related by:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}l'}\right)_{l} = \frac{\mathrm{d}^2E}{\mathrm{d}l\cdot\mathrm{d}l'} = \frac{\mathrm{d}^2E}{\mathrm{d}l'\cdot\mathrm{d}l} = \left(\frac{\mathrm{d}F'}{\mathrm{d}l}\right)_{l'}.$$

Note that the order of differentiation is interchangeable (SCHWARZ theorem). For simplicity, the brackets and indices for the two middle terms have been omitted. We will return to this equation later.

3.1.5. Primary and Coupling Effects

During the motion of the rods or, more generally, during a change in work coordinates, we observe various effects.

a) Primary effects and their coefficients:

The farther a rod is pushed in, or the larger l or l' becomes, the greater the corresponding force F or F', respectively. This observation is also valid when no coupling occurs. Such an effect, one that exhibits the interdependence of corresponding quantities, is called a *primary effect*. In our example it is expressed quantitatively by the positive coefficients

$$\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{l'}, \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_{F'}, \left(\frac{\mathrm{d}F'}{\mathrm{d}l'}\right)_{l}, \left(\frac{\mathrm{d}l'}{\mathrm{d}F'}\right)_{F} \cdots$$

These consist of derivatives of the corresponding main quantities such as (F, l) or (F', l'), and not (F', l) or (F, l') ; the index is unimportant here. We call these coefficients primary measures. In order to understand the significance of terms such as $(\mathrm{d}l/\mathrm{d}F)_{F'}$, one could investigate the functions $l(F, F')$ and $l'(F, F')$, instead of considering the dependence of F and F' on the positions of the rods. For instance, the term $(\mathrm{d}l/\mathrm{d}F)_{F'}$ indicates the "softness" of the elastic body in the direction l with F' held fixed.

b) Coupling effects and their coefficients:

The influence exerted by a change in position on the other positions and forces is called a *coupling effect*. The sign of a coupling effect depends on the type of coupling. In the absence of coupling this effect disappears, while the primary effects remain. Consider a system with counter-coupling, such as that illustrated by the left hand side of Figure 3.3. When one rod is pushed in, the other is pushed out, and vice versa. These coupling effects express themselves in two possible ways. If the right rod is held fixed (l' = const.) while the left rod is pushed in, then the force F' increases. If this rod is free to move (F' = const.), then its position l' decreases. This behavior may be described quantitatively by coefficients like

$$\left(\frac{\mathrm{d}F'}{\mathrm{d}l}\right)_{l'}, \left(\frac{\mathrm{d}l'}{\mathrm{d}l}\right)_{F'}, \cdots ,$$

where here the first term is positive and the second negative. In each case the quantity in the numerator and denominator are *not* corresponding main quantities, as seen here in (F', l) and (l', l). We call these kinds of derivatives coupling coefficients. The signs are reversed for co-coupling (right hand side of Figure 3.3). If one rod in that system is pushed in, the other tries to move in the same direction. If we push the rod on the left in and allow the rod on the right to move $(F' = \text{const.})$, its position l' increases. By holding this rod fixed $(l' = \text{const.})$, the force F' decreases. Note that the signs are reversed from those in our previous example.

c) Indirect effects:

It is clear that one rod is affected by the motion of the other rod in our two examples. In both cases, it is harder to push in the left rod if the other rod is held fixed $(l' = \text{const.})$. Conversely, it becomes easier if the other is free to move $(F' = \text{const.})$. This result is independent of the type of coupling (co or counter). Mathematically, this condition is expressed as follows:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{l'} > \left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{F'}, \qquad \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_{l'} < \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_{F'}.$$

In the first case the body appears less elastic, or stiffer, than in the second case. Although the second rod is not directly involved in the primary effect we are looking at, it still affects the motion of the first rod. We will call effects of these kind *indirect effects.* The coefficients differ, physically, because of the change of the constraints, formally, by the change of the index in the corresponding partial derivative.

One further comment about the equation from the end of the last section, $(\mathrm{d}F/\mathrm{d}l')_l = (\mathrm{d}F'/\mathrm{d}l)_{l'}$. The coupling effect described by the first term is numerically equal to that of the second term. This means that the first rod is coupled to the second as strongly as the second is coupled to the first. Stated concisely, the mutual coupling is equally strong, or in other words it is symmetric! This symmetry will be used when we apply the flip rule, or the SCHWARZ theorem, or the MAXWELL equations in traditional thermodynamics derivations (see sections 3.2.2 and 3.7.1).

In conclusion, when we know that the symmetry condition $(\mathrm{d}F/\mathrm{d}l')_l = (\mathrm{d}F'/\mathrm{d}l)_{l'}$ is satisfied, then for an arbitrary system with two coordinates l, l', and two forces $F(l, l')$, $F'(l, l')$, the differential $\mathrm{d}E = F{\cdot}\mathrm{d}l + F'{\cdot}\mathrm{d}l'$ is complete, i.e., we can say that the energy is a function of the coordinates $E = E(l, l')$. Physically, this means that we are dealing with an elastic system, as assumed earlier. Symmetric coupling is therefore a distinguishing feature of an elastic system.

3.1.6. Unstable Behavior

We have found that the coefficients for primary effects are positive for the elastic bodies in Figure 3.3. In general, it can be demonstrated that these coefficients should always be positive to avoid unstable behavior. An elastic system under the influence of constant, or zero external forces is referred to as unstable if a small perturbation can disturb its initial state of equilibrium. (See the examples shown in Figure 3.5; the weight on the left hand side does not form part of the system but only depicts graphically the constant external force.) Equilibrium can be achieved through a proper selection of the external force for any value of the position or work coordinate.

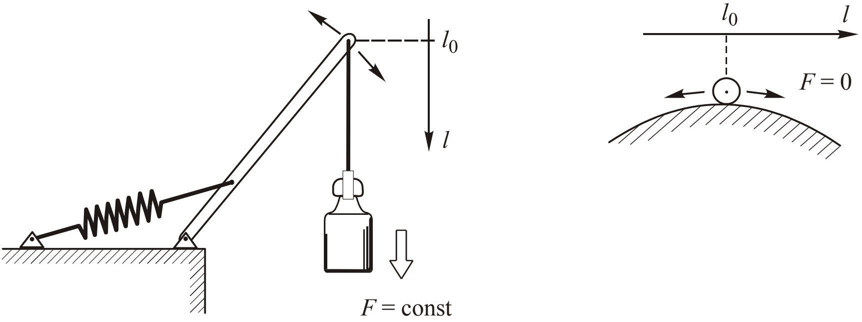

Fig. 3.5: Examples of unstable equilibrium

For clarification, let us consider a rubber band as in Figure 3.1, now with a body with weight G hanging from it. We now assume that, unlike in normal rubber bands, $\mathrm{d}F/\mathrm{d}l < 0$. In the initial state the opposing force F balances the weight: $F = G$. A small downward disturbance (increase in l) leads to a *reduction* in F such that $G > F$. The resulting force does not drive the weight up to its equilibrium position but farther away, aggravating the imbalance between F and G and accelerating the downward motion. An upward perturbation of the initial state will drive the weight up.

The reason for such unstable behavior is the assumption that $\mathrm{d}F/\mathrm{d}l < 0$. Clearly, we can expect unstable behavior in all cases where the force decreases with increasing work coordinate, or in other words, where the coefficient of the primary effect is negative.

So far statements regarding the sign and magnitude of the coefficients have been developed heuristically. These can be derived formally for a system, which is stable (which is almost always the case), and where the type of coupling between work coordinates is known. This means that the essential structure of a stable, elastic system is determined by the statements about coupling, independent of its mechanical, thermal, electrical or other properties. Structural conclusions can thus be extended from a familiar to a less familiar system with the same kind of coupling and stability. Therein lies the value of the current consideration.

3.2. Mathematical Rules for Derivatives

In this section we shall present some mathematical rules for expressing a derivative in terms of others, for example by derivatives that can be measured more conveniently. With an abundance of possible coefficients, any means of saving time is very useful. Although we are dealing with purely mathematical relationships here, we will highlight their physical significance. In the following, the variables u, v, w … describe the properties of the system, and the mutually independent parameters z_1, z_2, … z_n characterize the state of the system. Thus the quantities u, v, w … that can depend on each other in various ways are functions of z_i.

3.2.1. Change of Variable

In thermodynamics, where many equations are conveniently expressed in differential form, a change of variables is sometimes required for the derivatives. To make such a change to a derivative $(\mathrm{d}u/\mathrm{d}v)_{v'\,v''\ldots}$ of a function $u(v, v', v'' \ldots)$, it is useful to apply the fact that a derivative can be written as a ratio of two differentials:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_a = \frac{(\mathrm{d}u)_a}{(\mathrm{d}v)_a},$$

provided that the denominator does not vanish. The index a indicates, here and subsequently, an abbreviation for the quantities that are unimportant for the current development. In this example, a stands for the unimportant quantities v', v''... The symbols $(\mathrm{d}u)_a$ and $(\mathrm{d}v)_a$ denote differentials of u and v which can be functions of other variables — for instance, v, v', v'' ... or the parameters z_1, z_2, ... z_n — while a is held constant. A typical procedure involves the following: the two differentials are separately computed, based on mathematical or thermodynamic relations, and divided by each other. The resulting ratio of differentials is again represented by the usual derivative notation (see section 3.7.3). As a simple example, if we choose v, v', v'' ... as independent variables, then the total differential is given by

$$\mathrm{d}u = \left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_{v'v''\ldots} \mathrm{d}v + \left(\frac{\mathrm{d}u}{\mathrm{d}v'}\right)_{vv''\ldots} \mathrm{d}v' + \left(\frac{\mathrm{d}u}{\mathrm{d}v''}\right)_{vv'\ldots} \mathrm{d}v'' + \ldots$$

The requirement that a remains constant means that $(\mathrm{d}v)_a = \mathrm{d}v$, $(\mathrm{d}v')_a = 0$, $(\mathrm{d}v'')_a = 0$, ... , so that only the first term of the equation remains

$$(\mathrm{d}u)_a = \left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_a (\mathrm{d}v)_a .$$

By dividing by $(\mathrm{d}v)_a$, we regain the original expression.

In order to shorten the procedure further, it is useful to become familiar with some additional rules. Five simple operations will allow us to accomplish the task of changing derivatives to new variables. Section 3.2.2 discusses the fifth operation, and section 3.2.3 discusses the detailed applications. For ease of reference we shall give names to these operations.

a) *Inversion*:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_a = 1 \Big/ \left(\frac{\mathrm{d}v}{\mathrm{d}u}\right)_a$$

b) *Expansion*:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_a = \left(\frac{\mathrm{d}u}{\mathrm{d}w}\right)_a \left(\frac{\mathrm{d}w}{\mathrm{d}v}\right)_a$$

Note that the same index is used in each term!

c) *Inserting an index*:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_{wa} = -\left(\frac{\mathrm{d}u}{\mathrm{d}w}\right)_{va}\left(\frac{\mathrm{d}w}{\mathrm{d}v}\right)_{ua}$$

Note the minus sign, and that each term contains the complete set of variables u, v, w, a!

d) *Replacing an index*

$$\left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_{\underbrace{za}} = \left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_{\underbrace{wa}} + \left(\frac{\mathrm{d}u}{\mathrm{d}w}\right)_{\underbrace{va}}\left(\frac{\mathrm{d}w}{\mathrm{d}v}\right)_{\underbrace{za}}$$

If we wish to replace the index z with w in the original derivative $(\mathrm{d}u/\mathrm{d}v)_{za}$, we write down the derivative with the new variable w in the index, and then add the expansion of the original derivative with respect to the new variable w as a "correction term". The first factor in the "correction term" contains the new independent variables w, v, a, while the second factor contains the original set v, z, a.

For these rules to be valid, we require that the derivatives on both sides of the equation exist, i.e., the quantities in the numerator must be differentiable functions of the variables represented by the denominator and index.

For the following derivations, we use the property that a derivative can be represented by a ratio of differentials.

For a) $$\left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_a = \frac{(\mathrm{d}u)_a}{(\mathrm{d}v)_a} = 1\Big/\frac{(\mathrm{d}v)_a}{(\mathrm{d}u)_a} = 1\Big/\left(\frac{\mathrm{d}v}{\mathrm{d}u}\right)_a .$$

For b) $$\left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_a = \frac{(\mathrm{d}u)_a}{(\mathrm{d}v)_a} = \frac{(\mathrm{d}u)_a}{(\mathrm{d}w)_a}\frac{(\mathrm{d}w)_a}{(\mathrm{d}v)_a} = \left(\frac{\mathrm{d}u}{\mathrm{d}w}\right)_a\left(\frac{\mathrm{d}w}{\mathrm{d}v}\right)_a .$$

For c) By selecting u, v, a as independent variables, the differentials du, dv, da and dw of the quantities contained in the original expression are

$$\mathrm{d}u,\quad \mathrm{d}v,\quad \mathrm{d}a,\quad \mathrm{d}w = \left(\frac{\mathrm{d}w}{\mathrm{d}u}\right)_{va}\mathrm{d}u + \left(\frac{\mathrm{d}w}{\mathrm{d}v}\right)_{ua}\mathrm{d}v + \left(\frac{\mathrm{d}w}{\mathrm{d}a}\right)_{uv}\mathrm{d}a .$$

For constant w and a, $\mathrm{d}w = 0$ and $\mathrm{d}a = 0$, which leads to the relationship between du and dv

$$(\mathrm{d}u)_{wa} = -\left(\frac{\mathrm{d}w}{\mathrm{d}v}\right)_{ua} (\mathrm{d}v)_{wa} \Big/ \left(\frac{\mathrm{d}w}{\mathrm{d}u}\right)_{va} .$$

This results in the desired equation after dividing by $(\mathrm{d}v)_{wa}$ and inverting the denominator.

For d) With v, w, a as independent variables, we get

$$\mathrm{d}u = \left(\frac{\mathrm{d}u}{\mathrm{d}v}\right)_{wa} \mathrm{d}v + \left(\frac{\mathrm{d}u}{\mathrm{d}w}\right)_{va} \mathrm{d}w + \left(\frac{\mathrm{d}u}{\mathrm{d}a}\right)_{vw} \mathrm{d}a .$$

The differentials dv, dw, da are developed similarly by treating v, z, a as independent variables. For constant z and a, we obtain

$$(\mathrm{d}v)_{za} = \mathrm{d}v, \quad (\mathrm{d}w)_{za} = \left(\frac{\mathrm{d}w}{\mathrm{d}v}\right)_{za} \mathrm{d}v, \quad (\mathrm{d}a)_{za} = 0 .$$

By substituting into the differential equation for du, which yields $(\mathrm{d}u)_{za}$, and dividing by dv or $(\mathrm{d}v)_{za}$, we get the desired equation.

3.2.2. Flip Rule

Next we discuss a rule that is associated with the coupling phenomena in a special way. Let us start with a differential of n terms. We can consider this the main equation of an elastic system with n independent variables (n-actuator system):

$$\mathrm{d}E = y_1\mathrm{d}x_1 + y_2\mathrm{d}x_2 + y_3\mathrm{d}x_3 + \ldots + y_n\mathrm{d}x_n .$$

The x variables represent the position or work coordinates and the y variables, each of which can depend on all x variables due to coupling, represent the corresponding forces. All x variables are "of same type", just like the y variables. An x and y variable with the same subscript belong together as a pair, and we will refer to them as "paired".

There are a total of n^2 possible derivatives of y with respect to x

$$\left(\frac{\mathrm{d}y_i}{\mathrm{d}x_j}\right)_{x_{\hat{j}}} \qquad (i, j = 1, 2, 3 \ldots n, \quad x_{\hat{j}} \text{ stands for all } x \text{ without } x_j)$$

but they are not all different. Recall that the y_i variables can be expressed as derivatives of E with respect to x_i:

$$y_i = \left(\frac{\mathrm{d}E}{\mathrm{d}x_i}\right)_{x_{\hat{i}}} \qquad (i = 1, 2, 3 \ldots n, \quad x_{\hat{i}} \text{ stands for all } x \text{ without } x_i)$$

Since the order of differentiation is interchangeable, we get:

$$\left(\frac{\mathrm{d}y_i}{\mathrm{d}x_j}\right)_{x_{\hat{j}}} = \left(\frac{\mathrm{d}^2 E}{\mathrm{d}x_i\,\mathrm{d}x_j}\right) = \left(\frac{\mathrm{d}^2 E}{\mathrm{d}x_j\,\mathrm{d}x_i}\right) = \left(\frac{\mathrm{d}y_j}{\mathrm{d}x_i}\right)_{x_{\hat{i}}} .$$

Physically, this mathematical relationship may be interpreted as symmetry of coupling of the work coordinates, denoted here by x_i and x_j. We had done this previously. We can now formally describe the transition from the first to the last term. The procedure may seem a bit complicated, but we will see later that it is necessary for the multiple applications where we will employ it:

a) Exchange the variables in the numerator and denominator, and substitute these variables with their *paired* counterparts.

b) Reverse the sign in the case where the numerator and denominator contain variables of *the same type*.

c) The index consists of all *unpaired* variables in the original expression, and additionally of those *paired* variables that are absent.

The word "unpaired" means that one member of the pair is missing. We can clarify these rules with a concrete example ($n = 4$):

$$\left(\frac{\mathrm{d}y_1}{\mathrm{d}x_3}\right)_{x_1, x_2, x_4} \overset{\text{a)}}{\rightleftarrows} \left(\frac{\mathrm{d}y_3}{\mathrm{d}x_1}\right) \xrightarrow{\text{b)}} \left(\frac{\mathrm{d}y_3}{\mathrm{d}x_1}\right) \xrightarrow{\text{c)}} \left(\frac{\mathrm{d}y_3}{\mathrm{d}x_1}\right)_{x_2, x_3, x_4}$$

For a) The counterpart of y_1 is x_1 and that of x_3 is y_3. Consequently, x_1 goes into the denominator and y_3 into the numerator.

For b) The sign remains positive since y_3 represents a force and x_1 a work coordinate. They are not of the same type.

For c) Only x_2, x_3, x_4 are unpaired in the original expression, and therefore make up the new index. Additional pairs are not introduced because each of the four pairs x_i, y_i are represented by at least one member in the original expression.

We obtain the same result with the second derivatives of the energy function $E(x_1, x_2, \dots, x_n)$.

Steps a) through c) comprise a mathematical operation that we will call "*flipping*." This procedure allows us to go directly to the final expression without making a detour via energy derivatives. We say that a derivative can be "flipped" if the resultant derivative, as illustrated above, leads to the same numerical value. Before we focus on the properties of these operations, let us make an aside:

Instead of choosing the *x* variables as independent variables, one can, as a general rule, pick *n* quantities that depend on the *n* remaining variables. For example, for the elastic body with $n = 2$, where the energy differential is given by $\mathrm{d}E = F \cdot \mathrm{d}l + F' \cdot \mathrm{d}l'$:

$$\begin{array}{ccccc} l = l(F, F') & & F = F(l, F') & & l' = l'(F, l) \\ & \text{or} & & \text{or} & & \text{etc.} \\ l' = l'(F, F') & & l' = l'(l, F') & & F' = F'(F, l) \end{array}$$

Every differential quotient composed of $n + 1$ arbitrarily selected main quantities may be a derivative of such a function. Two of the quantities appear in the quotient itself, and the remaining $n - 1$ are indices. We can ignore degenerate cases, such as a system without coupling, where this statement is false. Applied to our example, this means that all differential quotients formally composed of $n + 1 = 3$ arbitrary chosen quantities from the whole set F, F', l, l' represent meaningful coefficients:

$$\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_{F'}, \quad \left(\frac{\mathrm{d}l'}{\mathrm{d}l}\right)_{F'}, \quad \left(\frac{\mathrm{d}F'}{\mathrm{d}F}\right)_{l}, \quad \text{etc.}$$

The "flip rule" states that each such derivative can be flipped. Thus, we immediately obtain via this rule a large number of important relationships that, as we will show later, may be considered all as results of an equally strong, symmetric coupling.

A prerequisite for applying the "flip rule" is that, for a system with $2n$ arbitrary variables $x_1, x_2 \dots x_n, y_1, y_2 \dots y_n$, where all y_k are functions of all x_k, the following relationship holds for all *i* and *j*

$$\left(\frac{\mathrm{d}y_i}{\mathrm{d}x_j}\right)_{x_{\hat{j}}} = \left(\frac{\mathrm{d}y_j}{\mathrm{d}x_i}\right)_{x_{\hat{i}}} \qquad (i, j = 1, 2, 3 \dots n). \qquad (*)$$

If this equation is valid, we can use the "flip" operation on any meaningful, but otherwise arbitrary derivative composed using x_k and y_k, without changing its value. We have seen previously that the main quantities of an elastic system satisfy this requirement. In other words, the two work coordinates x_i and x_j are symmetrically coupled. We will discuss the proof of the "flip rule" soon.

In order to practice using the flip rule, let us consider another example in detail ($n = 4$):

$$\left(\frac{\mathrm{d}y_2}{\mathrm{d}y_1}\right)_{x_2,x_3,y_3} \xrightarrow{\text{a)}} \left(\frac{\mathrm{d}x_1}{\mathrm{d}x_2}\right) \xrightarrow{\text{b)}} -\left(\frac{\mathrm{d}x_1}{\mathrm{d}x_2}\right) \xrightarrow{\text{c)}} \left(\frac{\mathrm{d}x_1}{\mathrm{d}x_2}\right)_{y_1,x_4,y_4}$$

For a) y_2 and y_1 are exchanged and simultaneously replaced by their counterparts, x_2 for y_2 and x_1 for y_1.

For b) The sign becomes negative since x_1 and x_2 are both work coordinates, and therefore are of the same type.

For c) Only y_1 is unpaired amongst the five variables in the original expression. It goes into the index along with the pair x_4, y_4 missing in the original term.

According to the flip rule, the left-hand and right-hand expressions are equal.

Let us now consider the still easy but particularly important case of $n = 2$ in order to demonstrate how the flip rule may be proofed*. We will do this simply by examining each of the 24 possible differential quotients. As starting point, we use, the condition that the four quantities x_1, x_2, y_1, y_2 are related by

$$\left(\frac{\mathrm{d}y_1}{\mathrm{d}x_2}\right)_{x_1} = \left(\frac{\mathrm{d}y_2}{\mathrm{d}x_1}\right)_{x_2} .$$

This equation is obtained from the general case (*) with $n = 2$, $i = 1$ and $j = 2$. The cases $i = 1$, $j = 1$ and $i = 2$, $j = 2$ as well as $i = 2$, $j = 1$ do not generate new relations and can therefore be left out.

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[*] Complete proof: G. Job, Z. Naturforsch. **25a** (1970) 1502

If we "expand" the derivative on the left-hand side by y_2 and "insert" the index x_2 into the derivative on the right-hand side, we get

$$\left(\frac{dy_1}{dy_2}\right)_{x_1}\cdot\left(\frac{dy_2}{dx_2}\right)_{x_1}=-\left(\frac{dy_2}{dx_2}\right)_{x_1}\cdot\left(\frac{dx_2}{dx_1}\right)_{y_2}\quad\text{or}\quad\left(\frac{dy_1}{dy_2}\right)_{x_1}=-\left(\frac{dx_2}{dx_1}\right)_{y_2}.$$

Continuing the transformation by inserting the index x_1 into the derivative on the left-hand side, and expanding the derivative on the right-hand side by y_1, we obtain

$$-\left(\frac{dy_1}{dx_1}\right)_{y_2}\cdot\left(\frac{dx_1}{dy_2}\right)_{y_1}=-\left(\frac{dx_2}{dy_1}\right)_{y_2}\cdot\left(\frac{dy_1}{dx_1}\right)_{y_2}\quad\text{or}\quad\left(\frac{dx_1}{dy_2}\right)_{y_1}=\left(\frac{dx_2}{dy_1}\right)_{y_2},$$

and from a similar computation with x_2, y_2

$$\left(\frac{dx_1}{dx_2}\right)_{y_1}\cdot\left(\frac{dx_2}{dy_2}\right)_{y_1}=-\left(\frac{dx_2}{dy_2}\right)_{y_1}\cdot\left(\frac{dy_2}{dy_1}\right)_{x_2}\quad\text{or}\quad\left(\frac{dx_1}{dx_2}\right)_{y_1}=-\left(\frac{dy_2}{dy_1}\right)_{x_2}.$$

By taking the inverse of all differential quotients in the last four equations on the right, we get four additional relations

$$\left(\frac{dx_2}{dy_1}\right)_{x_1}=\left(\frac{dx_1}{dy_2}\right)_{x_2},\qquad\left(\frac{dy_2}{dy_1}\right)_{x_1}=-\left(\frac{dx_1}{dx_2}\right)_{y_2},$$

$$\left(\frac{dy_2}{dx_1}\right)_{y_1}=\left(\frac{dy_1}{dx_2}\right)_{y_2},\qquad\left(\frac{dx_2}{dx_1}\right)_{y_1}=-\left(\frac{dy_1}{dy_2}\right)_{x_2}.$$

Finally, let us list all expressions containing the pairs x_1, y_1 or x_2, y_2 in the quotients itself:

$$\left(\frac{dy_1}{dx_1}\right)_{x_2},\left(\frac{dy_1}{dx_1}\right)_{y_2},\qquad\left(\frac{dx_1}{dy_1}\right)_{x_2},\left(\frac{dx_1}{dy_1}\right)_{y_2},$$

$$\left(\frac{dy_2}{dx_2}\right)_{x_1},\left(\frac{dy_2}{dx_2}\right)_{y_1},\qquad\left(\frac{dx_2}{dy_2}\right)_{x_1},\left(\frac{dx_2}{dy_2}\right)_{y_1}.$$

This list and the above eight equations comprise the total number of meaningful differential quotients that can be formed from the quantities x_1, x_2, y_1, y_2. Each derivative symbol involves three of the four variables. By applying the flipping operation, the expression either remain unchanged — as is the case for the last eight derivatives — or they change into the expression given on the other side of the equation. In all cases, the value of the derivative is unchanged. Thus, we have proved the validity of the flip rule for the two-dimensional case ($n = 2$).

3.2.3. Application Guidelines

Even the best tools are useless if one does not know how to work with them. Therefore, user instructions are just as important as the tools themselves. A frequently occurring task in thermodynamics is to express given coefficients in a known or more easily measurable form. For a systematic approach it makes sense to organize the used variables on the basis of accessibility. We will start with the main equation and establish a preferred sequence for its parameters. The most conveniently measured variable pair is listed first with "lowest rank" and the following ones possess increasing degrees of difficulty. Within each pair we will underline the one, which is more easily accessible. In this way the main quantities are split into two groups of equal size, "accessible" and "inaccessible" variables, and ranked on the basis of measurability (in addition to dividing them into forces and positions).

In our previous mechanical example (Figure 3.3) the differences are not very pronounced and the ranking of the variables becomes somewhat arbitrary. Let us assume that the positions of the rods are more easily determined than forces and the quantities referring to the rod on the left (without a prime) are simpler than those of the other rod (with a prime), then the main equation becomes:

$$\mathrm{d}E = F \cdot \mathrm{d}\underline{l} + F' \cdot \mathrm{d}\underline{l'}\,.$$

Under normal circumstances the familiar derivatives contain only easily measurable quantities as independent variables since these parameters can be more readily adjusted in an experiment. This gives the first rule for a systematic transformation procedure

a) The given derivative is transformed into expressions, which contain only derivatives, where only accessible variables appear in the denominator and the indices.

There are some simple but adequate aids available for performing this task. The first step depends on the type of the quotient:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_a, \quad \left(\frac{\mathrm{d}z}{\mathrm{d}u}\right)_a, \quad \left(\frac{\mathrm{d}z}{\mathrm{d}z'}\right)_a, \quad \left(\frac{\mathrm{d}u}{\mathrm{d}u'}\right)_a,$$

(z, z', … "accessible", u, u', … "inaccessible" main quantities as well as other variables, a, a', … serve as abbreviation for one or more quantities in the index, which are without interest at the moment). The first quotient is already in the correct form. We get the desired shape for the second quotient by *inverting* it. The desired result for the third quotient can be obtained by *inserting* a variable from the index and for the forth quotient by *expanding* it with an additional variable, and then – in both cases – *inverting* one of the new derivatives. At the same time, this procedure can be used to eliminate an unwanted variable u from the index $a = (u, a')$ of the third derivative $(\mathrm{d}z/\mathrm{d}z')_a$, and to introduce one missing desirable variable z in the forth derivative $(\mathrm{d}u/\mathrm{d}u')_a$:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_a$$

(Expression remains unchanged.),

$$\left(\frac{\mathrm{d}z}{\mathrm{d}u}\right)_a = 1\bigg/\left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_a$$

(Quotient is *inverted*.),

$$\left(\frac{\mathrm{d}z}{\mathrm{d}z'}\right)_{ua'} = -\left(\frac{\mathrm{d}z}{\mathrm{d}u}\right)_{z'a'} \cdot \left(\frac{\mathrm{d}u}{\mathrm{d}z'}\right)_{za'} = -\left(\frac{\mathrm{d}u}{\mathrm{d}z'}\right)_{za'} \bigg/ \left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_{z'a'}$$

(Index u is *inserted*, then the *first* factor in the intermediate result is *inverted*.),

$$\left(\frac{\mathrm{d}u}{\mathrm{d}u'}\right)_a = \left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_a \cdot \left(\frac{\mathrm{d}z}{\mathrm{d}u'}\right)_a = \left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_a \bigg/ \left(\frac{\mathrm{d}u'}{\mathrm{d}z}\right)_a$$

(The given quotient is *expanded* by the variable z, then the *second* factor in the intermediate result is *inverted*.).

If these "cleaned-up" expressions still have unwanted quantities such as u' in the index $a = (u', a')$, then these can be eliminated by using the rule for *replacing* an index combined with the other operations discussed above:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_{u'a'} = \left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_{z'a'} + \left(\frac{\mathrm{d}u}{\mathrm{d}z'}\right)_{za'} \cdot \left(\frac{\mathrm{d}z'}{\mathrm{d}z}\right)_{u'a'} = \ldots = \left(\frac{\mathrm{d}u}{\mathrm{d}z}\right)_{z'a'} - \left(\frac{\mathrm{d}u}{\mathrm{d}z'}\right)_{za'} \cdot \frac{\left(\frac{\mathrm{d}u'}{\mathrm{d}z}\right)_{z'a'}}{\left(\frac{\mathrm{d}u'}{\mathrm{d}z'}\right)_{za'}}$$

With practice, the intermediate steps may be skipped and we can go directly to the final result. But at the first stage of learning it may be better to proceed slowly step by step.

A derivative obtained by applying the flip rule is generally measurable if the variable in the numerator belongs to a higher-ranking pair than that in the denominator. This leads immediately to a second rule for the desired transformation:

b) All generated quotients that contain a numerator with higher rank than the denominator (“top-heavy” quotients) are flipped.

Let us consider briefly whether this step is consistent with our efforts to make all independent variables accessible. A quotient, prior to being flipped, must have the form $(\mathrm{d}u/\mathrm{d}z')_{a}$ where $a = (z, a')$ contains the force or work coordinate z associated with u, and a' consists of all unpaired main quantities. After flipping, we get

$$\left(\frac{\mathrm{d}u}{\mathrm{d}z'}\right)_{za'} = \left(\frac{\mathrm{d}u'}{\mathrm{d}z}\right)_{z'a'},$$

where u' relates to z'. Thus, the flipped expression has the desired form.

By transforming all derivatives according to these rules, we will eventually reach a point where all derivatives contain desirable variables in their denominators and indices, and the quantities in the numerator are of lower rank than those in the denominator. In general, we have reached our goal of turning an unfamiliar expression into a known one. If this is not the case and there are other, more easily measurable coefficients in the system, we can subject these new coefficients to the above procedure and hence obtain additional equations between the various terms. By means of these new equations we can replace any undesired coefficients with the more favorable ones. This procedure corresponds to the elimination of a variable from a system of equations with several unknowns.

To ease quotation, the frequently used procedure described by steps a) and b) is given a name. A derivative changed by this procedure is said to be "cut back" to the variables $v_1, v_2, v_3 \ldots$ (like cutting back a tree, shrub or hedge to a desired shape), where $v_1, v_2, v_3 \ldots$ denotes the selected accessible main quantities arranged according to increasing rank.

3.2.4. Applications

Let us return to the elastic body. We assume that the "stiffness" of this body in each direction, $s = (\mathrm{d}F/\mathrm{d}l)_{l'}$ and $s' = (\mathrm{d}F'/\mathrm{d}l')_{l}$, as well as the coupling coefficient $f = (\mathrm{d}F/\mathrm{d}l')_{l}$ are known. f is a measure for the strength of coupling. By definition, f is positive when the two rods oppose each other. All other coefficients can be related to these three coefficients, as can be shown by "cutting back": to the variables l and l'. Here are a few examples where the comments in parentheses clarify each computational step.

a) "Softness" while holding the second rod fixed:

$$\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_{l'} = 1\Big/\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{l'} = \frac{1}{s}\frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

(This is of type $(\mathrm{d}z/\mathrm{d}u)_a$, which has to be inverted). This coefficient simply equals the inverse of the "stiffness" s.

b) Displacement of the second rod caused by the first:

$$\left(\frac{\mathrm{d}l'}{\mathrm{d}l}\right)_{F'} = -\left(\frac{\mathrm{d}l'}{\mathrm{d}F'}\right)_{l}\cdot\left(\frac{\mathrm{d}F'}{\mathrm{d}l}\right)_{l'} = -\left(\frac{\mathrm{d}F}{\mathrm{d}l'}\right)_{l}\Big/\left(\frac{\mathrm{d}F'}{\mathrm{d}l'}\right)_{l} = -\frac{f}{s'}$$

(This is of type $(\mathrm{d}z/\mathrm{d}z')_a$, where we insert a variable from the index, here F', invert the first factor of type $(\mathrm{d}z/\mathrm{d}u)_a$, and flip the second factor since F' has higher rank than l). The coefficient is negative, as expected for opposing interactions.

c) "Stiffness" with a constant force on the second rod:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{F'} = \left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{l'} + \left(\frac{\mathrm{d}F}{\mathrm{d}l'}\right)_{l}\cdot\left(\frac{\mathrm{d}l'}{\mathrm{d}l}\right)_{F'} = s - f\left(\frac{\mathrm{d}l'}{\mathrm{d}F'}\right)_{l}\cdot\left(\frac{\mathrm{d}F'}{\mathrm{d}l}\right)_{l'}$$

$$= s - f\cdot\left(\frac{\mathrm{d}F}{\mathrm{d}l'}\right)_{l}\Big/\left(\frac{\mathrm{d}F'}{\mathrm{d}l'}\right)_{l} = s - \frac{f^2}{s'}$$

(This is of type $(\mathrm{d}u/\mathrm{d}z)_a$, where we replace the inaccessible F' by l' and process the second factor as in b) above). The term $-f^2/s'$, which measures the magnitude of the force on the second rod due to the motion of the first rod, is negative for both co-coupling $(f < 0)$ and counter-coupling $(f > 0)$. This result shows formally what we concluded intuitively earlier, i.e., the body appears more elastic when the second rod is allowed to move (F' is constant) than when it is held fixed (l' is constant):

$$\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{F'} < \left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_{l'}$$

d) Now assume that we know s, s' and the coefficient from c) denoted by s^* instead of s, s' and f. As before, let us compute the coefficients in a) and b). In the case of a) nothing changes because by "cutting back" to l, l' (see above), the final expression contains the familiar s. In the case of b) we have to cut back to s^* and l, l' in order to eliminate the undesirable quantity f via a new equation:

$$\left(\frac{\mathrm{d}l'}{\mathrm{d}l}\right)_{F'} = -\frac{f}{s'}, \quad s^* = s - \frac{f^2}{s'}$$

(Calculation as in b) and c)). We can eliminate the unknown f since $f = \sqrt{(s-s^*)s'}$ from the second equation, and substitution of this expression into the first gives the final result:

$$\left(\frac{\mathrm{d}l'}{\mathrm{d}l}\right)_{F'} = -\sqrt{\frac{s-s^*}{s'}}$$

3.2.5. Necessary Number of Known Coefficients

During the computation of the different coefficients for the elastic body we assumed that three of these coefficients were known. How many derivatives have to be known in order to express the remaining derivatives of first order composed of main quantities? The answer is

$$\frac{n\cdot(n+1)}{2}$$

for an n-actuator system. For $n = 2$, we get the value 3 used earlier. Now let us substantiate this claim:

By "cutting back" any derivative of that form constructed from main quantities, we end up with an expression consisting of derivatives with n accessible independent variables listed in order of increasing rank $z_1, z_2 \ldots z_n$. Since the remaining n main quantities $u_1, u_2 \ldots u_n$ can be differentiated with respect to each variable z, we obtain a total of n^2 derivatives:

$$\begin{array}{cccc}
\left(\frac{\mathrm{d}u_1}{\mathrm{d}z_1}\right)_{z_{\hat{1}}} & \left(\frac{\mathrm{d}u_1}{\mathrm{d}z_2}\right)_{z_{\hat{2}}} & \ldots & \left(\frac{\mathrm{d}u_1}{\mathrm{d}z_n}\right)_{z_{\hat{n}}} \\
\left(\frac{\mathrm{d}u_2}{\mathrm{d}z_1}\right)_{z_{\hat{1}}} & \left(\frac{\mathrm{d}u_2}{\mathrm{d}z_2}\right)_{z_{\hat{2}}} & \ldots & \left(\frac{\mathrm{d}u_2}{\mathrm{d}z_n}\right)_{z_{\hat{n}}} \\
\ldots & \ldots & \ldots & \ldots \\
\left(\frac{\mathrm{d}u_n}{\mathrm{d}z_1}\right)_{z_{\hat{1}}} & \left(\frac{\mathrm{d}u_n}{\mathrm{d}z_2}\right)_{z_{\hat{2}}} & \ldots & \left(\frac{\mathrm{d}u_n}{\mathrm{d}z_n}\right)_{z_{\hat{n}}}
\end{array}.$$

On the basis of the flip rule all derivatives that are symmetrically located relative to the diagonal have the same value. Thus, we can ignore all terms below the diagonal since, for each of these terms, the numerator has a higher rank than the denominator. By counting the remaining terms, we get

$$1+2+3\ldots+n=\frac{n(n+1)}{2}.$$

This number does not change even if one or more derivatives are replaced by more easily measurable ones or for any preferred ones, as illustrated in the previous section. However, when square roots are involved, this procedure introduces some uncertainty as to the sign.

3.3 Simple Examples of Mechanical-Thermal Coupling

After this thorough preparation, we now return to thermodynamics. Initially we shall examine the interrelationships between thermal and mechanical changes to a body. As a guide, we shall use the example of elastic coupling.

3.3.1. Deformation of a Body

Consider a system that is closely related to our mechanical ideal, the elastic body. As illustrated by Figure 3.6, one of the rods is replaced by an "entropy syringe" that allows us to overcome thermal tension and add entropy to the elastic body. The elastic body can be considered as an inflated, thermally insulated rubber ball. (Note: the rod and syringe in Figure 3.6 do not form part of the system).

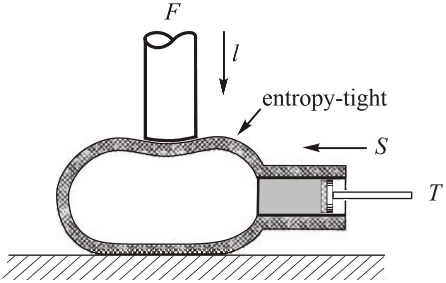


Fig. 3.6: Coupling of a mechanical coordinate *l* with a thermal *S*

The processes of "pushing in a rod" and "adding entropy" are not independent but are mutually coupled. Qualitatively they bear the same relationship as counter-coupling in our mechanical example. This follows readily from our earlier discussions of entropy, or heat*. The observed effects can be classified the same way as in the case of the elastic mechanical body (here, we will not consider the coefficients that describe quantitatively the individual effects).

a) Primary effects:

– The further the rod is pushed in, the greater the resistive force F becomes.

$$\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_S > 0\,, \qquad \left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_T > 0\;\ldots$$

– The more entropy is added, the higher the thermal tension rises inside the rubber ball.

$$\left(\frac{\mathrm{d}T}{\mathrm{d}S}\right)_l > 0\,, \qquad \left(\frac{\mathrm{d}T}{\mathrm{d}S}\right)_F > 0\;\ldots$$

b) Coupling effects:

– If we push in the rod, then entropy is forced out. If the entropy is sealed in, the temperature rises.

$$\left(\frac{\mathrm{d}S}{\mathrm{d}l}\right)_T < 0\,, \qquad \left(\frac{\mathrm{d}T}{\mathrm{d}l}\right)_S > 0\;\ldots$$

– If we add entropy, the rod is pushed out. If we hold the rod fixed, the force acting on it increases.

$$\left(\frac{\mathrm{d}l}{\mathrm{d}S}\right)_F < 0\,, \qquad \left(\frac{\mathrm{d}F}{\mathrm{d}S}\right)_l > 0\;\ldots$$

c) Indirect effects:

– It is easier to push in the rod if we allow entropy to escape; harder if entropy is sealed in.

$$\left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_S > \left(\frac{\mathrm{d}F}{\mathrm{d}l}\right)_T .$$

– It is easier to add entropy if we allow the rod to move, harder if the rod is held fixed.

$$\left(\frac{\mathrm{d}T}{\mathrm{d}S}\right)_l > \left(\frac{\mathrm{d}T}{\mathrm{d}S}\right)_F .$$

For a), b) and c) we first listed the observed mechanical effects and then the non-mechanical ones.

The formal description of the rubber ball and the elastic body are identical. Work is performed and stored in two ways:

– mechanical work to overcome the "tension" F when the rod is pushed in (l extent of depression):

$$\mathrm{d}W = F\cdot\mathrm{d}l .$$

– thermal work to overcome the thermal tension T when entropy is added (S entropy content of the ball):

$$\mathrm{d}W' = T\cdot\mathrm{d}S .$$

Therefore, the total energy increase is

$$\mathrm{d}E = F\cdot\mathrm{d}l + T\cdot\mathrm{d}S ,$$

where l and S denote work coordinates and F and T the corresponding forces. Since the condition of the ball, particularly the magnitude of the forces, is uniquely determined by the work coordinates, the system is elastic in the sense explained previously. The above energy differential represents the main equation.

The coefficients relating to the various effects now become meaningful. With the aid of our rules, we can determine signs in those cases where it is not apparent from our intuition, and derive relationships between the individual coefficients. From the flip rule, for example, we find that the two coupling coefficients $(\mathrm{d}F/\mathrm{d}S)_l$ and $(\mathrm{d}T/\mathrm{d}l)_S$ are equal. In other words, the change in rod position Δl and the exchange of entropy ΔS are symmetrically coupled.

The term $(\mathrm{d}S/\mathrm{d}T)_x = Ç_x$ represents the entropy capacity of the elastic body as explained earlier. We have already seen (section 2.2.7) that this quantity can assume different meanings depending on the conditions specified by the subscript x. The letter x can denote l or F, for example. It is harder to add entropy to the ball when l is held fixed than when the force F is held constant, as expressed by the inequality:

$$\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_l < \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F \qquad \text{or} \qquad Ç_l < Ç_F\ .$$

The entropy capacity of the system with a fixed rod is smaller than that with a constant force on the rod. A similar result applies to the heat$^\bullet$ capacity C (which is the entropy capacity $Ç$ multiplied by the factor T):

$$C_l < C_F\ .$$

This result may be obtained formally by manipulating $Ç_F$ in the following way:

$$Ç_F = \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F = \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_l + \left(\frac{\mathrm{d}S}{\mathrm{d}l}\right)_T \cdot \left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F = Ç_l + \left(\frac{\mathrm{d}F}{\mathrm{d}T}\right)_l \cdot \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T \cdot \left(\frac{\mathrm{d}F}{\mathrm{d}T}\right)_l$$

(Computational steps: Definition of $Ç_F$, change of index from F to l, flipping of first factor of additional term and insertion of index F into the second factor). Since the final three-factor term is definitely positive — of the three factors, $(\mathrm{d}l/\mathrm{d}F)_T$ is a primary measure and therefore positive and $(\mathrm{d}F/\mathrm{d}T)_l$ appears squared — we conclude that $Ç_F > Ç_l$.

The above transformations basically involve cutting $Ç_F$ back to l and T. Only the term $(\mathrm{d}l/\mathrm{d}F)_T$ still needs to be flipped. In this example, a ranking for accessibility is easily established. While it is clear that the mechanical quantities l, F are more readily measurable than the thermal parameters S, T, and T is more accessible than S, one can argue about the ranking order of l and F. Above we decided to prefer l:

$$\mathrm{d}E = F\cdot\mathrm{d}\underline{l} + \underline{T}\cdot\mathrm{d}S\ .$$

3.3.2. Rubber Band

Let us now examine the relationship between mechanical and thermal quantities in our first example, a rubber band, where we can readily test the various effects. As in the case of the rubber ball, we can perform mechanical work on the rubber band, namely, by extension dl against the force F, and thermal work by adding entropy while overcoming the tension T:

$$\mathrm{d}E = F\cdot\mathrm{d}l + T\cdot\mathrm{d}S \ .$$

The system is elastic and F, l, T and S are its main quantities. We found earlier that stretching the rubber band causes a temperature increase. It follows that the coupling between S and l is opposing, or counter-coupled.

On the basis of this characteristic we can predict several observable and verifiable effects:

a) If we heat the rubber band, or, in other words, if we add entropy, it should decrease in length (this represents a coupling effect of an entropy input on mechanical quantities):

$$\left(\frac{\mathrm{d}l}{\mathrm{d}S}\right)_F < 0 \, .$$

b) It should be easier to stretch the rubber band if we allow entropy to escape and harder if we do not (indirect effect of thermal quantities on mechanical ones):

$$\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_S < \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T \, .$$

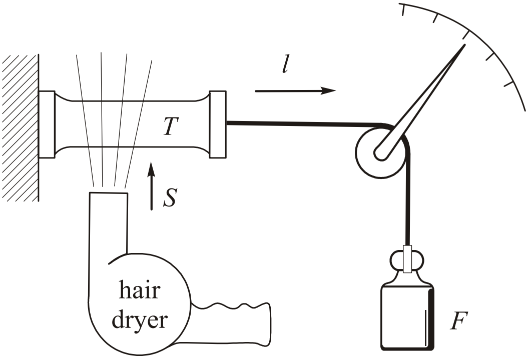


Fig. 3.7: Measuring heat effects in a rubber band

In order to prove these statements we will use the setup pictured in Figure 3.7. First we stretch a strong rubber band with a heavy weight suspended from a pulley. A gauge attached to the pulley indicates the extension of the rubber band. When we suspend the weight, we note a significant increase in length and a sudden rise in temperature by several degrees. Then l increases more slowly as the temperature returns to its initial value. It is easy to interpret this result. The first step happens so quickly that entropy does not have time to escape. Subsequently, it slowly escapes to its surroundings as indicated by the temperature drop. When T reaches its initial value ($T = \text{const.}$), the stretching of the rubber band is noticeably longer than during the first step ($S = \text{const.}$). Thus, the inequality predicted by b) is indeed true. If our thought process is correct, then adding entropy with a blow drier, for example, should shorten the rubber band as in a). This result may also be verified in an experiment.

3.3.3. Steel Wire

If we replace the rubber band with a metal wire (Figure 3.8), the main equation remains unchanged:

$$\mathrm{d}E = F\cdot\mathrm{d}l + T\cdot\mathrm{d}S\ .$$

While the rubber ball and rubber band have no practical applications and there is no data on the associated coefficients, this is not the case for the steel wire. The

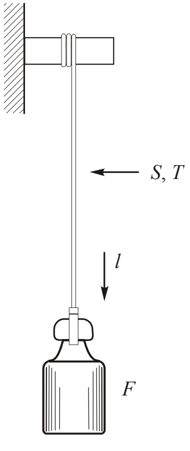


Fig. 3.8: Thermal effects in a steel wire

derivatives $(\mathrm{d}l/\mathrm{d}F)_T$, $(\mathrm{d}l/\mathrm{d}T)_F$ and $(\mathrm{d}S/\mathrm{d}T)_F$ are associated with the elasticity of the wire or more specifically, the coefficient of elasticity ε, the coefficient of linear expansion α and the specific heat$^\bullet$ capacity c_F. (The coefficient ε is the inverse of the elasticity modulus that is a measure of the "stiffness" of the material rather than the elasticity. The coefficient c_F for $F = 0$ is equal to the "usual" specific heat$^\bullet$ c in the absence of tension and is not much different from it otherwise). If we denote the length of the wire by l, the cross sectional area by A and the density by ρ, then $\rho{\cdot}l{\cdot}A$ is the mass and we have:

$$\varepsilon = \frac{A}{l}\cdot\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T, \quad \alpha = \frac{1}{l}\cdot\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F, \quad c_F = \frac{T}{\rho l A}\cdot\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F .$$

The factors, which multiply the derivatives are included so as to make these coefficients descriptive of material properties but independent of the size and shape of the body. For example, the derivative $(\mathrm{d}l/\mathrm{d}T)_F$ is proportional to the initial length of the wire l_0. Similarly, c_F, the heat$^\bullet$ capacity $T\,(\mathrm{d}S/\mathrm{d}T)_F$ divided by mass, is independent of the mass.

It is known that a wire expands on heating. Therefore, unlike the case of the rubber band, the quantities S and l are co-coupled such that they reinforce each other. It follows that a wire absorbs entropy from its surroundings during an extension. If we stretch it quickly, not allowing enough time for entropy to flow in, it should cool down.

Let us estimate the magnitude of this effect for a steel wire. For a temperature change at constant S, we can express this change by $\mathrm{d}T = (\mathrm{d}T/\mathrm{d}F)_S \cdot \mathrm{d}F$. If we start without tension ($F = 0$) and remain within the linear regime (Figure 3.9), we

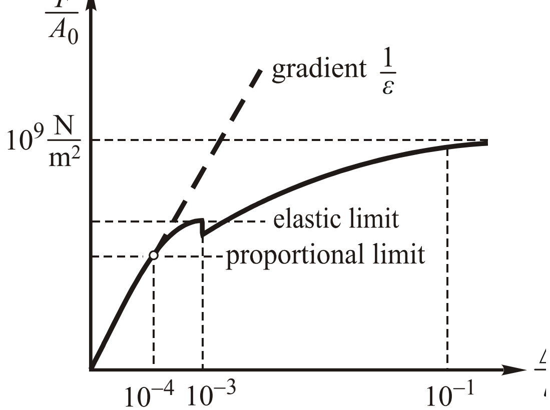


Fig. 3.9: Tensile stress-stra
curve for a steel
wire

can write F instead of dF or ΔF. After "cutting back" the derivative to F, T, and substituting for α and c_F, we obtain:

$$\Delta T = \left(\frac{\mathrm{d}T}{\mathrm{d}F}\right)_S \cdot F = -\left(\frac{\mathrm{d}T}{\mathrm{d}S}\right)_F \left(\frac{\mathrm{d}S}{\mathrm{d}F}\right)_T \cdot F = -\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F \Bigg/ \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F = -\frac{F}{A}\cdot\frac{\alpha T}{\rho\, c_F}$$

Even for a maximum load up to the limit of linearity, i.e., up to half of the tensile strength $F/A = 0.5 \cdot 10^9$ N/m^2, we compute a small temperature change of -0.4 K using $\alpha = 10 \cdot 10^{-6}$ K^{-1}, $T = 300$ K, $\rho = 8000$ kg/m^3, $c_F = 500$ J K^{-1} kg^{-1}. With the aid of the setup illustrated by Figure 3.10, we can convince ourselves that this estimate is right.

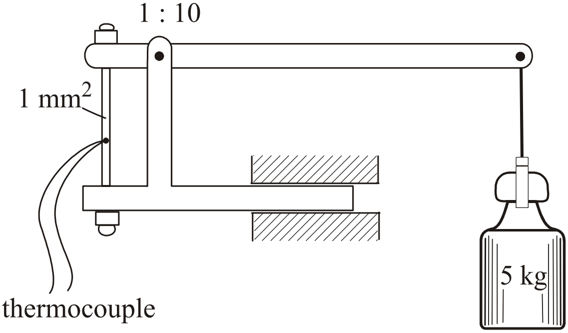


Fig. 3.10: Measuring heat effects in a steel wire

The wire is harder to stretch under adiabatic conditions (S = const.) than under isothermal conditions (T = const.):

$$\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_S < \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T .$$

In order to compute the relative difference with respect to $(\mathrm{d}l/\mathrm{d}F)_T$, we cut back to F, T, and insert ε, α and c_F:

$$\frac{\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T-\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_S}{\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T}=\frac{-\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F\cdot\left(\frac{\mathrm{d}T}{\mathrm{d}F}\right)_S}{\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T}=\frac{\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F\cdot\left(\frac{\mathrm{d}T}{\mathrm{d}S}\right)_F\cdot\left(\frac{\mathrm{d}S}{\mathrm{d}F}\right)_T}{\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T}=$$

$$=\frac{\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F^2}{\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T\cdot\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F}=\frac{T\alpha^2}{c_F\ \rho\varepsilon}.$$

Using the modulus of elasticity $\varepsilon^{-1}=0.2\cdot10^{12}\ \mathrm{N/m^2}$ for steel and the above values of coefficients, the relative difference is 0.0015. Since the difference caused by thermally indirect effects is less than one-tenth of a percent, it is usually neglected in mechanics. The elasticity modulus is generally given as $l/A\cdot\mathrm{d}F/\mathrm{d}l$, although strictly we should distinguish between an isothermal and an adiabatic modulus.

3.4. Body Under Isotropic Pressure

The next example of mechanical-thermal coupling is for a uniform body subjected to isotropic ambient pressure. This body could be a wooden cube, a hollow iron ball or the liquid enclosed in a hydraulic cylinder. Since this last one is an especially important case, we will cover it in detail.

3.4.1. Main Equation and Coupling

Mechanical work is required to compress a body. This work increases with increasing volume increment $-\mathrm{d}V$, and with applied pressure p, and can be expressed as

$$\mathrm{d}W=-p\cdot\mathrm{d}V\ .$$

Figure 3.11 illustrates these relationships. Since p is the force acting on unit area, the total force applied to a flat area A is $F=p\cdot A$. The work can now be written as

$$\mathrm{d}W=F\mathrm{d}l=\frac{F}{A}A\mathrm{d}l=p(-\mathrm{d}V)\,,$$

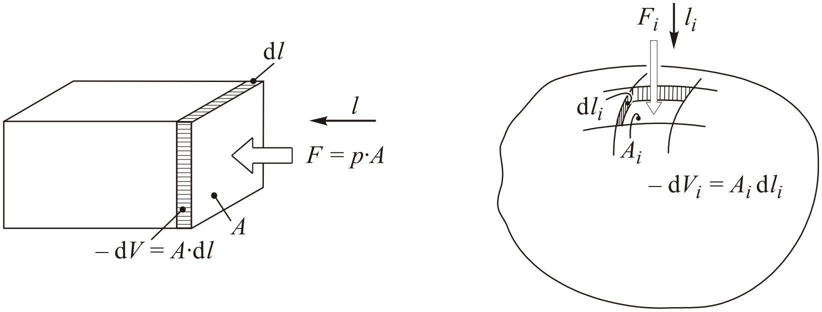


Fig. 3.11: Pressure, force, and work on an arbitrary body

since the area moves by an amount dl due to the external pressure. As a result, the volume decreases by $A{\cdot}\mathrm{d}l$. If the surface is curved, it can be divided into many small, nearly flat pieces. In order to obtain the total work, the contributions from all pieces must be summed:

$$\mathrm{d}W = F_i\mathrm{d}l_i = \sum \frac{F_i}{A_i} A_i \mathrm{d}l_i = \sum p(-\mathrm{d}V_i) = p(-\mathrm{d}V)\,.$$

Similarly, the energy added as a result of entropy inputs at different surface locations can be computed as the sum of all individual contributions

$$\mathrm{d}W' = \sum T\mathrm{d}S_i = T\mathrm{d}S\ .$$

The mechanical and thermal work performed on the body due to compression or heating is stored and can be regained in one form or another by letting the body relax or cool down. This is true for compact, heat-resistant materials over a wide pressure and temperature range, but decomposing, porous materials must be handled with care. By stipulating volume and entropy, V and S, the condition of the material is usually fully determined if we exclude all influences other than changes in pressure and temperature. Thus, we have an elastic system with main equation

$$\mathrm{d}E = (-p)\mathrm{d}V + T\mathrm{d}S.$$

If we select V and S as work coordinates, then $-p$ and T become the corresponding forces. According to our sign convention (section 3.1.2), a positive external force will tend to increase the corresponding coordinate. It should be noted, however, that p and V are not paired, but rather V with $-p$ or $-V$ with p.

While volume and pressure characterize the state of compression of a substance, entropy and temperature determine its thermal state. These phenomena, as we already know, are interrelated. For example, if we add entropy to a body by bringing it into contact with a hotter substance, then its temperature rises (the primary effect of an entropy input) and the volume tries to increase (coupling effect). If, on the other hand, the body is compressed into a smaller space, then its pressure increases (the primary effect of a volume decrease) and also the thermal tension T increases and forces out entropy (coupling effect). As mentioned earlier, the body behaves like a sponge towards water. It "swells up" when entropy is absorbed and it releases entropy when it is squeezed. The quantities V and S are co-coupled. Cold water is an exception because it contracts when it is heated from 273 to 277 K.

3.4.2. Volume

Since the quantities p and T may be easily adjusted, one usually treats the remaining quantities as functions of these variables. Figure 3.12 presents a rough overview of the variation in volume of a solid body with p and T. In general, the volume V decreases with increasing pressure; the decrease is steep initially and

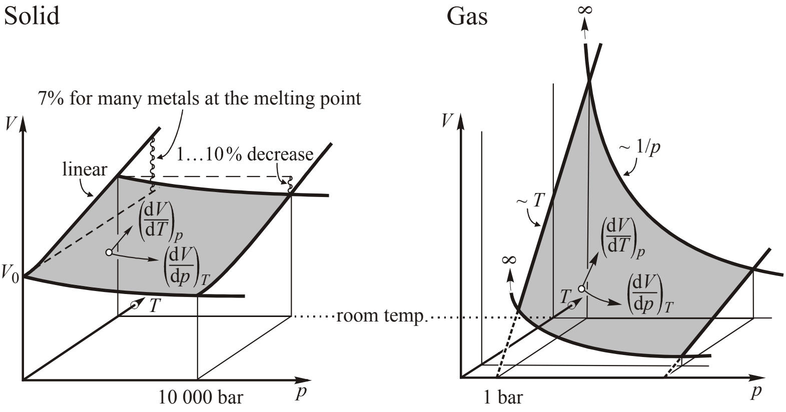


Fig. 3.12: $V(p,T)$-diagram

becomes less pronounced later. However, it takes several thousand atmospheres of pressure to cause noticeable changes in volume for solids. Gases, by contrast, lose about half of their volume when the pressure is doubled (BOYLE-MARRIOTTE Law: $V \sim 1/p$). In the T-direction, the $V(p,T)$-surface often rises linearly. For gases, it is directly proportional to temperature (GAY-LUSSAC Law). For many metals, the increase in volume from 0 K to the melting point is about 7 % (GRÜNEISEN Rule). At low temperatures the variation in volume approaches a horizontal tangent. Of course, gases will condense before reaching the absolute zero of temperature so that nothing can be said about the change in volume.

3.4.3. Entropy Content

Entropy can be described as a quantity of work / temperature ($S = W/T$) and consequently has units of J/K = Joule/Kelvin for which no other abbreviation exists. One J/K has a concrete and intuitive meaning. It is almost exactly the amount of entropy required to melt 1cm^3 of ice or to bring 1cm^3 of water, initially at room temperature, to boil.

If we consider that 1cm^3 of a liquid or solid under normal conditions (room temperature and normal atmospheric pressure) contains several J/K of entropy, we have a good grasp of this amount. A solid loses approximately 1 to 10 % of its entropy if the pressure is raised to 10 000 bar and the temperature is held constant. When the temperature reaches 0 K, the entropy S goes to zero in the ideal case. In practice, this only happens for perfect crystals with a regular structure down to the atomic level; all other matter always traps in a certain amount of entropy that can be as large as 1 J/K in a volume of 1 cm^3.

Figure 3.13 illustrates the dependence of the entropy content on p and T. The $S(p,T)$-surface for solids starts out from the p-axis with a horizontal or nearly horizontal tangent and then passes over into a more or less logarithmically rising slope. In this range S increases by several J/K for each 1 cm^3 of matter while the temperature rises by a power of ten. The entropy decrease parallel to the p-axis is similar to the loss in volume with increasing pressure. The behavior of gases is essentially the same. However, the entropy density at room temperature, which is 10 J/K per liter, is a thousand times lower for gases than for solids or liquids. The $S(p,T)$-surface cannot be extended to $T = 0$ due to unavoidable condensation, nor down to $p = 0$ because S approaches infinity there. The loss of entropy with increasing pressure is small, only 1 J/K for a tenfold increase in pressure starting

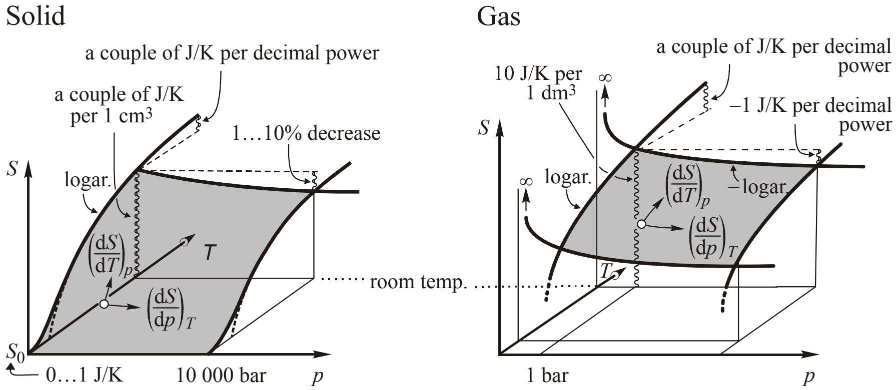


Fig. 3.13: $S(p,T)$-diagram

from 1 dm^3 of gas at normal conditions. In the T-direction the entropy increase is also logarithmic but steeper, several J/K for each power of ten.

Since a cold body at absolute zero contains no or no retrievable entropy, the amount of entropy cannot be influenced by other variables; all derivatives of S at constant T must be zero. All non-adiabatic temperature coefficients $(\mathrm{d}h/\mathrm{d}T)_{\cancel{S}\ldots}$ or $(\mathrm{d}h'/\mathrm{d}T)_{\cancel{S}\ldots}$ of any non-thermal work coordinate h or its corresponding force h' also vanishes due to the symmetry of coupling . Applying the flip rule gives

$$(\mathrm{d}h/\mathrm{d}T)_{\cancel{S}\ldots} = (\mathrm{d}S/\mathrm{d}h')_{T\ldots} = 0 \quad \text{and} \quad (\mathrm{d}h'/\mathrm{d}T)_{\cancel{S}\ldots} = -(\mathrm{d}S/\mathrm{d}h)_{T\ldots} = 0\,.$$

S does not appear in the first term (as indicated by the crossed out $\cancel{S}$) therefore T is unpaired there. Consequently, T appears in the index of the second derivative. For thermal expansion, for example, this yields:

$$\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p = -\left(\frac{\mathrm{d}S}{\mathrm{d}p}\right)_T = 0\,.$$

This result is illustrated in Figure 3.12 where the $V(p,T)$-surface starts in T-direction with a horizontal tangent. Conversely, since temperature goes to zero when all entropy is released (except for the trapped in amounts), derivatives of the type $(\mathrm{d}h/\mathrm{d}S)_{\cancel{T}\ldots}$ must vanish, as can be shown with the flip rule. In summary, the coupling between thermal and all other phenomena disappears at the absolute zero of temperature.

3.4.4 Compressibility, Coefficient of Expansion, and Specific Heat•

If entropy and volume are specified at a point p, T, one can compute approximately the values in the vicinity of this point as long as the slopes along the p-axis and T-axis, $(\mathrm{d}V/\mathrm{d}p)_T$ and $(\mathrm{d}V/\mathrm{d}T)_p$, as well as $(\mathrm{d}S/\mathrm{d}p)_T$ and $(\mathrm{d}S/\mathrm{d}T)_p$ are known. The first coefficient measures the compressibility of the material, the second the thermal expansion, the third the loss in entropy with increasing pressure and the fourth the entropy capacity $Ç_p$ (also denoted by $Ç$). This data is available in the literature for uniform materials.

Mostly one does not find the desired data directly but related values of coefficients, defined such that they are independent of a particular body. For example, we have the compressibility χ, the coefficient of volume expansion γ, the specific heat• c ("specific thermal work capacity"), the pressure coefficient β, etc.:

$$\chi = -\frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_T, \quad \gamma = \frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p, \quad c = \frac{T}{\rho V}\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_p, \quad \beta = \frac{1}{p}\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_V \quad \ldots$$

where ρ is the density. Unfortunately, these definitions are not consistent. The observed changes of material properties are sometimes referred to the current value of V, in some cases to the initial volume V_0 (typically for γ) or to the mass $m = \rho \cdot V$. It would be more logical to use the entropy capacity normalized by the volume, $e = V^{-1}(\mathrm{d}S/\mathrm{d}T)_p$, in connection with χ and γ instead of c. Then one could eliminate the multiplying factor p^{-1} from β, as is sometimes done, because $(\mathrm{d}p/\mathrm{d}T)_V$ is already independent of the size of the body. If we flip the derivative in the definition of γ and recall that $-p$ and V are paired, we get

$$\gamma = -\frac{1}{V}\left(\frac{\mathrm{d}S}{\mathrm{d}p}\right)_T .$$

This indicates that γ describes not only the relative increase in volume of a body due to heating, but simultaneously the loss in entropy per unit volume due to compression.

The three coefficients, χ, γ and c, are sufficient to compute all possible derivatives or coefficients composed thereof. For example, if we cut back β to p, T, we get

$$\beta = \frac{1}{p}\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_V = -\frac{1}{p}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p \Big/ \left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_T = \frac{\gamma}{p\chi}$$

The specific heat• at constant volume $c_V = T\rho^{-1}V^{-1} \cdot (\mathrm{d}S/\mathrm{d}T)_V$ is smaller than that for constant pressure $c_p = c$ because adding entropy is more difficult when coupled volume changes, either positive or negative, are prevented. In order to compute the difference $c - c_V$ relative to c, that may be considered as a measure of the indirect effect of mechanical behavior on thermal behavior, we cut back $(c - c_V)/c$ to p, T without flipping the derivative just this once:

$$\frac{c - c_V}{c} = \frac{(\mathrm{d}S/\mathrm{d}T)_p - (\mathrm{d}S/\mathrm{d}T)_V}{(\mathrm{d}S/\mathrm{d}T)_p} = \frac{-(\mathrm{d}S/\mathrm{d}p)_T \cdot (\mathrm{d}p/\mathrm{d}T)_V}{(\mathrm{d}S/\mathrm{d}T)_p} =$$

$$= \frac{-(\mathrm{d}S/\mathrm{d}p)_T \cdot (\mathrm{d}V/\mathrm{d}T)_p}{-(\mathrm{d}V/\mathrm{d}p)_T \cdot (\mathrm{d}S/\mathrm{d}T)_p} = \frac{T\gamma^2}{c\rho\chi} .$$

The same expression can be obtained by comparing the compressibility of the body with and without entropy exchange, similarly to the above. The compressibility is described by the usual isothermal $\chi_T = \chi$ and adiabatic $\chi_S = -V^{-1}(\mathrm{d}V/\mathrm{d}T)_S$ definitions. Note that this is an indirect effect of thermal side on mechanical changes:

$$\frac{c - c_V}{c} = \frac{\chi - \chi_S}{\chi} = \frac{\gamma^2}{\chi e} \le 1 .$$

The more suitable density of entropy capacity "*e*" has been substituted for *c* in order to simplify the final expression. This result is not only valid for *c* and χ but also for the primary measures, entropy capacity $(\mathrm{d}S/\mathrm{d}T)_x$ and compressibility $-(\mathrm{d}V/\mathrm{d}p)_x$. Since primary measures cannot be negative for stable behavior, the expression $\gamma^2/(e\cdot\chi)$ has to be less than one. The second to last equation indicates that the relative strength of the indirect effect is determined by a quotient of coupling and primary measures (formed from the same independent variables).

For solids under normal ambient conditions, typical values for χ are $10^{-5} \ldots 10^{-6}$ /bar, γ lies in the range of $10^{-4} \ldots 10^{-5}\ \mathrm{K}^{-1}$ and *e*, including liquids, has a value near 10^{-2} (J/K)/K per cm^3 of matter.

3.5 Other Systems

The above method can be applied qualitatively and quantitatively to completely different systems and processes such as the magneto-thermal effect, piezoelectric crystals, lateral expansion of a rod on compression, bending of a heated bimetallic strip, pyroelectric effect, etc. This list includes examples that have no relation to thermodynamics. This is understandable; it is only required that we can apply our mathematical model. In the following it is assumed that we are dealing with elastic systems even if it is not justified in each case. Since the thought process and computational methods are the same, it is adequate to outline the approach and present a few sample calculations.

3.5.1. Galvanic Cell

Electric work is stored by charging a storage battery (Figure 3.14). The work performed when transferring a charge dq across the terminal voltage U is given by

$$\mathrm{d}W = U \cdot \mathrm{d}q$$

and may be retrieved without significant loss if care is taken. Furthermore, the thermal work $\mathrm{d}W' = T{\cdot}\mathrm{d}S$ is added or removed by heating or cooling the battery simultaneously. The total energy thus becomes

$$\mathrm{d}E = U \cdot \mathrm{d}q + T \cdot \mathrm{d}S.$$

Since the voltage U depends on temperature, the state of charge and the thermal state apparently influence each other; q and S are coupled. If q and S are counter-coupled, we can predict that the terminal voltage will increase for a lossless battery when the external temperature rises. This is so since the emission of entropy and therefore the charging are made more difficult (q and S are counter-coupled).

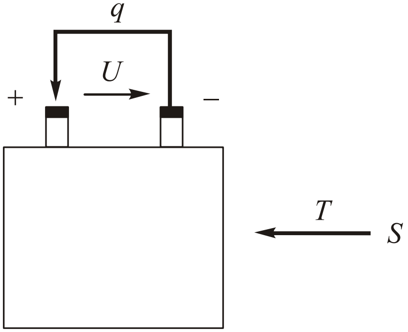


Fig. 3.14: Charge and entropy flow in a galvanic cell

By applying the flip rule we obtain the temperature coefficient β:

$$\beta = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_q = -\left(\frac{\mathrm{d}S}{\mathrm{d}q}\right)_T .$$

For a lead battery, β has the relatively small value of 0.2 mV/K for a terminal voltage of 2 V. This value corresponds to an entropy decrease of $2 \cdot 10^{-4}$ (J/K)/C at constant temperature. As a further example, a battery with a charging capacity of 50 A·h = 180 000 C (starter battery) has to reduce its entropy content by 35 J/K during the charging process. This amount is sufficient to melt 35 cm^3 of ice.

3.5.2. Piezoelectric and Pyroelectric Effects

When a piezoelectric material, such as a quartz or tourmaline crystal, is compressed or extended, certain crystal surfaces are charged. This mechanical-electrical coupling can be used in many ways. As an example consider a capacitor with an appropriately aligned piezoelectric dielectric. If we compress the dielectric with a force F, an electric potential difference appears across the terminals of the capacitor, or a pulse of current appears if the terminals are short-circuited. If we apply an additional external voltage U to the capacitor, charge q is transferred from one plate to the other, and the plate separation l tends to decrease further. The charge flows back completely after the removal of the external force and voltage. One can excite the body into periodic mechanical oscillations by applying an alternating voltage. These electrically driven oscillators have been used to produce ultrasound and to control clocks and watches (quartz watch).

In setting up the main equation, we need to consider that thermal work can be performed in addition to electrical and mechanical work (Fig. 3.15) :

$$\mathrm{d}E = U \cdot \mathrm{d}q + (-F) \cdot \mathrm{d}l + T \cdot \mathrm{d}S.$$

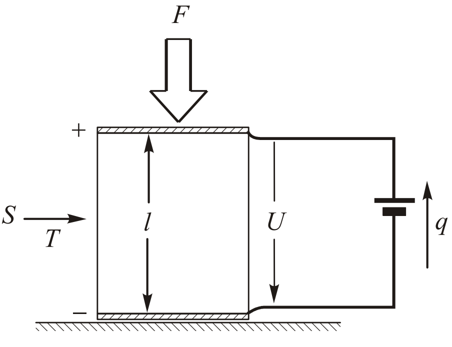


Fig. 3.15: Piezoelectric crystal With applied force F and voltage U

Furthermore, q and S may be coupled. Depending on the type of coupling, the capacitor is charged in one direction or the other (pyroelectric effect).

As a numerical example let us choose a 1 cm^3 cube of "sintered" $\mathrm{BaTiO_3}$ which, following polarization at high temperatures in an electric field, becomes piezoelectric. The capacitor plates are made by plating two opposite sides perpendicular to the polarization direction. Since this is a three-actuator system ($n = 3$), we need $(n + 1)\cdot n/2 = 6$ independent coefficients for a complete description. In addition to the elasticity modulus ($10^{11}\ \mathrm{N/m^2}$), the coefficient of expansion (10^{-5}/K) and density of entropy capacity ($10^4 \mathrm{J/K^2} \cdot \mathrm{m^3}$), we could select the electric capacitance in addition to the piezo- and pyroelectric charge coefficients:

$$\left(\frac{\mathrm{d}q}{\mathrm{d}U}\right)_{F,T} = 10^{-10}\,\frac{\mathrm{C}}{\mathrm{V}}; \qquad \left(\frac{\mathrm{d}q}{\mathrm{d}F}\right)_{U,T} = 10^{-10}\,\frac{\mathrm{C}}{\mathrm{N}}; \qquad \left(\frac{\mathrm{d}q}{\mathrm{d}T}\right)_{U,F} = 10^{-9}\,\frac{\mathrm{C}}{\mathrm{K}}.$$

Now let us squeeze our system slowly but strongly ($F = 1000$ N) by applying a pair of pliers to the metallic ends. Since the entropy has time to escape (T = const.), a voltage develops between the open electrodes ($q = 0$):

$$U = F\left(\frac{\mathrm{d}U}{\mathrm{d}F}\right)_{q,T} = -F\left(\frac{\mathrm{d}q}{\mathrm{d}F}\right)_{U,T} \Bigg/ \left(\frac{\mathrm{d}q}{\mathrm{d}U}\right)_{F,T} = -1000\mathrm{V}$$

This is large enough to produce a 1/2 mm long spark. Similarly, a high voltage can be reached by heating ($\Delta T = 100$ K) instead of applying pressure:

$$U = \Delta T\left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_{q,F} = -\Delta T\left(\frac{\mathrm{d}q}{\mathrm{d}T}\right)_{U,F} \Bigg/ \left(\frac{\mathrm{d}q}{\mathrm{d}U}\right)_{F,T} = -1000\mathrm{V}\,.$$

Conversely, by applying a voltage of −1000 V to the electrodes while holding l and S constant, the resulting expansion force is 100 N with a temperature rise of $1.1 \cdot 10^{-3}$ K.

3.5.3. Magneto-Caloric Effect

If we heat a piece of iron within a constant external magnetic field, then the induced magnetic dipole moment j decreases and vanishes almost completely at 1040 K (770 ºC), implying that S and j are coupled. In fact, a magnetized body can be treated as an elastic system provided it does not exhibit significant hysteresis.

In the simple case of a uniform region, parallel to an external homogeneous magnetic field H, the main equation becomes

$$\mathrm{d}E = (-p)\cdot\mathrm{d}V + H\cdot\mathrm{d}j + T\cdot\mathrm{d}S \ .$$

In order to show that the work $H\cdot\mathrm{d}j$ is expended during magnetization, consider a thin resistanceless solenoid having a solid core. It has a cross section A, length l, Volume $V = A\cdot l$, and n turns with the current I flowing through the coil (Fig. 3.16). The approximately uniform field in the core, with an intensity of $H = (n\cdot I)/l$, induces a magnetic polarisation J and a magnetic flux density $B = \mu_0\cdot H + J$. The magnetic dipole moment j of the body is given by $j = V\cdot J$ and the magnetic flux Φ in the solenoid by

$$\Phi = n\,A\cdot B = \frac{n}{l}\cdot(V\mu_0 H + j) \ .$$

A change in magnetic flux $\mathrm{d}\Phi$ induces a voltage surge $U\cdot\mathrm{d}t = \mathrm{d}\Phi$ (t time) across the coil that the current has to overcome by expending work:

$$\mathrm{d}W = I\cdot U\cdot\mathrm{d}t = \frac{nI}{l}(V\mu_0\mathrm{d}H + \mathrm{d}j) = V\mu_0 H\cdot\mathrm{d}H + H\cdot\mathrm{d}j$$

Since the energy $V\mu_0 H\cdot\mathrm{d}H$ is present even in the case of a hollow core ($j = 0$), only the second term $H\cdot\mathrm{d}j$ represents the work of magnetization of the body. This work may be retrieved in the case of a lossless system, providing that j follows precisely the rise or fall in field intensity and is not delayed due to hysteresis.

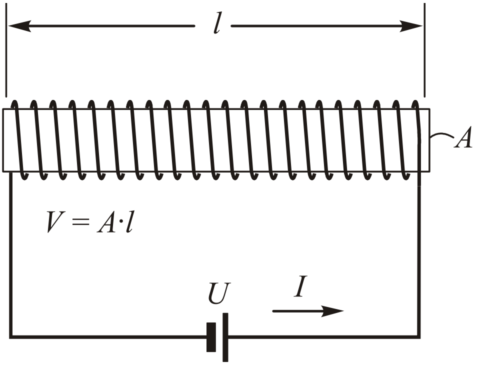


Fig. 3.16: Magnetization experiment

For a paramagnetic, condensed material above the CURIE temperature T_C, one can describe the (volume) susceptibility χ and therefore indirectly, also the magnetic dipole moment $j = V{\cdot}J = V{\cdot}\mu_0\,\chi{\cdot}H$ via the CURIE-WEISS Law

$$\chi = \frac{C}{T - T_C} \;,$$

where C is the CURIE constant, and the magnetic polarization J is small relative to its saturation value J_∞ (of the order of 1 $\mathrm{Wb/m^2}$) reached at very high field intensities. Since j drops with increasing temperature, i.e., the magnetic dipole moment j and entropy S are counter-coupled, an increase in j leads to a decrease in S. Such a body releases entropy when a magnetic field is applied (magneto-caloric effect). By using this process after pre-cooling a body with liquid helium, very low temperatures (10^{-3} K and lower) can be reached which would not be feasible otherwise.

Let us estimate this effect for a paramagnetic salt (e.g. $FeSO_4 \cdot 7\,H_2O$ or $MnSO_4 \cdot 4\,H_2O$) in the field of a strong electromagnet: $\chi_{300\mathrm{K}} \approx 10^{-3}$, $T_c \approx 0$ K, $H \approx 10^6$ A/m . Using $j = V \cdot \mu_0 H \cdot C/T$, where $C = T\chi \approx 0.3$ K, we get:

$$\left(\frac{\mathrm{d}S}{\mathrm{d}H}\right)_{T,p} = \left(\frac{\mathrm{d}j}{\mathrm{d}T}\right)_{H,p} = -V\mu_0 H \frac{C}{T^2} \;.$$

The amount of entropy "received" during the increase in magnetic field from 0 to H, at constant p and T, is obtained by integration. The term $(\mathrm{d}S/\mathrm{d}H)_{T,p}$ cannot be treated as a constant:

$$\Delta S = \int_0^H \left(\frac{\mathrm{d}S}{\mathrm{d}H}\right)_{T,p} \mathrm{d}H = -V\mu_0 \frac{H^2}{2}\cdot\frac{C}{T^2} = -2\cdot 10^{-6}\,\mathrm{J/K}\;.$$

This value applies to a 1 $\mathrm{cm^3}$ cube of salt at room temperature, and corresponds to the minute temperature drop of $2 \cdot 10^{-4}$ K during adiabatic demagnetization using an entropy capacity of 1/100 (J/K)/K. However, the above formula indicates that the cooling process becomes substantially more effective at low temperatures due to the relation $\Delta S \sim 1/T^2$, provided that CURIE's Law is valid.

3.5.4. Bimetallic Strip

A bimetallic strip (Fig: 3.17) bends when it is heated. Bending and heating — or more formally expressed, the work coordinates l and S — are co-coupled. If the strip is bent back, it must release entropy or its mean temperature must rise.

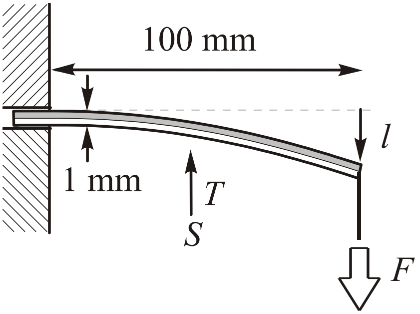


Fig. 3.17: Work at a bimetallic strip

The main equation can be expressed as

$$\mathrm{d}E = F\,\mathrm{d}l + T\mathrm{d}S,$$

where F is the applied force at the tip of the strip and l is the deflection in the direction of the force.

For a strip 100 mm long, 10 mm wide and 1 mm thick consisting of invar (alloy of iron and 36% nickel) on one side and nickel or brass on the other, we have the following approximate results:

$$\left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T = \text{a few }\frac{\text{mm}}{\text{N}}; \quad \left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F = 10^{-1}\,\frac{\text{mm}}{\text{N}}; \quad \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F = 10^{-2}\,\frac{\text{J/K}}{\text{K}}.$$

In order to calculate how much the metal heats up internally when straightened out, we consider the coefficient $(\mathrm{d}T/\mathrm{d}l)_S$, cut back to F, T, and substitute the numerical values:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}l}\right)_S = \frac{1}{\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_S} = \frac{1}{\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F + \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T \cdot \left(\frac{\mathrm{d}F}{\mathrm{d}T}\right)_S} = \frac{\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F}{\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F^2 - \left(\frac{\mathrm{d}l}{\mathrm{d}F}\right)_T \cdot \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F} =$$

$$= \text{a few }\frac{\text{K}}{\text{m}}.$$

While we must heat up the strip by 100 K in order to obtain a deflection of 10 mm without applying a force, we only get a temperature rise $\Delta T = (\mathrm{d}T/\mathrm{d}l)_S \cdot \Delta l$ of several hundredths of a degree when we bend the strip back adiabatically over the same distance ($\Delta l = -10$ mm).

3.6. Traditional Concepts

In addition to the quantities used so far, various other concepts are frequently utilized in thermodynamics, such as internal energy, enthalpy, useful work, free energy, etc., for the purpose of facilitating computation and theory. The reason for introducing these concepts goes back to the historical development of treating thermal work performed on a body as a measure of added heat. Heat became a special form of energy either transferred to or, under certain conditions, residing in a body and was grouped with other forms of energy. Since one could not interpret entropy intuitively — it was perceived as an abstract quantity derived from thermal work — computational methods that avoided this concept were preferred. As far as possible, entropy was expressed by energetic quantities in the final result. Therefore, the shortest and most reasonable approach to obtain the desired relationships appeared to be energy considerations. The traditional framework of thermodynamics was developed with this goal in mind and, as a result, appears more akin to an energy theory than to a theory of heat.

In our presentation, in which entropy is introduced with more or less known and intuitive properties, we can dispense with many of these artificial aids without sacrificing anything. However, since the energy approach is widely used, it is difficult to avoid reference to some of its most important concepts. In the following sections these are explained within the context of our viewpoint.

3.6.1. Forms of Energy

If we bring a body from state I to II — some concrete examples are a stretched wire, a gas in a cylinder, a piezoelectric crystal — then the total work W expended is given as the difference in energy E between the two states:

$$W = E_{\mathrm{II}} - E_{\mathrm{I}} .$$

The form in which the energy is exchanged, such as mechanical or thermal, depends in general on the intermediate states in going from I to II. In Figure 3.18, we consider a gas in a cylinder. We can describe graphically different ways of moving from one state to another. Along the solid line in the diagram, the gas is easily compressed but heated up with difficulty, i.e., the required mechanical work W' is

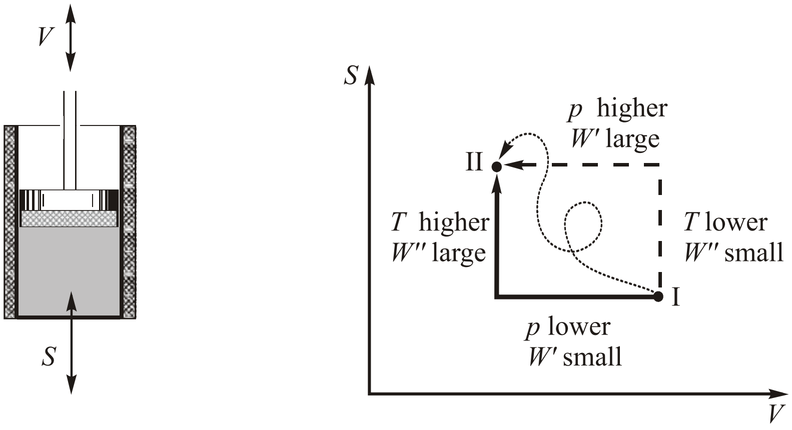


Fig. 3.18: The ratio of mechanic and thermal work depends on the path

small and the thermal work W'' required is large. The dashed line indicates the opposite trend. And along an arbitrary path (for example, the dotted line) the ratio of the two forms of energy can attain any given value. One cannot simply say that the body in state II, for instance, has a distinct amount of thermal work exceeding that in state I.

The total energy cannot be easily divided into separate mechanical, thermal, electrical, etc., energy parts. It represents a common supply from which one form of energy flows off while another form is supplied. We say that energy is "converted" from one transfer form to another. Suppose that the gas in Figure 3.18 repeatedly follows a "cycle": from state I to II via the solid path, and back from state II to I via the dashed path. For each complete cycle, thermal work is supplied ($\sum W'' > 0$) and mechanical work is emitted ($\sum W' > 0$). In 1824 S. Carnot examined energy transformations of this kind in reversible cycles where heat is added at a high temperature and released at a lower temperature, or vice versa. Such "Carnot cycles" were used frequently in the past to derive thermodynamic relationships.

For a system in which the work coordinate x is not appreciably coupled to other coordinates, or it is the only coordinate, the corresponding force y depends only on x and the resulting work $W^\dagger = \int_{\mathrm{I}}^{\mathrm{II}} y(x)\mathrm{d}x$ has a definite value. In such a case, one could state that the system actually contains energy in the form $W^\dagger$ as received. One can define an independent supply of work $E^\dagger$ such that

$$W^{\dagger} = E_{\mathrm{II}}^{\dagger} - E_{\mathrm{I}}^{\dagger}.$$

This possibility is readily achieved, allowing us to distinguish between stored and transferred forms of energy. For example, for a body with constant mass, the work for elevation in a gravitational field is determined only by the height it acquires, and the work for acceleration is determined only by the momentum it acquires, regardless of whether the body receives additional energy from heating or deformation. Consequently, in mechanics we can treat potential and kinetic energy separately, without considering other contributions to the energy.

The "internal energy" U of a body or system is the remainder of the total energy E after subtracting the kinetic and potential energies due to external fields,

$$E = U + E_{\mathrm{kin}} + E_{\mathrm{pot}} .$$

The quantity U describes the total work due to deformations, heating, electrification, magnetization, surface tension, etc. In contrast to other contributions to E, it represents the energy associated with the material structure — the inner structure or internal motion of a system. This energy is of primary interest in thermodynamics so that most concepts are derived from U rather than from E.

3.6.2. Heat, Work, and First Law of Thermodynamics

Thermal work, commonly referred to as heat$^{\bullet}$ and denoted by the symbol Q, has its own supply provided that the coupling of entropy with other work coordinates is negligible within the energy balance. If this holds for all parts of a substance ($i = 1,2,3$ ... in Figure 3.19) as approximated by liquids and solids under ordinary conditions, then each part can be assigned a definite content of heat$^{\bullet}$. The darkness of shading in Figure 3.19 indicates the amount of Q_i. When Q_i decreases in one part and increases in another, this process can be described as the transfer or flow of heat$^{\bullet}$ from one part to another. When the body is thermally insulated, the total heat$^{\bullet}$ content $\sum Q_i$ cannot decrease, but it can be increased by an internal electric heater, for example. Heat is thus produced but not destroyed, and is distributed over the entire substance. Any given part appears hotter the more heat$^{\bullet}$ it "contains". Heat$^{\bullet}$ under these circumstances possesses the properties assigned to heat* as discussed earlier in this book.

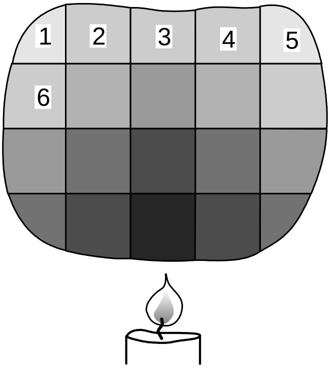


Fig. 3.19: Heat• distribution in a heated body

This peculiarity is undoubtedly the most important reason why the term "heat" was established and retained for the quantity Q. Unfortunately, this name is responsible for many conceptual difficulties because it suggests properties possessed by Q which apply only under special circumstances. Many properties appear to be valid, but in the strictest sense, they are hardly ever satisfied. In general thermodynamics, where the coupling of entropy to other work coordinates is investigated, these properties are absent so that recourse to intuition often leads to mistakes, and abstract language is preferred.

The thermal work performed on a body or, in other words, the heat• Q transferred to it, can be measured without knowing anything about entropy. In order to determine the amount of heat• required to raise the temperature of a body — let's say bath water — by 1 degree, it is sufficient to compute the energy W_p expended by an electric heater used for the process. As illustrated by Figure 3.20, W_p is easily calculated from the applied current, voltage and duration of heating. The heating coil receives electric work and gives off thermal work. If we submerge a hot body in the bath water, then we can conclude from the observed rise in temperature how much heat• was given off by this object. Most "calorimeters" work on the basis of such a procedure.

The interpretation of Q as heat• obscures the meaning of the corresponding work coordinate S. Q is considered measurable directly. This explains why Q is not perceived as work, which is usually determined by the product of force times displacement. Instead, heat• is given a special meaning and it is contrasted with "work." For example, we say that the internal energy U of a body increases by the

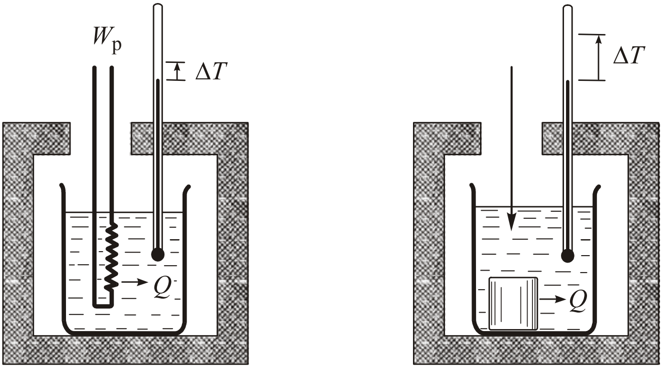


Fig. 3.20: Measuring heat$^\bullet$ (thermal work)

addition of heat$^\bullet$ Q and work W performed on transition from state I to II:

$$U_{II} - U_I = Q + W \qquad \text{or} \qquad dU = dQ + W \;.$$

This equation represents a mathematical form of the "First Law of Thermodynamics" as a special case of the energy principle. In essence, it says that heat$^\bullet$ and work are interchangeable, but their sum, the energy, cannot be created or destroyed.

3.6.3. Temperature, Entropy, and Second Law of Thermodynamics

Since Q is measurable, the increase of the entropy of a substance on transition from state I to II can be calculated from the thermal work expended, provided that a) no entropy is produced internally, and b) the absolute temperature is known throughout the incremental steps:

$$dS = \frac{dQ_{rev}}{T} \qquad \text{or} \qquad S_{II} - S_I = \int_I^{II} \frac{dQ_{rev}}{T}$$

The first condition a) is satisfied if the process is "reversible", i.e., no work losses occur due to friction as indicated by the subscript "rev". The second condition b) assumes that T is already defined. A rigorous definition is not easy within the traditional approach. As an aid, a temporary temperature scale T^* is introduced. It is not practical to use mercury or alcohol for the thermometer. Instead, a dilute gas whose temperature T^* is proportional to the volume at constant pressure is used

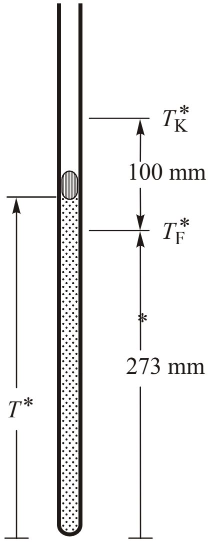


Fig. 3.21: Gas thermometer

(Figure 3.21). If we select the difference between the freezing point T_F^* and boiling point T_K^* of water under normal pressure as 100 degrees, then T_F^* becomes 273 degrees.

Now we know that Q, or the integral $\int_I^{II} \mathrm{d}Q$, depends on the path taken in going from state I to II. There is no reason why the expression $\int_I^{II} \mathrm{d}Q/T^*$ should not behave similarly. The Second Law of Thermodynamics states that there exists a quantity S^* for any macroscopic body possessing a unique value in any state such that the following relationship is satisfied:

$$S_{II}^* - S_I^* \geq \int_I^{II} \frac{\mathrm{d}Q}{T^*} \qquad \text{or} \qquad \mathrm{d}S^* \geq \frac{\mathrm{d}Q}{T^*}$$

The equal sign applies in the case where the change from state I to II is reversible. This theorem only states that the abstract quantity S^* exists, and offers no intuitive interpretation. Nevertheless, one can draw far-reaching conclusions. For instance, since $S_{II}^* - S_I^*$ is equal to the integral $\int_I^{II} \mathrm{d}Q_{\text{rev}}/T^*$ this difference is independent of the path taken. The integral contains only measurable quantities and consequently, S^* can be calculated for any state II of a body once S^* is known or is somehow fixed for state I. In the case of a body which is thermally insulated from its environment, $\mathrm{d}Q = 0$ and hence $S_{II}^* - S_I^* \geq 0$. When this body changes from state I to state II, S_{II}^* cannot be less than S_I^*. If internal processes such as diffusion, electric currents, chemical transformations, etc. occur in such a body, S^* can only increase and never decrease. And so on.

Later we will see that T^* is equivalent to T when we consider the properties of dilute gases (see section 4.7.2). As a result, S^* and the now-familiar quantity S are also equivalent for the appropriate choice for the zero point. The abstractly formulated content and correspondences of the Second Law of Thermodynamics should become intuitively understandable. If we consider, for example, that $\mathrm{d}Q/T$ represents the entropy transferred into a system from the outside, and that some entropy can also be produced internally, then the inequality $\mathrm{d}S \geq \mathrm{d}Q/T$ becomes more meaningful.

3.6.4. Enthalpy, Heat Functions

For a system with coupled work coordinates, we can generally obtain the individual contributions to work arising from a change in state by summing all contributions along the path from state I to II. This applies in particular to thermal work Q. However, since Q is readily determined calorimetrically and is usually interpreted as a measure of heat•, we are inclined to look for the possibility of calculating Q by simpler methods. One possibility is to associate Q with other variables such as U^* which can represent a heat• content under certain conditions:

$$Q = U^*_{\mathrm{II}} - U^*_{\mathrm{I}} \ .$$

In fact, variables called "heat functions" or "enthalpy", from the Greek word for heat content, are easily declared. The simplest example is the total or internal energy for systems that can only exchange thermal work with their surroundings. Consequently, it follows that

$$Q = E_{\mathrm{II}} - E_{\mathrm{I}} = U_{\mathrm{II}} - U_{\mathrm{I}} \, .$$

A cylinder filled with gas reduces to such a system when the piston is fixed. As a result, no work arising from volume changes is performed. Even if the external pressure vanishes and the piston moves "blindly", the outward motion is only restrained by the friction between the piston and the cylinder wall. In this case, no mechanical work is done on the surroundings. Unlike our previous examples, this system is no longer lossless. The mechanical work due to the expansion of the gas is lost as heat• — in a sense via a detour because the regular path for mechanical work is blocked. Here the variable $\mathrm{d}Q$ consists of two parts arising from different sources. One part is the increase in entropy content $\mathrm{d}S$, and the other part is the thermal work representing the lost energy or the newly produced entropy $\mathrm{d}S_\mathrm{p}$:

$$\mathrm{d}Q = T\mathrm{d}S - T\mathrm{d}S_\mathrm{p}\ .$$

If we go one step further and consider the system illustrated by Figure 3.22, where the work coordinates and force functions of the internal process are unknown, but only heat$^\bullet$ can be exchanged, the equation $Q = \Delta U$ can nevertheless be used. We shall see later that the process of moving the piston against internal friction forces corresponds to a change in the work coordinate x with a missing external force. The useful work is lost and exchanged for heat$^\bullet$ via a bypass. If we extinguish the flame and bring the process to a stop (x = const.), then we have a system with a fixed piston in the work cylinder and $Q = \Delta U$ is still valid.

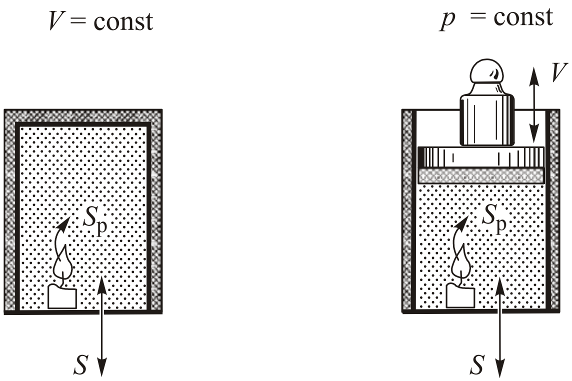


Fig. 3.22: Entropy as a work coordinate

The most important case is that of a body moving against a constant pressure — perhaps air pressure — and performing thermal work, but otherwise not exchanging any energy with its surroundings. Here the auxiliary quantity

$$H \equiv U + pV$$

(or more explicitly, $U - (-p)V$), where H is called enthalpy, plays the role of a heat$^\bullet$ content. If we consider that under these conditions $\Delta U = W_\mathrm{therm} + W_\mathrm{mech} = Q - p \cdot \Delta V$ and $\Delta H = \Delta U + p \cdot \Delta V$, then we obtain the equation

$$Q = H_\mathrm{II} - H_\mathrm{I}\,.$$

This relationship remains valid even if energy is lost internally due to friction or other processes and turned into heat$^\bullet$, in addition to the usual thermal work. (Note:

the weight on the right side of Figure 3.22 is not part of the system but only helps to visualize the constant pressure).

The above result can be generalized to multi-actuator systems. If, besides $x_1 = S$, all other work coordinates $x_2, x_3, x_4 \ldots$ are fixed, then U is a heat function. By holding some of the corresponding forces $y_2, y_3, y_4 \ldots$ fixed, say y_2 and y_4, but not the corresponding work coordinates x_2 and x_4, the following quantity

$$U^* = U - y_2 x_2 - y_4 x_4$$

assumes the role of the heat function. Under these circumstances

$$\Delta U = Q + y_2 \Delta x_2 + y_4 \Delta x_4 ,$$

and

$$\Delta U^* = \Delta U - y_2 \Delta x_2 - y_4 \Delta x_4 ,$$

yielding the result $Q = \Delta U^*$. This equation is also valid in the case of "blind" coordinates as covered previously. For example, if we eliminate the external force y_3 suddenly and x_3 drifts "blindly" under the influence of opposing forces of friction, the previously useful work produces entropy internally. "Blind" coordinates, those with a missing external force like x_3, are sometimes called "internal parameters" and are not interpreted as work coordinates in the same sense as we use this notion.

It is apparent that we can introduce heat functions in numerous special cases. For each set of forces $y_\alpha, y_\beta, y_\gamma \ldots \neq T$ (T may be constant or variable), the following is defined as the "associated" enthalpy U^*:

$$\psi_{\alpha\beta\gamma\ldots} = U - y_\alpha y_\alpha - y_\beta y_\beta - y_\gamma y_\gamma - \ldots .$$

If $y_\alpha, y_\beta \ldots$ are kept constant and heat• and energy exchange are allowed only via the associated coordinates $x_\alpha, x_\beta \ldots$, then $\psi_{\alpha\beta\gamma\ldots}$ becomes a heat function. (There are many other functions such as $U^* = \psi_{\alpha\beta\gamma\ldots} + f(y_\alpha, y_\beta \ldots)$, where f is an arbitrary function.) If not specified differently, the independent variables of $\psi_{\alpha\beta\gamma\ldots}$ include T, the forces named in the index $y_\alpha, y_\beta, y_\gamma \ldots$, and the work coordinates $x_\mu, x_\nu \ldots$ which are neither associated with T nor the forces named in the index:

$$\psi_{\alpha\beta\gamma\ldots} = f(T, y_\alpha, y_\beta, y_\gamma \ldots x_\mu, x_\nu \ldots) .$$

This equation reduces to the special form $U = f(T,V)$ or $H = f(T,p)$ for a body that can be compressed and heated ($\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$), and is often referred to as the "caloric equation of state", compared to the so-called "thermal equation of state" of a body, i.e., $p = f(T,V)$ or $V = f(T,p)$ where applicable. In section 3.4 we compared $V(p,T)$ and $S(p,T)$ for similar reasons, but were guided by different interpretations of heat. The most important heat• capacities can be viewed as temperature coefficients of properly chosen enthalpy functions. For the case under consideration we have $(\mathrm{d}U)_V = (\mathrm{d}Q)_V$ and also $(\mathrm{d}H)_\mathrm{p} = (\mathrm{d}Q)_\mathrm{p}$ which yields

$$\left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_V = \frac{(\mathrm{d}Q)_V}{(\mathrm{d}T)_V} = C_V , \qquad \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_p = \frac{(\mathrm{d}Q)_p}{(\mathrm{d}T)_p} = C_p \ .$$

Since entropy is considered an abstract and not directly measurable quantity, it is understandable that this special representation of the coefficients $C_a = T(\mathrm{d}S/\mathrm{d}T)_a$ is preferred, where a denotes arbitrarily chosen conditions.

3.6.5. Maximum Useful Work

When a system is in equilibrium, all forces compensate, and therefore all work performed due to small changes of the work coordinates compensate for each other. There is no driving force for a spontaneous change. When the system is not balanced, a net force remains which can start a process that runs in one direction, even against some resistance. In the unbalanced system, the greater forces on one side perform more work (release more energy) than is gathered by the opposing forces on the other side. We will call the difference "free work" W_f, and consider it as emitted and therefore negative, $W_\mathrm{f} < 0$. This free work is burned up (as far as not parts of it are stored as kinetic energy, intermediately or finally), by producing entropy in overcoming forces of friction. The lost work may be absorbed by the system together with the produced entropy or may be released to the environment as thermal work. In the first case W_f cancels in the energy balance of the system. In the second case it shows up as a smaller (more negative) term Q. Under some conditions it is possible to calculate the energy released in a desired change without knowing the individual forces. Therefore, one can identify the effective driving forces of a process and predict whether or not a process is feasible.

If one succeeds in counteracting the excess forces, for example by intervention with an external force, then one can stop or even reverse the processes running in the system. In doing so, the previously released free energy W_f has to be expended and it becomes positive. Such intervention allows us to make the free work, which

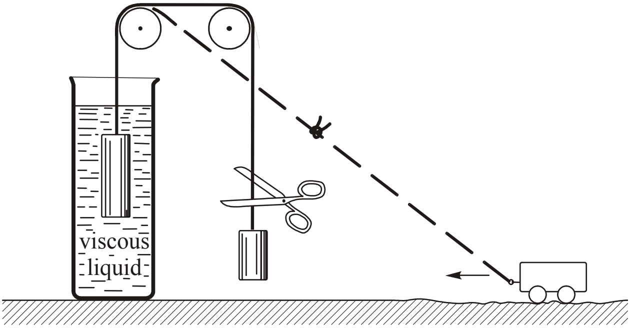


Fig. 3.23: Mechanical example for usable work

would otherwise be lost, partially or totally used for some purpose. How W_f is divided into amounts of lost and used work depends on the skill of the experimenter. In each case, W_f determines the maximum amount of usable free energy, which led to the name "maximum useful work" for $|W_f|$. A galvanic battery is a familiar example where the energy released by a chemical reaction is used for "electric power generation" through a suitable arrangement of electrodes, plates, etc. The electric work gained … can be further utilized to lift a weight, to generate light, to produce entropy, to perform electrolysis, etc.

A simple mechanical example (Fig. 3.23) may serve to clarify the concept of useful work. The suspended weight and the counterweight in the fluid are initially in equilibrium. The vector sum of the forces is zero and the system is at rest. If the equilibrium is disturbed by eliminating a force (cutting the string), the remaining forces are not fully compensated and the system can perform work. This work is not stored but instead used for producing entropy in overcoming the forces of friction in the fluid. By some intervention we can use the work for other purposes (pull a wagon, drive a generator, etc.) or re-establish equilibrium (hold the string). We can even reverse the process (pull the string) and replace the energy released.

3.6.6. Free Energy, Thermodynamic Potentials

Can we predict what part of the energy content of a body or system is usable? Can we define a definite supply $\mathcal{E}$ of free work from which, under certain conditions, energy is available for any arbitrary purpose we want, even to be wasted:

$$W_f = \mathcal{E}_{II} - \mathcal{E}_I \,?$$

It turns out that this is generally not feasible because that part of the total energy which can be considered "free" depends strongly on specific circumstances for each body. There is no separate work supply, but under certain conditions auxiliary variables $\mathcal{E}$ can assume this role. As an example, if we drop a rock with mass m from an elevation h to ground level (Fig. 3.24), then the available work supply $\mathcal{E}$ consists of the potential energy $E = mgh$:

$$\mathcal{E} = E.$$

This amount is available for producing entropy, for instance. On the other hand, if the rock is dropped within a water column, in a pool for instance, then $\mathcal{E}$ is reduced by the work $F_b\, h$ required to overcome the buoyancy F_b:

$$\mathcal{E} = E - F_b\, h.$$

We can consider $\mathcal{E} = E$ or, depending from the conditions, $\mathcal{E} = E - F_b\, h$, as auxiliary quantities for our purpose.

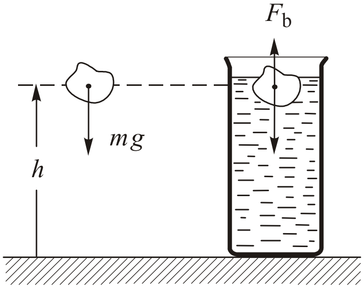


Fig. 3.24: "Free energy" of a raised stone

A similar difficulty arises when we attempt to partition the internal energy of a body or system. If the system has no possibility of energy exchange other than the release of free work to the surroundings (this work is usually burned up producing entropy), then

$$W_f = U_{II} - U_I \qquad = \underbrace{\Delta U}_{"\mathcal{E}"}.$$

This case occurs when we hold S constant — the produced entropy S_p must then be transferred out — and block any other exchange of energy. The energy U generally increases by the amount of work W_f required to reverse the spontaneous state change back from state II → I by intervention, and by the additional work W due to possible changes of work coordinates:

$$U_{II} - U_I = W_f + W.$$

As an illustration let us use the equilibration of pressure between two gas containers (Figure 3.25). Since the system exchanges entropy with its surroundings, it also performs thermal work. With the restriction that the temperature T remains fixed, and no energy is released to the surroundings except through S (and W_f), we can set $W = T \cdot \Delta S$. The term $\Delta S = S_{II} - S_I$ describes the entropy received from the outside. The correct determination of W_f requires that the processes are conducted in such a way that no work is wasted and no entropy is produced. Therefore, we obtain

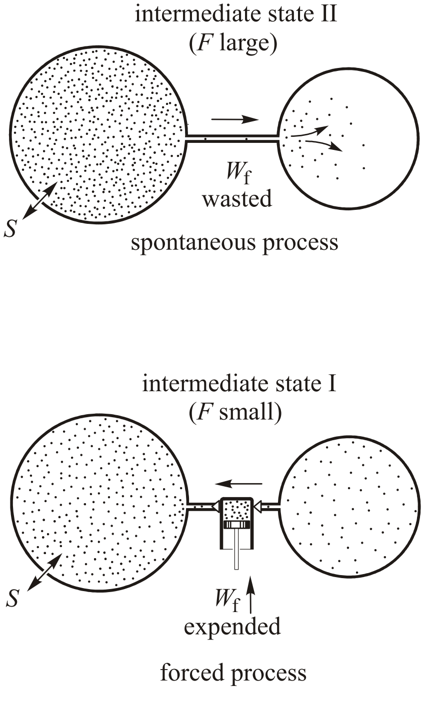


Fig. 3.25: Equilibration of pressure, and the reverse process

$$W_f = \Delta U - W \quad = \Delta U - T \cdot \Delta S \qquad\qquad = \Delta(\underbrace{U - T \cdot S}_{"\mathcal{E}"}) .$$

For this special case it is no longer U but a new quantity A whose change determines the free work:

$$A = U - TS, \qquad W_{\mathrm{f}} = A_{\mathrm{II}} - A_{\mathrm{I}} .$$

Similar auxiliary functions — different ones depending on the situation — are called "free energies" or "thermodynamic potentials" (or better, "thermodynamic potential energies"), because they have properties similar to the potential energy in mechanics. The quantity A, as introduced by H. V. HELMHOLTZ, is called "HELMHOLTZ free energy", "HELMHOLTZ energy" or simply "free energy".

In the more important practical case in which a body expands against a constant pressure p (perhaps air pressure) we have $W = T{\cdot}\Delta S + (-p){\cdot}\Delta V$ and

$$W_{\mathrm{f}} = \Delta U - W \;= \Delta U - T{\cdot}\Delta S - (-p){\cdot}\Delta V \qquad = \Delta(\underbrace{U - T{\cdot}S + p{\cdot}V}_{\text{"}\mathcal{E}\text{"}})$$

Here a new quantity G, introduced by W. J. GIBBS and called "GIBBS free energy", "GIBBS energy" or simply "free enthalpy”, assumes the role of A.

$$G = U - TS + pV, \qquad W_{\mathrm{f}} = G_{\mathrm{II}} - G_{\mathrm{I}} .$$

If we hold S constant rather than T, then we have $W = (-p)\Delta V$. In this way we obtain

$$W_{\mathrm{f}} = \Delta U - W \;= \Delta U - (-p){\cdot}\Delta V \qquad = \Delta(\underbrace{U + p{\cdot}V}_{\text{"}\mathcal{E}\text{"}})$$

We remember $U + p{\cdot}V \equiv H$. The quantity H that was previously got to know as enthalpy, now serves as a thermodynamic potential.

Just as in the case of the heat functions, we can immediately generalize these results. If we fix all work coordinates x_i of a multi-actuator system, or allow the corresponding external forces y_i to vanish, then U serves as thermodynamic potential. Note that in addition to W_{f} (as thermal waste or dissipation heat$^{\bullet}$) no energy is exchanged with the surroundings in this system. However, if some forces, say y_2 and y_4, are held constant instead of the corresponding coordinates x_2 and x_4, then we have $W = y_2\Delta x_2 + y_4\Delta x_4$, and

$$W_{\mathrm{f}} = \Delta U - W \;= \Delta U - y_2\Delta x_2 - y_4\Delta x_4 \qquad = \Delta(\underbrace{U - y_2x_2 - y_4x_4}_{\text{"}\mathcal{E}\text{"}})$$

Thermodynamic potentials can be defined for numerous special cases. For each set of constant forces $y_\alpha, y_\beta, y_\gamma \ldots$ (unlike the heat functions, T is included here), we can define a new energetic variable, which acts as a free energy. We can define as "associated" free energy $\mathcal{E}$ the quantity $\Psi_{\alpha\beta\gamma\ldots}$. This is similar to how we defined enthalpies $\psi_{\ldots}$ in section 3.6.4. The free energy is viewed as a function of the variables $y_\alpha, y_\beta, y_\gamma \ldots$ appearing as subscripts in $\Psi_{\alpha\beta\gamma\ldots}$, and all the work coordinates $x_\mu, x_\nu \ldots$ that are not paired with the y's:

$$\Psi_{\alpha,\beta,\gamma\ldots} = g(y_\alpha, y_\beta, y_\gamma \ldots x_\mu, x_\nu \ldots).$$

$\Psi_{\alpha,\beta,\gamma\ldots}$ as a function of its "natural" variables $y_\alpha, y_\beta, y_\gamma \ldots x_\mu, x_\nu \ldots$ becomes also a characteristic function (see section 3.7.1). The ability to act as a thermodynamic potential in the above sense is not absolutely tied to a particular choice of independent variables.

3.6.7. Equilibrium Conditions

Natural processes occurring without intervention release energy, and consequently, the supply $\mathcal{E}$ of free work, if definable, decreases with each spontaneous change. For instance, the HELMHOLTZ free energy A diminishes if for a body or system of bodies the temperature T is constant, and all energy exchanges are blocked except via S. An uninhibited internal process only comes to rest if the system has reached a state 0 in whose immediate vicinity there are no states having smaller free energy. In other words, A represented as some function of the parameter z that defines the state of the system, has a local minimum. The graph on the left in Figure 3.26 applies to our gas example from Figure 3.25. As a parameter, the graph utilizes the amount of gas in the smaller gas container. The sketch on the right in Figure 3.26 presents a mechanical analog for the graph. A ball rolls in a water-filled hollow where the "free energy" $\mathcal{E}$ is equal to the potential energy $mgh - F_b h. = \mathcal{E}$.

Similarly to the mechanical analog, where the derivative $-\mathrm{d}\mathcal{E}/\mathrm{d}z$ describes the force acting on the ball in the z-direction, one can use $-\mathrm{d}A/\mathrm{d}z$ as the driving force for the internal process of the gas example under consideration. As long as this driving force is not counteracted externally, the process comes to rest at equilibrium when the forces vanish by themselves. This is equivalent to the above requirement that the system has to reach the minimum point of its "potential" curve. One can also interpret z as a work coordinate and $\mathrm{d}A/\mathrm{d}z$, as well as $\mathrm{d}\mathcal{E}/\mathrm{d}z$, as a force that has to be overcome by doing work on the system. If one succeeds in changing z by external intervention without energy losses (without friction), then $\mathrm{d}W_\mathrm{f} = (\mathrm{d}A/\mathrm{d}z)\,\mathrm{d}z$, and $\mathrm{d}W_\mathrm{f} = (\mathrm{d}\mathcal{E}/\mathrm{d}z)\,\mathrm{d}z$, respectively, describes the energy input to the system due to the change in the work coordinate z by $\mathrm{d}z$.

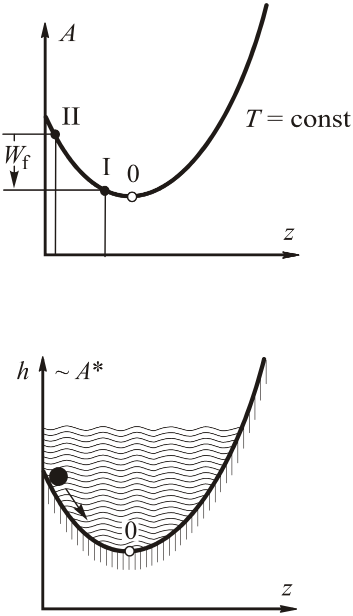


Fig. 3.26: Equilibrium at the minimum of the free energy

If we need further parameters z_i in order to define the state of the system (assuming T = const. and no energy transfer occurs except via S!), then the forces $(\mathrm{d}A/\mathrm{d}z_i)_{z_{\hat{i}}}$ must vanish in all directions in the final state of a completed process. The condition for equilibrium of the system at point $(z_1, z_2 \ldots)$ is given by

$$\left(\frac{\mathrm{d}A}{\mathrm{d}z_i}\right)_{z_{\hat{i}}} = 0 \qquad (i = 1,\ 2\ \ldots).$$

Since $\mathrm{d}A = (\mathrm{d}A/\mathrm{d}z_1)_{z_{\hat{1}}}\mathrm{d}z_1 + (\mathrm{d}A/\mathrm{d}z_2)_{z_{\hat{2}}}\mathrm{d}z_2 + \ldots$, we can express the "equilibrium condition" in simpler form without referring to the parameters z_i:

$\mathrm{d}A = 0$ (T = const. and no energy transfer except via S).

Under different conditions, A is replaced by other thermodynamic potentials but nothing else is changed. Of particular interest are systems under constant pressure and temperature that are otherwise insulated, where the most frequently used equilibrium condition is

$\mathrm{d}G = 0$ (p, T = const. and no energy transfer except via S,V).

This condition is widely used in chemical thermodynamics. The equilibrium conditions discussed above make it possible to describe the equilibrium state of a system via energy balances as preferred by the energetic approach to thermodynamics.

3.7 Common Mathematical Procedures

Mathematical procedures used in traditional thermodynamics differ from those employed here in essentially two respects:

a) Instead of directly transforming the derivatives, one usually goes back to the differentials.

b) In place of the flip rule, one uses various characteristic functions or appropriately selected cycles.

Let us first consider the computational aids in b).

3.7.1. Characteristic Functions, MAXWELL Relations

It was noted in section 3.1.2 that the energy E as a function of the work coordinates $x_1, x_2 \ldots x_n$ is the characteristic function for a lossless or elastic system. That means that all properties described by its main quantities can be computed as long as $E(x_1, x_2 \ldots x_n)$ is known. In particular, one can find the missing forces F_i from the derivatives of E with respect to x_i. A similar conclusion is valid for U.

This feature of E or U is lost on choosing other independent variables such as, for example, the forces y_1 and y_3 instead of the corresponding coordinates x_1 and x_3. However, in this case the already familiar intermediate variable $\psi_{1,3}$, known as the free energy with y_1 and y_3 held constant, assumes this role. By definition, we have $\psi_{1,3} = U - y_1 x_1 - y_3 x_3$ and its differential becomes:

$$\mathrm{d}\psi_{13} = \mathrm{d}U - \mathrm{d}y_1 \cdot x_1 - y_1 \cdot \mathrm{d}x_1 - \mathrm{d}y_3 \cdot x_3 - y_3 \cdot \mathrm{d}x_3 .$$

By substituting this $\mathrm{d}U$ with the main equation $\mathrm{d}U = y_1\,\mathrm{d}x_1 + y_2\,\mathrm{d}x_2 \ldots$, we obtain the so-called "fundamental equation" of the quantity $\psi_{1,3}$:

$$\mathrm{d}\psi_{13} = -x_1\mathrm{d}y_1 + y_2\mathrm{d}x_2 - x_3\mathrm{d}y_3 + y_4\mathrm{d}x_4 + \ldots\ .$$

This equation differs from the energy differential in two respects. For the variables identified by the index of the quantity ψ (here 1 and 3), x and y are interchanged and the sign is also changed. Now the differential of $\psi_{1,3}(y_1, x_2, y_3, x_4 \dots)$ can generally be expressed as:

$$\mathrm{d}\psi_{13} = \left(\frac{\mathrm{d}\psi_{13}}{\mathrm{d}y_1}\right)_{\dots} \mathrm{d}y_1 + \left(\frac{\mathrm{d}\psi_{13}}{\mathrm{d}x_2}\right)_{\dots} \mathrm{d}x_2 + \left(\frac{\mathrm{d}\psi_{13}}{\mathrm{d}y_3}\right)_{\dots} \mathrm{d}y_3 + \dots$$

Comparison of the coefficients in the last both equations shows an important result. By taking the derivatives of $\psi_{1,3}(y_1, x_2, y_3, x_4 \dots)$ with respect to any of the variables inside the brackets, we always get the corresponding main quantity with either positive or negative sign. This way we can compute the missing work coordinates and forces, and other expressions consisting of main quantities, as long as the function $\psi_{1,3}(y_1, x_2, y_3, x_4 \dots x_n)$ is known. Therefore, we can consider $\psi_{1,3}$, just as $U(x_1 \dots x_n)$, to be a characteristic function of the system under consideration. With a different choice of independent variables $z_1 \dots z_n$ ($z_i = x_i$ or y_i), $U(x_1 \dots x_n)$ is replaced by the corresponding function $\psi(z_1 \dots z_n)$, which we have already met in our earlier discussion about thermodynamic potentials.

The real significance of the characteristic function lies in the fact that it enables us to perform, either directly or indirectly, those operations that we completed by using the flip rule. For example, in order to carry out the transformation

$$\left(\frac{\mathrm{d}v}{\mathrm{d}u}\right)_{yw} = -\left(\frac{\mathrm{d}x}{\mathrm{d}y}\right)_{uw}$$

for a system with the main equation $\mathrm{d}U = u\mathrm{d}x + v\mathrm{d}y + w\mathrm{d}z$, we start with the fundamental equation of the function $\psi_{uw} = U - ux - wz$, where the independent variables u, y, w are the same as on the left side of the above equation. Then

$$\mathrm{d}\psi_{uw} = -x\,\mathrm{d}u + v\,\mathrm{d}y - z\,\mathrm{d}w\,.$$

From this equation, we get $v = (\mathrm{d}\psi_{uw}/\mathrm{d}y)_{uw}$ and $x = -(\mathrm{d}\psi_{uw}/\mathrm{d}u)_{yw}$. Then by changing the order of differentiation (SCHWARZ theorem), we obtain the final result:

$$\left(\frac{\mathrm{d}v}{\mathrm{d}u}\right)_{yw} = \left(\frac{\mathrm{d}}{\mathrm{d}u}\left(\frac{\mathrm{d}\psi_{uw}}{\mathrm{d}y}\right)_{uw}\right)_{yw} = \left(\frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{\mathrm{d}\psi_{uw}}{\mathrm{d}u}\right)_{yw}\right)_{uw} = -\left(\frac{\mathrm{d}x}{\mathrm{d}y}\right)_{uw}.$$

If the index and numerator of the initial derivative contain paired variables, then this procedure fails. In this case, one has to make an appropriate transformation of the original derivative.

Equations derived in this way are often called "MAXWELL relations". J. C. MAXWELL derived them originally by considering a reversible cycle for a body undergoing compression and heating. It is described by the main equation $\mathrm{d}U = -p\mathrm{d}V + T\mathrm{d}S$. The characteristic functions are $U(V,S)$, $\psi_p = H(p,S)$, $\psi_T = A(V,T)$ and $\psi_{pT} = G(p,T)$ with corresponding fundamental equations:

$$\mathrm{d}U = -p\mathrm{d}V + T\mathrm{d}S, \qquad \mathrm{d}H = V\mathrm{d}p + T\mathrm{d}S,$$

$$\mathrm{d}A = -p\mathrm{d}V - S\mathrm{d}T, \qquad \mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T.$$

By taking derivatives "diagonally", i.e., $-p$ with respect to S, and T with respect to V in the first equation, etc., and by using the SCHWARZ theorem, we obtain the following four equations:

$$-\left(\frac{\mathrm{d}p}{\mathrm{d}S}\right)_V = \left(\frac{\mathrm{d}T}{\mathrm{d}V}\right)_S, \qquad \left(\frac{\mathrm{d}V}{\mathrm{d}S}\right)_p = \left(\frac{\mathrm{d}T}{\mathrm{d}p}\right)_S,$$

$$-\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_V = -\left(\frac{\mathrm{d}S}{\mathrm{d}V}\right)_T, \qquad \left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p = -\left(\frac{\mathrm{d}S}{\mathrm{d}p}\right)_T.$$

These equations can be derived directly by flipping. In this sense the flip rule can be considered as a tool for deriving all possible MAXWELL relations.

3.7.2. Reversible Cycles

The same results can be obtained with energy balance equations applied to appropriate cycles, as MAXWELL himself did. As an example, consider a piece of wire of length l that is stretched by the force F and whose entropy content can be increased by adding entropy against the temperature T (Figure 3.27). In order to derive the MAXWELL Equation

$$\left(\frac{\mathrm{d}S}{\mathrm{d}l}\right)_T = -\left(\frac{\mathrm{d}F}{\mathrm{d}T}\right)_l,$$

we perform the following lossless procedure with the wire:

a. Stretch the wire by $\mathrm{d}l$ at constant temperature T as described by the first derivative, and thereby add the entropy $\mathrm{d}S = (\mathrm{d}S/\mathrm{d}l)_T\,\mathrm{d}l$ to the wire.

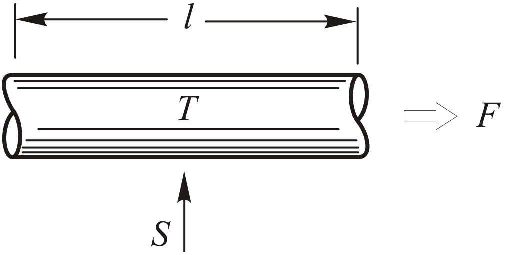


Fig. 3.27: Deriving a MAXWELL Equation by his method

b. Heat the wire by dT while holding the length $(l + \mathrm{d}l)$ constant as required by the second derivative. As a result, the force changes by $\mathrm{d}F = (\mathrm{d}F/\mathrm{d}T)_l\,\mathrm{d}T$. (Actually d$F$ is negative!)

c. Reverse stage a): Shorten the wire by dl while holding the temperature $(T + \mathrm{d}T)$ constant and thus release the entropy dS.

d. Reverse stage b): Cool down the wire by dT at fixed length such that F and the wire return to their initial state.

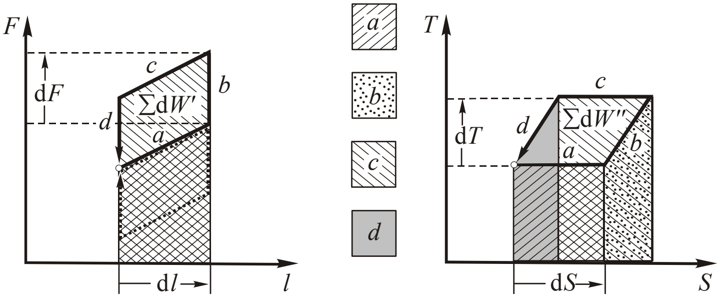


Fig. 3.28: Work- and heat-diagrams for an infinitesimal cycle

Figure 3.28 illustrates this process by a so-called "work diagram" on the left and a "heat diagram" on the right. Since dF is actually negative, the process follows the dotted path on the left. Each increment of mechanical work dW' or increment of thermal work dW'' performed on the body is equal to the hatched area under the respective curve segment. It is positive if the corresponding work coordinates increase, and negative otherwise. The sum of the work increments for the four parts of each cycle, $\sum \mathrm{d}W'$ and $\sum \mathrm{d}W''$, represents the area of each parallelogram (with sides abcd), both with a negative sign for this case. Their values can be computed geometrically as $^{\sim}\mathrm{d}F\cdot\mathrm{d}l$ and $^{\sim}\mathrm{d}S\cdot\mathrm{d}T$, respectively, by taking into account the proper signs. It follows that

$$\sum\mathrm{d}W' + \sum\mathrm{d}W'' = -\mathrm{d}F\cdot\mathrm{d}l - \mathrm{d}S\cdot\mathrm{d}T = 0$$

because the wire has the same energy at the beginning and the end of the process. By substituting the expressions for dS and dF derived earlier, we get

$$\left[\left(\frac{\mathrm{d}S}{\mathrm{d}l}\right)_T \mathrm{d}l\right]\mathrm{d}T = -\left[\left(\frac{\mathrm{d}F}{\mathrm{d}T}\right)_l \mathrm{d}T\right]\mathrm{d}l \qquad \text{or} \qquad \left(\frac{\mathrm{d}S}{\mathrm{d}l}\right)_T = -\left(\frac{\mathrm{d}F}{\mathrm{d}T}\right)_l .$$

Since actually $\sum\mathrm{d}W' < 0$ and $\sum\mathrm{d}W'' > 0$, we can say that work is reversibly converted to heat• in this process.

Similar reversible cycles are, of course, possible when entropy is not mentioned. CARNOT cycles, which are composed of two isothermal and two adiabatic segments, were frequently used in earlier days, in spite of their complexity, because the computations can be made without using the entropy concept. Figure 3.29 depicts a CARNOT cycle for our wire example. As before, the circumscribed areas represent the "converted" energies $\sum\mathrm{d}W'$ and $\sum\mathrm{d}W''$. The rectangle for the heat• diagram of a CARNOT process is usually skipped, and $\sum\mathrm{d}W'' = \Delta S\cdot\Delta T$, with $\Delta T = T_\mathrm{h} - T_\mathrm{l}$, is computed by the formula

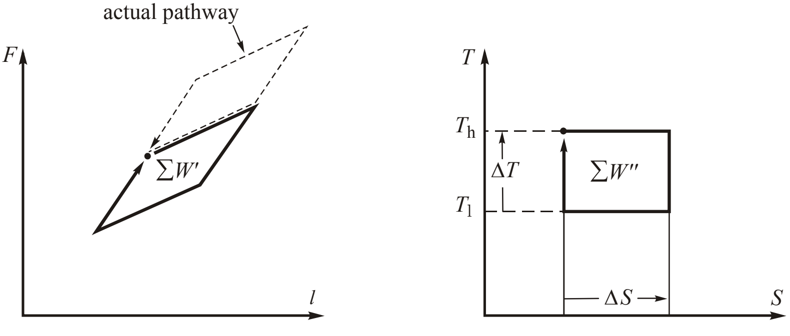


Fig. 3.29. Work- and heat-diagrams for an infinitesimal CARNOT cycle

$$\sum\mathrm{d}W'' = Q_\mathrm{h}\cdot\frac{\Delta T}{T_\mathrm{h}},$$

where Q_h is the heat$^\bullet$ $T_\mathrm{h}\Delta S$ flowing into the system at the high temperature T_h. Since part of the heat$^\bullet$, namely $T_\mathrm{l}\Delta S$, flows out of the system in each cycle at the low temperature T_l, and only the part $\sum \mathrm{d}W''/Q_\mathrm{h} = \Delta T/T_\mathrm{h}$ is "converted" to mechanical work, the "efficiency" of a CARNOT cycle is expressed as

$$\eta = \frac{\Delta T}{T_\mathrm{h}}\,.$$

The desired thermodynamic relationships are obtained by computing the work $-\sum \mathrm{d}W'$ gained from a CARNOT process by means of the work diagram, and the "converted" heat from $\eta \cdot Q_\mathrm{h}$. In this way, no reference is made to the word entropy:

$$-\sum W' = Q_\mathrm{h} \cdot \frac{\Delta T}{T_\mathrm{h}}\,.$$

3.7.3. Systematic Procedure for Calculations

To demonstrate that our guidelines apply also to the energetic approach, let us revisit the task formulated in section 3.2.3, namely, to express the coefficients $(\mathrm{d}u/\mathrm{d}v_1)_{v_2 \ldots v_n}$ in terms of known or more easily measurable quantities.

In preparation, using the First Law, we write down the energy balance for our thermodynamic system arising from small changes in the work coordinates $x_2 \ldots x_n$ ($x_1 = S$ is not treated as a work coordinate):

$$\mathrm{d}U = \mathrm{d}Q + y_2\mathrm{d}x_2 + \ldots + y_n\mathrm{d}x_n\,.$$

If all state changes are reversible, implying that no entropy is produced internally, then on the basis of the Second Law, $\mathrm{d}Q$ can be replaced by $T\,\mathrm{d}S$:

$$\mathrm{d}U = T\mathrm{d}S + y_2\mathrm{d}x_2 + \ldots + y_n\mathrm{d}x_n\,.$$

Expressed in our terminology, this is the main equation of an elastic system. As before, a systematic procedure is advantageous. On the right side of the equation, let us establish a ranking order for each term or pair of variables, and choose from each pair the "more accessible" variable z_i. The quantities $z_1 \ldots z_n$ are considered as independent variables. We recall step a) from section 3.2.3:

"The given derivative is transformed into expressions which contain only derivatives, where only accessible variables appear in the denominator and the indices".

This procedure may be carried out in the following systematic way:

a) Write down the differentials of all variables appearing in the derivative $(\mathrm{d}u/\mathrm{d}v_1)_{v_2 \ldots v_n}$ and select z_i as the independent variables:

$$\mathrm{d}u = \left(\frac{\mathrm{d}u}{\mathrm{d}z_1}\right)_{z_{\hat{1}}} \mathrm{d}z_1 + \ldots + \left(\frac{\mathrm{d}u}{\mathrm{d}z_n}\right)_{z_{\hat{n}}} \mathrm{d}z_n ,$$

$$\mathrm{d}v_1 = \left(\frac{\mathrm{d}v_1}{\mathrm{d}z_1}\right)_{z_{\hat{1}}} \mathrm{d}z_1 + \ldots + \left(\frac{\mathrm{d}v_1}{\mathrm{d}z_n}\right)_{z_{\hat{n}}} \mathrm{d}z_n ,$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$\mathrm{d}v_\mathrm{n} = \left(\frac{\mathrm{d}v_n}{\mathrm{d}z_1}\right)_{z_{\hat{1}}} \mathrm{d}z_1 + \ldots + \left(\frac{\mathrm{d}v_n}{\mathrm{d}z_n}\right)_{z_{\hat{n}}} \mathrm{d}z_n .$$

b) The differentials $\mathrm{d}v_2 \ldots \mathrm{d}v_n$ vanish since the parameters $v_2 \ldots v_n$ are constant, resulting in $n + 1$ equations with $n + 2$ "unknowns", namely, $\mathrm{d}u$, $\mathrm{d}v_1$, $\mathrm{d}z_1 \ldots \mathrm{d}z_n$. By eliminating $\mathrm{d}z_i$ and solving for $\mathrm{d}u$, we obtain:

$$\mathrm{d}u = B\,\mathrm{d}v_1 \quad \text{or} \quad \frac{\mathrm{d}u}{\mathrm{d}v_1} = \left(\frac{\mathrm{d}u}{\mathrm{d}v_1}\right)_{v_2 \ldots v_n} = B ,$$

where B is composed of the coefficients from the system of equations, and therefore contains only derivatives with respect to z_i as desired.

This procedure, explained above in general form, appears cumbersome, but often leads to the solution relatively quickly. We have already encountered one application during the derivation of the rule for "inserting an index" (see section 3.2.1). If the specified derivative contains auxiliary variables ψ (enthalpies, thermodynamic potentials, etc.), its total differentials are written with the help of the fundamental equation before being expanded in terms of z_i.

We also recall step b) from section 3.2.3:

> "All generated quotients that contain a numerator with higher rank than the denominator (top-heavy quotients) are flipped".

This procedure can be performed by utilizing the characteristic function for all z_i or the corresponding MAXWELL relations. The procedure was explained in the previous section and will not be repeated here.

If some differential quotients in the final result are to be replaced by more accessible coefficients, we can as before, repeat the procedure for the new coefficients and thus eliminate the undesirable ones. This might arise if entropy appears in the final result and a heat function is preferred in its place. Textbooks typically skip some steps in this computational procedure, change the sequence, use previously derived results, or resort to other aids. This can give the procedure described above, which is fairly straightforward, a completely new appearance.

3.7.4. Applications

As an example, we wish to demonstrate in detail the systematic procedure for calculating the derivative $(\mathrm{d}T/\mathrm{d}F)_S$. This coefficient arose in section 3.3.3 where we determined the change in temperature of a piece of wire (length l, cross section A, mass density ρ) upon stretching. As before, we assume that the elasticity coefficient ε, the coefficient of linear expansion α and the specific heat• c_F are known.

a) Preparatory steps:

On the basis of the First Law: $\mathrm{d}U = \mathrm{d}Q + F\mathrm{d}l$.

By consideration of the Second Law: $\mathrm{d}U = T\mathrm{d}S + F\mathrm{d}l$.

Ranking order of accessible variables: F, T.

b) Express $(\mathrm{d}T/\mathrm{d}F)_S$ with F, T as independent variables:

List the differentials:

$$\mathrm{d}F, \qquad \mathrm{d}T, \qquad \mathrm{d}S = \left(\frac{\mathrm{d}S}{\mathrm{d}F}\right)_T \mathrm{d}F + \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F \mathrm{d}T = 0\,.$$

Solve for $\mathrm{d}T$ and divide by $\mathrm{d}F$:

$$\mathrm{d}T = -\left(\frac{\mathrm{d}S}{\mathrm{d}F}\right)_T \mathrm{d}F \bigg/ \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F, \qquad \left(\frac{\mathrm{d}T}{\mathrm{d}F}\right)_S = -\left(\frac{\mathrm{d}S}{\mathrm{d}F}\right)_T \bigg/ \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F .$$

c) "Flip" the derivative $(\mathrm{d}S/\mathrm{d}F)_T$ because S has a higher rank than F:

Select characteristic function: $\psi_{FT}(F,T) = U - TS - Fl$.

Write down fundamental equation: $\mathrm{d}\psi_{FT} = -S\,\mathrm{d}T - l\,\mathrm{d}F$.

Obtain MAXWELL relation: $\left(\frac{\mathrm{d}S}{\mathrm{d}F}\right)_T = \left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F .$

Substitute into result of step b): $$\left(\frac{\mathrm{d}T}{\mathrm{d}F}\right)_S = -\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F \Big/ \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F . \quad (*)$$

d) Introduce new coefficients α, c_F:

$\alpha = l^{-1}(\mathrm{d}l/\mathrm{d}T)_F$ is the linear expansion coefficient, c_F the specific heat capacity, defined as the derivative of the heat function (or enthalpy) $\psi_F(T, F) = U - Fl$ with respect to temperature, while holding the force F constant, and dividing the result by the mass $m = \rho \cdot lA$

$$\alpha = \frac{1}{l}\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right)_F , \qquad c_F = \frac{1}{\rho lA}\left(\frac{\mathrm{d}\psi_F}{\mathrm{d}T}\right)_F . \qquad (**)$$

The coefficient α is in the desired form, but c_F must be modified by repeating the procedure above as far as necessary (here only step a):

a′) Write down the differentials using the fundamental equation:

$$\mathrm{d}\psi_F = T\mathrm{d}S - l\mathrm{d}F, \qquad \mathrm{d}T, \qquad \mathrm{d}F = 0 .$$

Solve for $\mathrm{d}\psi_F$, divide by $\mathrm{d}T$ and multiply by $\frac{1}{\rho lA}$:

$$\mathrm{d}\psi_F = T\mathrm{d}S, \qquad \left(\frac{\mathrm{d}\psi_F}{\mathrm{d}T}\right)_F = T\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F , \qquad c_F = \frac{T}{\rho lA}\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_F . \qquad (***)$$

By using the additional equations (**) and (***), we can eliminate the terms $(\mathrm{d}l/\mathrm{d}T)_F$ and $(\mathrm{d}S/\mathrm{d}T)_F$ in equation (*) to obtain the final result:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}F}\right)_S = -\frac{1}{A}\cdot\frac{\alpha T}{\rho c_F} .$$

It is obvious that this procedure can be shortened considerably through practice and experience. For example, the last part could be omitted completely by realizing from the beginning that c_F (like all other heat capacities) can be expressed best as an entropy derivative. The effort may be reduced further of course if we can fall back on earlier results. In conclusion, let us derive the often discussed volume and pressure coefficients of the heat functions $U(V,T)$ and $H(p,T)$, respectively, using this streamlined procedure by applying the derived MAXWELL relations from section 3.7.1.

$$\left(\frac{\mathrm{d}U}{\mathrm{d}V}\right)_T = \left(\frac{\mathrm{d}(T\mathrm{d}S - p\mathrm{d}V)}{\mathrm{d}V}\right)_T = T\left(\frac{\mathrm{d}S}{\mathrm{d}V}\right)_T - p\left(\frac{\mathrm{d}V}{\mathrm{d}V}\right)_T = T\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_V - p ,$$

$$\left(\frac{\mathrm{d}H}{\mathrm{d}p}\right)_T = \left(\frac{\mathrm{d}(T\mathrm{d}S + V\mathrm{d}p)}{\mathrm{d}p}\right)_T = T\left(\frac{\mathrm{d}S}{\mathrm{d}p}\right)_T + V\left(\frac{\mathrm{d}p}{\mathrm{d}p}\right)_T = -T\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_p + V\ .$$

Collecting and numbering hundreds of formulas for later usage is a standard method in conventional textbooks. One aim of the new approach is to reduce this apparatus to a minimum.

4. CHEMICAL THERMODYNAMICS

The area of physics that deals with the macroscopic description of systems of reactive matter is called "chemical physics" or "chemical thermodynamics". This subject can be developed conceptually and formally in a manner similar to that used in Chapter 2 for pure thermodynamics. The most important quantities, the counterparts of entropy and temperature, are the amount of substance and its chemical potential, and we consider these quantities first.

The concept of chemical potential used here is a somewhat generalized version of that found in standard chemical thermodynamics. A more descriptive term might be substance potential (the potential of a substance, where substance can even refer to light), but here we shall use the well-known expression chemical potential.

4.1. Introduction

The term "substance" generally refers to a uniform substance described by a chemical formula and identified by certain properties such as color, density, solubility, melting point, emission and absorption spectra, reactivity, etc. Our surroundings comprise many different substances, distributed uniformly or non-uniformly. Rarely does an object consist of only one kind of substance such as a piece of pure sugar or a copper wire. Generally we find mixtures of substances.

In simple cases, bodies such as an air bubble, a water drop, a drinking glass and an emerald are uniform. Some bodies comprise a number of separate uniform parts, such as a granite block made up of feldspar, quartz and mica minerals, or a steel beam consisting of a microscopic mixture of iron and iron carbide crystals, or a copper coin having a structure of differently arranged crystals each with the same chemical composition. In addition, bodies such as a cell, a leaf or a wooden block are structured down to the submicroscopic scale. Others change continuously from place to place such as a colorful agate mineral, or the atmosphere that becomes thinner and contains relatively more hydrogen at higher elevations.

The compositions of bodies are not fixed but exchange substances more or less slowly with the environment. Such substances, particularly the more volatile ones, tend to act like entropy by penetrating their surroundings and spreading uniformly within the available space, although often slowly or imperceptibly. For example, wood, fabric, and bricks absorb water in a moist environment and release it in a dry one. In a closed room the different amounts of moisture in individual objects equilibrate just as temperature does (Figure 4.1). If we put a fresh slice of bread in a bag of zwieback or crackers, the bread turns hard and brittle. Conversely, a piece of zwieback or a cracker put together with fresh bread becomes soft and flexible. The air in the bag — more precisely, nitrogen and oxygen — behaves like water. The air-saturated condition of objects in our surroundings is normal. In contrast, boiled water is deprived of air and it slowly absorbs gases from its environment when left standing. If too much air is dissolved, then it is expelled, as in the case of fresh tap water that often contains rising bubbles and forms gas bubbles on container walls. Beer in an uncovered glass turns flat because the concentrated carbon dioxide is released into the atmosphere. Food items with a strong odor gradually transfer this odor to other items in the same storage container. Even a crystallized, compact body is not impenetrable. For instance, an iron rod can gain carbon up to 1% of its weight when carburized in glowing hot coals or graphite powder. Conversely, it can lose this carbon again in an oxidizing flame.

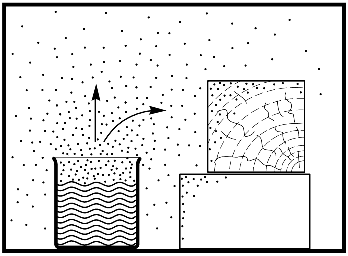


Fig. 4.1: Humidity in a closed room

The amount of substance, which penetrates a given layer of a solid, liquid or gaseous substance can vary enormously. For example, polyethylene lets *n*-heptane pass a thousand times more easily than water — even though *n*-heptane has a similar boiling point as water. Therefore, one can store aqueous solutions in such containers but not gasoline, since the latter will noticeably vanish within a few days. Similarly, a soap film is about one hundred times more impenetrable to nitrogen than to carbon dioxide. There are large differences in the ability to penetrate a layer of air above a salt solution: Water can easily cross this layer but the less volatile salt is almost completely blocked.

For a homogeneous body, a substance penetrating it distributes itself uniformly over the entire volume after a sufficient amount of time. The capacity to absorb foreign substances varies over a wide range, just like the penetrability. One liter of water at room temperature can absorb an unlimited amount of ethanol since water and ethanol are miscible. On the other hand, 500 liters of hydrochloric acid gas at one bar pressure can dissolve only approximately 10 mm^3 of limestone or only 10^{-10} mm^3 of silver sulfide, an amount not perceptible with an optical microscope.

Amounts of substance are not constant since the substances can be converted into one another, or decomposed into their fundamental parts, the elements. They can also be rebuilt from the elements. During familiar chemical transformations the amount of elements remains unchanged, i.e., under the same conditions one obtains the same amount of elements when the mixture is analyzed before and after the transformation. However, processes in nuclear reactors and particle accelerators show that the elements themselves may be transformed and can be split into hydrogen (including the neutrons!), or reconstituted from it with the amount of hydrogen remaining constant. If we wish, we can interpret all transformations of substances as changes of state of a single kind of matter.

4.2. Amount of Substance

Since various measures are used to quantify amounts of substance, let us first consider what properties we should expect of such a quantity.

It is reasonable to assume that an amount of substance within a given space can only change by releasing or receiving substances to or from its environment. In addition, a chemical transformation can consume or create a substance. Its quantity cannot change simply by storing, heating, insulating or separating it from other substances. If we impose this property, certain measures are eliminated immediately, such as the volume used in everyday transactions — a liter of water, a cubic meter of gas, etc. — and in a strict sense also the mass m that increases whenever work is performed on a particular substance due to EINSTEIN's equation

$$E = m c^2 .$$

E is the energy content and c is the speed of light. Because these changes in mass are far below the available accuracy of measurement under normal circumstances, this measure of quantity of substance, the mass m, has been widely accepted in science and in business. However, it is unsatisfactory when one considers that by increasing the temperature of 1 cm^3 of water by 1° Celsius, its mass increases by $5 \cdot 10^{-14}$ g. This corresponds to the mass of around one billion water molecules.

It is a convincing assumption that two amounts of the same substance are equal, provided they occupy the same volume or weigh the same under the same external conditions, such as the shape of the volume, pressure, temperature, field strength, etc.,. In order to measure the available amount of a substance, it is sufficient — as we did for entropy — to divide the substance into equal pieces or fill up equal containers with it under identical conditions, and then count the parts. Basically, any arbitrary quantity can serve as a unit, provided it can be uniquely identified for a given substance. The unit for an amount of gas as "standard cubic meter" is basically such a procedure.

Due to the atomic structure of matter, it seems natural to divide up a portion of substance into its component atoms or groups of atoms. It is therefore natural to use "particle" as a basic unit. By doing so, the concepts of the amount of substance and the number of particles overlap. The usual unit of measurement in chemistry, the "mole", is consistent with the above. The mole may be defined as

$$1 \text{ mol} = 0.6023 \cdot 10^{24} \text{ particles},$$

where the right-hand side represents the so-called LOSCHMIDT or AVOGADRO number. More accurately, the mole may be defined so that a portion with a mass $m = 12$ g of the pure carbon isotope with a mass number of 12 represents exactly an amount of substance $n(^{12}\mathrm{C}) = 1$ mol. Since it is possible to count directly or indirectly the atoms or groups of atoms, the amount of substance n defined by this rule is a measurable quantity. Nevertheless, our measurement procedure is applicable whether or not we know anything about the existence of atoms.

If we consider all matter to be of the same kind, then this definition is not adequate. Logically, all substances must be brought into a consistent material state, such as hydrogen for instance, whose quantity can be determined by counting atoms. The number of nuclear building blocks, in other words the nucleon number, becomes a measure of the amount of substance of a body. Expressed in "mol", the numerical value of this quantity agrees approximately with the mass given in grams. More precisely, a portion of $n = 1$ mol of matter in the form of hydrogen H weighs 1.008 g, as graphite C it weighs 1.000 g and as iron Fe it weighs 0.999 g. According to this measurement procedure, there is a law of conservation of substance (antimatter might be count as negative) similar to that for electric charge. If we identify the amount of substance by its mass, essentially a measure of energy, then matter and energy can be treated as interchangeable due to EINSTEIN's equation. Thus, we encounter relationships here that are similar to those we learned from heat concepts (entropy or energy).

4.3. Chemical Potential

As mentioned earlier, the dispersion of matter in space reminds us of thermal processes. Past researchers were guided by this similarity and spoke of heat as a fluid. It seems obvious that we should use the conceptual framework for thermal phenomena as a model for our current topic.

4.3.1 Energy and Potential

We are already familiar with the fact that a body can exchange various substances with surrounding objects. In order to transfer substances in a controlled fashion, we can utilize a kind of syringe as we did for entropy. If we use this device to deliver a small quantity dn of any substance from one body to another — for example, water in the form of steam from a dry wooden block to a moist brick (Figure 4.2) — it requires work. This work is totally retrievable if all losses due to friction or other entropy-producing processes are avoided. Losses can be avoided, at least in an idealized thought process, by ensuring that all steps are reversible.

In order to determine the work dW required for the substance under consideration, we must transfer only this amount and avoid any additional work. Specifically, we should not transfer other substances simultaneously, nor produce any entropy, nor transfer any extra electric charge. Neither should the bodies be deformed in the process. We are assured that no parameter or component was overlooked when a body ends up in its original state after returning the transferred amount of substance. In practice, this transfer can be carried out as follows: First the desired substance is extracted from a body through a rigid wall (the bottom) of the syringe that is permeable only to the substance. Then the syringe is used to inject the substance into the second body and the expended work is measured. Unfortunately, there is no such permeable wall that holds back entropy. However,

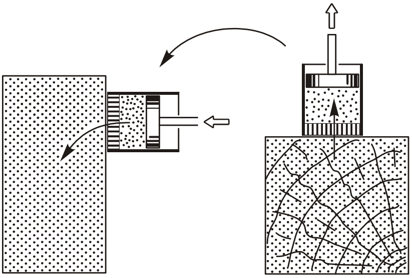


Fig. 4.2: Transport work and chemical potential

we can easily return the unwanted entropy and subtract the corresponding work gained from the initial value. Other unwanted substances can be treated similarly.

The work d*W* does not depend on the path nor the method used because of energy conservation. We could transfer the substance in a single step or via several bodies. We could use our special syringe or any other aid. Consequently, we can state that a small amount of substance d*n* from one body, or part of it, possesses a potential energy d*E* relative to a quantity d*n* from a reference body. The energy d*E* at locations I and II differs by the work expended in bringing d*n* from I to II:

$$\mathrm{d}E_{\mathrm{II}} - \mathrm{d}E_{\mathrm{I}} = \mathrm{d}W \qquad (\mathrm{d}W = \text{"transfer" work}).$$

Let us now consider multiple bodies, which may be parts of a whole, and they may contain larger or smaller amounts of a particular substance. Then we define the "chemical potential" μ for this substance in each body as the ratio

$$\frac{\mathrm{d}E}{\mathrm{d}n} = \mu \,,$$

where d*E* is the potential energy of an incremental amount d*n* compared to an arbitrary but properly selected reference body. Although d*E* depends on d*n*, the parameter μ is a property of the body, or a selected part of it, and is determined by its state. A corresponding chemical potential can be defined and measured for any substance, provided that it is sufficiently mobile.

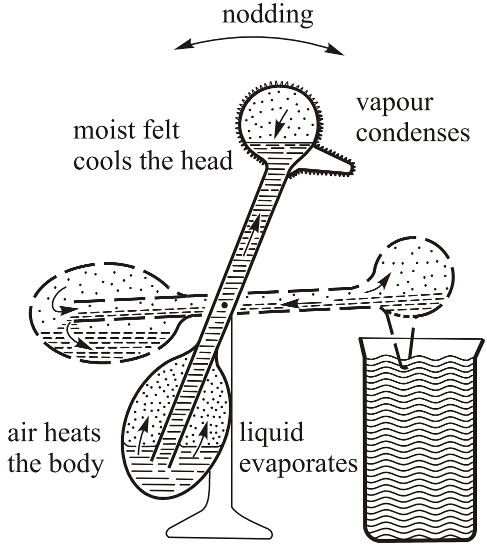


Fig. 4.3: The drinking duck as a chemical engine

Just as for a heat engine where the potential drop of entropy is utilized to perform work, one can construct a corresponding "chemical engine". A simple setup of this kind is the toy known as the "drinking duck" (Figure 4.3), which is driven by the difference of the chemical potential of water in a glass and in the ambient air. The duck slowly sways back and forth, dips its beak into the water, backs up again and after a few oscillations restarts the game. For a lossless engine working between two reservoirs with fixed potentials μ_1 and μ_0, the energy W can be utilized (negative sign!) when the amount of substance n is transferred from μ_1 to μ_0:

$$W = -n\,(\mu_1 - \mu_0)\ .$$

Basically, one could compute the energy increase dE of a body due to transfer of substance dn from EINSTEIN's equation $E = m\,c^2$ by measuring the increase in mass, and thus determine a value for the absolute chemical potential $\mu = \mathrm{d}E/\mathrm{d}n$. However, the body should not lose or receive energy in alternative ways so that dE represents the energy transferred with the syringe — this is the only energy we have to measure. This is accomplished by holding the volume, the entropy content, and remaining amounts of substances in the body constant:

$$\mu = \left(\frac{\mathrm{d}E}{\mathrm{d}n}\right)_{SVn'n''\ldots}.$$

This relationship shows that μ (for matter at rest and not exposed to external fields) agrees with the chemical potential μ from traditional thermodynamics. But this procedure for measuring absolute chemical potential is impractical, as shown by the numerical examples in section 4.3.3, because it requires precise mass measurements of up to 10 to 15 decimal places in order to determine the small potential differences that are important for chemical processes.

4.3.2. The Tendency of Matter to Disperse

The chemical potentials of substances have descriptive properties similar to those of temperature. They indicate how difficult it is to squeeze a substance into a body. The greater the potential difference between two locations, the harder the transfer of a substance. It is convenient to think of μ as a form of tension that wants to distribute the considered substance throughout a given space. In order to move a small amount dn into the body, we have to perform work $\mu \cdot \mathrm{d}n$ to overcome this tension:

$$\mathrm{d}W = \mu \cdot \mathrm{d}n.$$

Since this work changes the composition of a body, we will refer to it as "chemical" in order to distinguish it from mechanical work, $-p\cdot\mathrm{d}V$, thermal work, $T\cdot\mathrm{d}S$, electric work, $\varphi\cdot\mathrm{d}q$, etc. This should not be confused with work arising from a potential energy difference ("lifting work").

The chemical potential μ, as mentioned above, is the driving force for diffusion and flow processes. It measures the drive to disperse. As long as potential differences exist, energy is released due to the flow of substances from locations with higher μ-values to locations with lower ones (Figure 4.4). Flow in the opposite direction requires work. The first process occurs naturally and the energy released is used for entropy production. In contrast, the second process is only possible by external intervention. The larger the potential difference or, in other words, the more powerful the driving force, the stronger the flow of substances and also the more work is wasted. The speed of the process depends on the driving force and on the resistance that has to be overcome. Resistance can vary widely and be so high that no movement is perceived over long periods of time. In order to avoid work losses, the resistance has to be as small as possible and the movement of substances very slow, so that the currents exist practically without driving

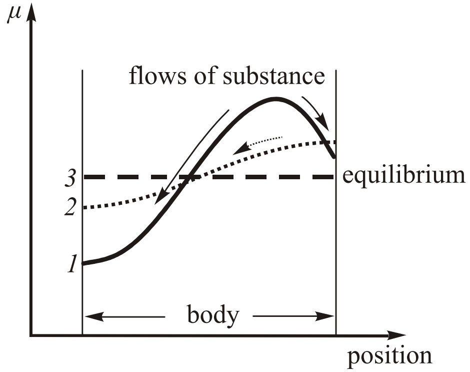


Fig. 4.4: Flows of substance down the of chemical potential slops

force. The substance should not "drop" down but it should be "lifted down" whilst the released energy is captured. Equilibrium exists when all potential differences vanish and the drive to disperse is the same everywhere, at least as long as no separation walls or low temperatures hinder the diffusion and flow, and no other energy-releasing processes are active:

$\mu = \text{const.}$ equilibrium condition.

The behavior of water in a humid room is easily understood in terms of chemical tension. As long as the water potential in the air is higher than that in adjacent objects, the objects absorb moisture. They lose moisture to the air when the potential difference reverses:

$\mu_{\text{inside}} < \mu_{\text{outside}}$ inflow,

$\mu_{\text{inside}} > \mu_{\text{outside}}$ outflow.

Similar behavior is valid for nitrogen, oxygen and carbon dioxide when they are dissolved in water or are separated from it. Another example is the accumulation of carbon on a glowing piece of iron and its subsequent removal. If a portion of ether is added to water, both substances mix (Figure 4.5). The dispersion drive is exhausted, i.e., the chemical potentials of water and ether equalize, when the upper layer contains 1% water and the lower one nearly 8% ether. At that point the mixing process stops.

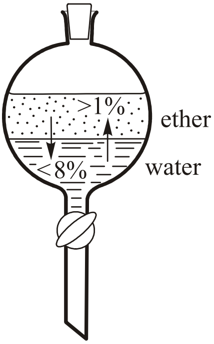


Fig. 4.5: Behavior of adding ether to water

The greater the amount of substance that is added to a body, the higher the rise in the corresponding chemical potential (under some special conditions it may remain constant):

$$\frac{\mathrm{d}\mu}{\mathrm{d}n} \geq 0 .$$

If the opposite were true, the behavior would be unstable. Under such conditions equilibrium exists between two parts of a body provided that the μ-values are equal. However, if a small perturbation accidentally transfers some extra substance to one part and thus lowers the "drive" there, then the imbalance causes additional substance to follow until all of the substance is transferred, or at some point the assumed behavior $\mathrm{d}\mu/\mathrm{d}n < 0$ is no longer valid. The body would disintegrate by itself into such parts that satisfy our initial statement. The always positive, rarely used, inverse $\mathrm{d}n/\mathrm{d}\mu$ of the above derivative, corresponds to the entropy and charge capacities, $(\mathrm{d}S/\mathrm{d}T)_x$ and $(\mathrm{d}q/\mathrm{d}\varphi)_x$. Just like these other examples, it depends upon the given constraints (x):

$$\left(\frac{\mathrm{d}n}{\mathrm{d}\mu}\right)_x \qquad \text{"substance capacity".}$$

4.3.3. Water as a Numerical Example

In contrast to temperature, the numerical values of the chemical potential provide no intuitive feel because they are not used in everyday life. In order to partially close this gap, we select as an example the most familiar substance, water, in various bodies. An amount of water of $n = 1$ mol under normal room conditions has a molar mass $M_\mathrm{m} = 18$ g/mol, occupies a molar volume $V_\mathrm{m} = 18\ \mathrm{cm}^3/\mathrm{mol}$, and contains a molar entropy of $S_\mathrm{m} = 66$ J/(K·mol). The subscript $_\mathrm{m}$ refers to the word "molar" (see section 4.4.1).

a) Different shape and elevation (Figure 4.6)

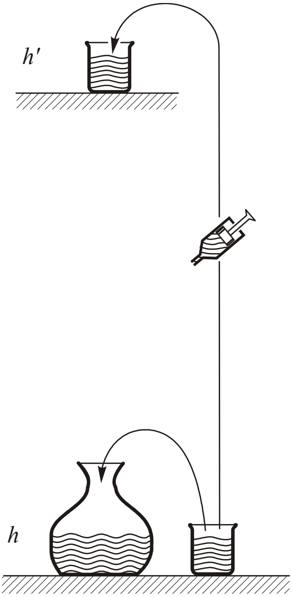


Fig. 4.6: Water transfer — lifting

In order to lift an amount of water dn with a mass $M_\mathrm{m}\cdot\mathrm{d}n$ from the lower-right container to either the upper container or the left container, work $\mathrm{d}W = M_\mathrm{m}\cdot\mathrm{d}n\cdot g\cdot\Delta h$ is required, where Δh is finite in the first case and zero in the second. Since we assume the water to be pure and the temperature to be uniform, we do not need "selectively permeable" walls to keep out unwanted substances, and we do not need to return entropy. The chemical potential $\Delta\mu = \mathrm{d}E_\mathrm{II}/\mathrm{d}n - \mathrm{d}E_\mathrm{I}/\mathrm{d}n = \mathrm{d}W/\mathrm{d}n$ is independent of the size and shape of the body and is given by

$$\Delta\mu = M_\mathrm{m}\cdot g\cdot\Delta h.$$

For an elevation difference of 1 m, we get $\Delta\mu \approx 0.000\,18$ kJ/mole. Some textbooks use the name "gravito-chemical potential" for the quantity μ in this case, to indicate that it combines both gravitational and chemical influences.

b) Different pressure (Figure 4.7)

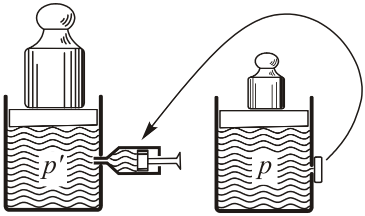


Fig. 4.7: Water transfer — pressure

Let us extract an amount of water dn with volume $V_m \cdot \mathrm{d}n$ from the right container and add it to the left one, expending work $\mathrm{d}W = -p \cdot V_m \cdot \mathrm{d}n + p' \cdot V_m \cdot \mathrm{d}n$. This result assumes that the pressure difference is not too high and that we can treat V_m as constant. Otherwise, we must include the work of compression $\mathrm{d}W'$ in transferring the amount dn from p to p'. Again, entropy is of no concern. It is true that the volume of our system changes as the water in the container displaces the weights, and thus the system exchanges energy with the weights. But this is unimportant for the measurement process. Therefore, we have

$$\Delta\mu = V_m \cdot \Delta p.$$

For a pressure difference of 1 bar, we get $\Delta\mu \approx 0.0018$ kJ/mol.

c) Different temperatures (Figure 4.8)

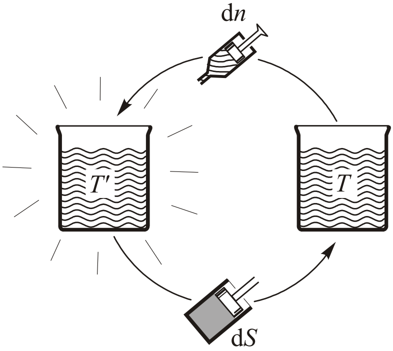


Fig. 4.8: Water transfer — temperature.

Let us remove an amount of water dn from the right container, accompanied by an entropy flow $S_m \cdot \mathrm{d}n$. We cannot mix cold and warm water because the process is irreversible. In order to raise the temperature of the water in the syringe from T to T', we add a small amount of entropy dS' from the hotter container with an entropy syringe and obtain the work dW'. We then transfer the water to the left container. In violation of our measurement procedure, the entropy $S_m \cdot dn$ was also passed from the right to the left container. As part of the return transport we have to perform work $-S_m \cdot dn \cdot \Delta T$. If the temperature differences are small, dW' is negligible and the total expenditure of work becomes $dW = -S_m \cdot \Delta T \cdot dn$. The final expression for $\Delta\mu$ is given by

$\Delta\mu = -S_m \cdot \Delta T$ for small ΔT.

For a temperature difference of 1 K, we get $\Delta\mu \approx -0.066$ kJ/mol.

d) Different chemical milieu (Figure 4.9)

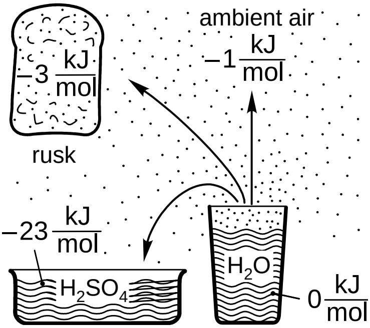


Fig. 4.9: Water potential of water in different chemical milieus

Compared to the value of a glass of water, the chemical potential in air with a relative humidity of 60…70%, typical of living room conditions, is roughly 1 kJ/mol lower, about 3 kJ/mol lower for fresh zwieback or crackers, and about 23 kJ/mol lower for concentrated sulfuric acid, a strong water-extracting agent. Fresh bread, with a chemical potential nearly equal to that of a glass of water, will dry out if left exposed to ambient air, while a piece of zwieback or cracker will lose its crispiness by absorbing water.

e) Absolute value

If we add 10^{-3} mol of water to a 1 m^3 cube filled with water at constant elevation, volume, entropy content, etc., the mass increases by $\Delta m = 18.0153\ldots$ mg and the energy by $\Delta E = \Delta m \cdot c^2 = 1.62 \cdot 10^{12}$ J. Therefore the chemical potential μ of water has the absolute value of $1.62 \cdot 10^{12}$ kJ/mole.

The result that cold water has a higher chemical potential than warm water, indicating a stronger tendency to disperse, seems to contradict our experience. We know that wet clothes dry out near the oven and water condenses on cold windowpanes. For those cases with a large temperature difference, a strong entropy flow dictates the flow of substances, and supplies sufficient energy to transfer substances against opposing potential drops.

4.4. Coupling of Substance Transfer to Other Processes

An object that receives substances increases its volume, energy and entropy content in most cases. However, it can also bend, distort, accept or reject another substance, change its state of charge and so on. The following sections present a description of such processes.

4.4.1. Volume and Entropy Demands of a Substance, "Molar Mass"

A gelatine cube, a wooden block and even a granite block swell when wet and shrink when dried. We can attribute these changes in volume to the space requirements of the water inside the respective bodies. If we add 1 cm^3 of water to one liter of concentrated sulfuric acid and also to the same amount of half-concentrated sulfuric acid, then the volume increases by 0.48 cm^3 in the first case and by 0.97 cm^3 in the second. Evidently water does not always require the same space even when the temperature and pressure remain constant, so it becomes necessary to define this concept more precisely.

We will consider the volume required for a given amount of substance as the volume by which a body expands when the substance is added. For a more rigorous treatment, we will add only an incremental quantity $\mathrm{d}n$ in order to avoid significant changes to the composition of the body. The resulting volume increase $\mathrm{d}V$ can be computed for a convenient amount of substance, say a mole, as $V_\mathrm{m} = \mathrm{d}V/\mathrm{d}n$. The quantity V_m is called the (partial) molar volume of the substance in the body. Let us now specify the conditions under which this procedure has to be performed. It is required that pressure, temperature, field strength, etc. remain constant in order to avoid errors due to thermal expansion, compressibility, electrostriction and similar effects. Simultaneously, no other substances can be introduced. Finally, we define

$$V_i \equiv \left(\frac{\mathrm{d}V}{\mathrm{d}n_i}\right)_{pT\ldots n_{\hat{i}}} \quad ,$$

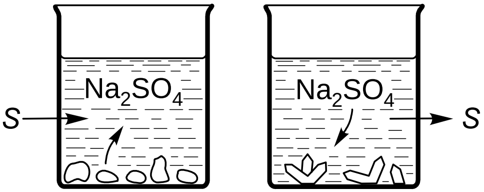
where the subscript i replaces the subscript m in order to refer to the molar volume of a *particular* substance under consideration. The symbol $n_{\hat{i}}$ with $\hat{i}$ denotes the amounts of all other substances besides i.

Note that the molar volume V_i may be negative in the exceptional case where the total volume drops when a substance penetrates a body. Therefore, we prefer the name "volume demand" for V_i because it is more descriptive. For an estimate of V_i, we can start with the fact that 1 mol of atoms in the condensed state occupies a volume of around 10 cm^3, and about a thousand times more volume in the gaseous form under normal room conditions. For homogeneous bodies consisting of a single pure substance, the volume demand is given by the total volume V divided by the total amount of substance n, because under the specified conditions $V \sim n$:

$$V_\mathrm{m} = \frac{V}{n} \qquad \text{for a pure substance.}$$

As a general rule, if the volume of a body increases when a substance is added, the entropy content also increases. This entropy increase is due not only to the contribution from the substance, but also to the additional entropy exchanged to keep the temperature from rising or falling. For example, by dissolving a teaspoonful of Glauber salt ($Na_2SO_4 \cdot 10H_2O$), sodium nitrate ($NaNO_3$) or potassium nitrate (KNO_3) in a glass of water, the solution turns so cold that water condenses on the glass. In order to keep the temperature constant, entropy has to be received from the environment. The entropy is released when the salts precipitate from a super-saturated solution, and as a result the solution becomes noticeably warmer (Figure 4.10). The same amount of a substance has a different entropy content depending on whether it is pure or dissolved in another substance. The molar

Fig. 4.10: Entropy change when a substance dissolves (lef or precipiates (right)



entropy of a pure substance S_m, or the (partial) molar entropy S_i of a substance i, distributed in another substance, is defined in a similar fashion to V_m and V_i by the equation:

$$S_i \equiv \left(\frac{\mathrm{d}S}{\mathrm{d}n_i}\right)_{pT\ldots n_{\hat{i}}}$$

For homogeneous bodies consisting of a single substance, S_m is computed similarly to V_m by dividing the total entropy S by the total amount of substance n:

$$S_m = \frac{S}{n} \qquad \text{for a pure substance.}$$

It can be estimated from V_m and values of entropy density. If a substance is evaporated or mixed with other substances, then the entropy demand increases significantly.

Similarly we can describe the energy increase dE of a body due to the addition of the incremental amount of substance dn, and define a (partial) molar energy E_i of a substance in that body: $E_i = (\mathrm{d}E/\mathrm{d}n_i)_{pT\ldots n_{\hat{i}}}$. This and a number of related quantities (partial molar enthalpy, free energy, free enthalpy, etc.) play an important role in traditional thermodynamics, but they are dispensable here. On the basis of EINSTEIN's equation $m = E/c^2$, we can assign via E_i a (partial) molar mass to each substance (or more concisely, "molar mass") $M_i = E_i/c^2 = (\mathrm{d}m/\mathrm{d}n_i)_{pT\ldots n_{\hat{i}}}$. The relative changes of this quantity under different conditions are so small that M_m is considered constant for most applications. As such, we speak of the mass $m = n \cdot M_m$ of the amount n of a substance. If we know the elemental composition, i.e., the chemical formula of a substance, the molar mass can be calculated with sufficient accuracy by adding the M_i-values or "atomic weights" for the elements. Since masses can be easily and precisely determined from weight measurements, and the amounts of substance n_i by dividing by the molar mass, this method tends to be used almost exclusively.

4.4.2. Main Equation and Coupling

If we change the volume, entropy or amount of substances in a body, then its energy content is modified by the mechanical, thermal and chemical work expended in the process:

$$\mathrm{d}E = (-\underline{p})\,\mathrm{d}V + \underline{T}\,\mathrm{d}S + \mu_1\mathrm{d}\underline{n_1} + \mu_2\mathrm{d}\underline{n_2} + \ldots + \mu_k\mathrm{d}\underline{n_k}\ .$$

If we subject the body to an electric or magnetic field, and charge or accelerate it, then additional terms have to be included in the above equation. For simplicity, we will omit these terms. By proceeding at a sufficiently slow rate to avoid wasting energy on diffusion, all contributions to the work are retrievable and the system can be considered as elastic. The parameters p, T and n_i are easily measured and are hence usually selected as independent variables. We already know that V and S are coupled with the amounts of substance n_i, and V and S are themselves coupled, so that we can expect various relationships among the main quantities. Let us now evaluate some of these relationships.

a) Coupling between V and n_i

If the volume increases on addition of substance i, i.e., V_i is positive, then an increase in pressure p makes the addition more difficult, and the corresponding value of μ_i increases. By using the flip rule, we get

$$\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}p}\right)_{Tn_i n_{\hat{i}}} = \left(\frac{\mathrm{d}V}{\mathrm{d}n_i}\right)_{pTn_{\hat{i}}} = V_i \,.$$

V_i not only describes the volume demand of substance i, but also the pressure coefficient of its chemical potential. For solids and liquids, for which V_i is not influenced much by pressure, the $\mu_i(p)$-curve varies linearly with p. For gases, the $\mu_i(p)$-curve is approximately logarithmic and much steeper (Figure 4.11).

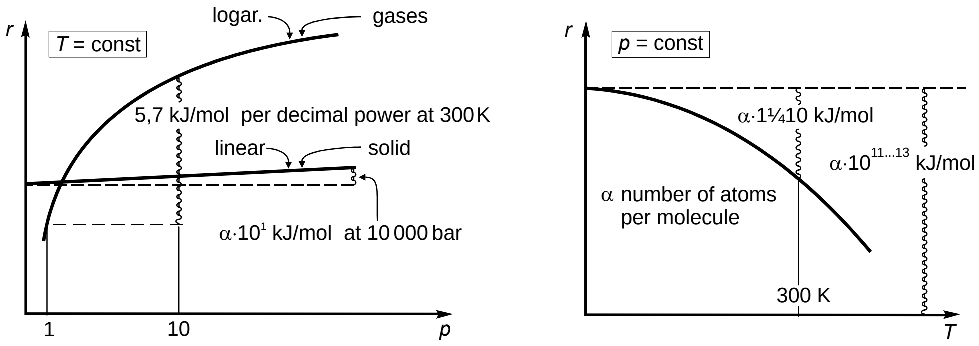


Fig. 4.11: Pressure- and temperature dependence of μ

b) Coupling between S and n_i

A positive S_i denotes that entropy tends to flow into the body as the substance i is added. An increase in temperature not only increases S but also aids the addition of the substance. As a result, the chemical potential μ_i is lowered provided that no additional amount of substance i is added (n_i = const.):

$$\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}T}\right)_{pn_in_{\hat{i}}} = -\left(\frac{\mathrm{d}S}{\mathrm{d}n_i}\right)_{pTn_{\hat{i}}} = -S_i\,.$$

S_i not only represents the entropy demand of the substance i but also the negative temperature coefficient of its chemical potential μ_i. Figure 4.11 depicts the temperature variation of μ. The $\mu(T)$-curve starts with a horizontal tangent, as it should since the entropy content vanishes for $T = 0$, and then drops off more and more steeply. This drop-off is faster for gases and substances in dilute solutions than for solids or liquids because the first two contain more entropy.

c) Coupling between n_i and n_j

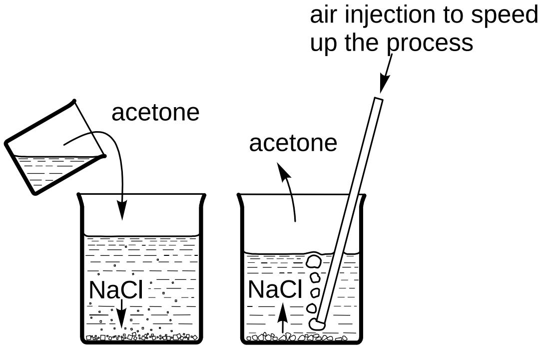


Fig. 4.12: Interplay between acetone and NaCl in water

If we add drops of acetone to a saturated solution of table salt, then the salt begins to precipitate. As the acetone evaporates, the salt slowly dissolves again (Figure 4.12). This is an example of counter-coupling between two amounts of substance n_i and n_j, where one substance tries to drive out the other. On the other hand, a small amount of solid lead chloride $PbCl_2$ at the bottom of a glass of water will dissolve on addition of potassium nitrate KNO_3 ("salting-in effect"). This provides an example of co-coupling. The change of the chemical potential of one substance indicates the strength of the effect caused by a second substance. This is expressed more precisely by the coefficient $\left(\mathrm{d}\mu_i/\mathrm{d}n_j\right)_{pTn_{\hat{j}}}$. Due to the symmetry of the coupling, the reverse effect of the second substance on the first, measured by the coefficient $\left(\mathrm{d}\mu_j/\mathrm{d}n_i\right)_{pTn_{\hat{i}}}$, is equally strong, as can be shown with the flip rule:

$$\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}n_j}\right)_{pTn_{\hat{j}}} = \left(\frac{\mathrm{d}\mu_j}{\mathrm{d}n_i}\right)_{pTn_{\hat{i}}} .$$

Qualitatively it is easy to demonstrate the inverse effect with our first example: By adding table salt to an acetone-water mixture with a 1:1 ratio, the acetone separates into a second layer above the solution ("salting-out effect").

For a substance that exists in pure form in a homogeneous body, it is possible to evaluate μ as a function of p and T compared to a reference value $\mu(p_0, T_0)$ since V_m and S_m can be measured readily:

$$\mu = \mu(p_0, T_0) + \int_{p_0}^{p} V_\mathrm{m}\mathrm{d}p - \int_{T_0}^{T} S_\mathrm{m}\mathrm{d}T .$$

Sometimes it is easier to investigate a simpler piece of matter that is in chemical equilibrium with the body in question, since both substances have the same chemical potential. For example, we can determine the potential of water in a cane sugar solution by evaluating the potential of the pure water vapor above the solution when isolated from the outside air. Its μ -value can be computed as that of a pure substance using the above equation.

4.5. Transformations of Substances

This section deals with the laws that govern the chemical conversions and transformations of different forms of substances.

4.5.1. Conditions for Chemical Conversion

So far we have ignored the fact that a substance penetrating a body may be changed chemically, either destroyed or produced. If a small amount of substance dn disappears in the process, its potential energy $\mu \cdot \mathrm{d}n$ is released, provided that it is not captured by the reaction products. Since this energy may be used to produce entropy and cannot be recovered, the chemical potential μ in a way forces the substance to destroy or transform itself. The quantity μ therefore assumes a new meaning as a "self-destructive drive ". Without conservation of matter this drive would destroy the substance into nothing, or rather, radiate it away. Instead, the destruction of one substance leads to the formation of another. During chemical conversions, excluding element changes, the amounts of the participating elements must remain unchanged. In a chemical equation this requirement is met by ensuring that the total number of atoms of each kind is equal on both sides.

According to this idea the conversion $A \rightarrow B$ should only take place spontaneously if the "destructive" or "transforming" drive μ_A of the reactant is greater than that of the product μ_B. In other words, $\mu_A > \mu_B$. Several substances may be involved in the reaction,

$A + B \rightarrow 2\,C$ or more generally $\nu_A\,A + \nu_B\,B + \nu_C\,C \ldots = 0$.

The above notation includes "stoichiometric coefficients" ν_i which are negative for the reactants and positive for the products ($\nu_A = -1$, $\nu_B = -1$, $\nu_C = +2$). Since the total "destructive drive" of the vanished substance must be greater than that of the newly formed ones, we impose the following requirement:

$\mu_A + \mu_B > \mu_C + \mu_C$ or more generally $\nu_A\mu_A + \nu_B\mu_B + \ldots < 0$.

In the opposite case, the drive of the reaction is reversed. Since chemical potentials vary with pressure, temperature, composition, etc., it is likely that the same chemical reaction can run in either direction depending on these conditions.

In order to confirm our assumption, let us consider what happens with the energy. The progress of a reaction is usually described by a variable ξ called "extent of reaction" that is explained by the equation

$\Delta n_i = \nu_i \xi$,

where Δn_i is the change of the amount of the substance i. If ν_i is negative, Δn_i indicates a loss of the substance i. We can denote the common expression "unit conversion" more precisely by $\xi = 1$ mol. In our example, 1 mol of A and B each are used up to create 2 mol of C. If the reaction progresses by the small amount $d\xi$ and the components change by $dn_i = \nu_i\,d\xi$, then the potential energy $\mu_A \cdot d\xi + \mu_B \cdot d\xi$ is released during the destruction of the reactants. Simultaneously, energy $2\mu_C \cdot d\xi$ has to be supplied for the newly created products. The total expenditure of work or "chemical work" is therefore given by

$$\mathrm{d}W = (-\mu_A - \mu_B + 2\mu_C)\,\mathrm{d}\xi \quad \text{or more generally} \quad \mathrm{d}W = (\nu_1\mu_1 + \nu_2\mu_2 + \ldots)\,\mathrm{d}\xi.$$

The reaction can only run by itself ($\mathrm{d}\xi > 0$) if energy is released, or in other words $\mathrm{d}W$ is negative. The expression in parentheses in the equation above must be negative, as we suspected earlier. This difference of the "chemical potentials of products minus reactants", $-\mu_A - \mu_B + 2\mu_C$ or $\sum \nu_i \cdot \mu_i$, is usually abbreviated by the symbol $\Delta_R\mu$ where the general R (R for reaction) can be replaced with other symbols for a particular reaction. The term $-\Delta_R\mu$ represents the forward drive or so-called "affinity" $\mathcal{A} = -\Delta_R\,\mu$ of a reaction, while $+\Delta_R\,\mu$ is the reverse drive. The conversion conditions can now be simply expressed as

$$\left.\begin{array}{ll} \Delta_R\,\mu < 0 & \text{reaction driven forwards,} \\ \Delta_R\,\mu = 0 & \text{equilibrium,} \\ \Delta_R\,\mu > 0 & \text{reaction driven backwards.} \end{array}\right\} \quad (\Delta_R\,\mu \equiv \textstyle\sum \nu_i \cdot \mu_i)$$

In order to describe the dispersion of a substance D, we can arbitrarily fix the zero point for its chemical potential since only the difference $\Delta\mu_D$ is important for the spread of D. That is convenient for many calculations. As soon as we include chemical conversions, however, we only have this freedom for the elements. All other substances consist of combinations of the elements:

$$a\mathrm{A} + b\mathrm{B} + c\mathrm{C} + \ldots \rightarrow \mathrm{A}_a\,\mathrm{B}_b\,\mathrm{C}_c\,\ldots\,.$$

During the formation (indicated by f) of a compound $\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c\ldots$ from its elements, which exist in some (well defined) standard state ($^\ominus$), the following work is expended for each mole produced:

$$W_m = \mu_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c\ldots} - a\mu_A^\ominus - b\mu_B^\ominus - c\mu_C^\ominus - \ldots \equiv \Delta_f\,\mu_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c\ldots}$$

By using the chemical potential $\mu_i^\ominus$ of the elements in their standard states and measuring $W_m = \Delta_f\,\mu$, the quantity $\mu_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c\ldots} = \Delta_f\,\mu_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c\ldots} + a\mu_A^\ominus + b\mu_B^\ominus + \ldots$ becomes fixed and can no longer be freely chosen. Conversely, because the terms $a \cdot \mu_A^\ominus + b \cdot \mu_B^\ominus + \ldots$ drop out during affinity calculations, we are free to do what we want with the $\mu^\ominus$-values. The chemical potential of a pure substance at 1.013 bar pressure and 298 K temperature, compared to that of its elements in pure, stable form under the same pressure and temperature, is tabulated for many substances (standard free enthalpies of formation). By setting the $\mu^\ominus$-values of the elements to zero, we can identify the quantity $\Delta_f\,\mu_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c\ldots}$ for any compound using the chemical potential $\mu_{\mathrm{A}_a\mathrm{B}_b\mathrm{C}_c\ldots}$ of this compound, which simplifies the notation and evaluations. This possibility is removed if we allow changes to the elements themselves (i.e., nuclear reactions) because differences in chemical potentials between them would become important.

4.5.2. Coupling of *V*, *S* and ξ

Let us now consider a homogeneous or non-homogeneous body consisting of various substances A_i. This body can be compressed and heated and has the reaction $\sum \nu_i A_i = 0$ running internally. The effect of such a chemical reaction is identical to that of an exchange of substance with the environment, except that the quantities n_i are no longer independent, but are related by the extent of reaction ξ: $\mathrm{d}n_i = \nu_i \cdot \mathrm{d}\xi$. As a result of this relation and $\Delta_\mathrm{R}\mu = -\mathcal{A}$, the main equation has the form

$$\mathrm{d}E = -p\mathrm{d}V + T\mathrm{d}S + \sum \mu_i\, \mathrm{d}n_i = (-p)\mathrm{d}V + T\mathrm{d}S + (-\mathcal{A})\mathrm{d}\xi\,.$$

On the basis of the above relation we can consider *S*, *V* and ξ as elastically coupled. We are already familiar with some of the possible primary and coupling effect indicators such as $(\mathrm{d}S/\mathrm{d}T)_{p\xi}$ representing the entropy capacity *Ç*. The index ξ merely indicates that the substances of the body will not change. Other coefficients such as $(\mathrm{d}V/\mathrm{d}\xi)_{pT}$ and $(\mathrm{d}S/\mathrm{d}\xi)_{pT}$ that describe the change in volume and entropy content during the reaction can easily be calculated. Applying the chain rule to the function $V(p, T, n_1(\xi), n_2(\xi)...)$ and its counterpart for *S*, we get:

$$\left(\frac{\mathrm{d}V}{\mathrm{d}\xi}\right)_{pT} = \left(\frac{\mathrm{d}V}{\mathrm{d}n_1}\right)_{pTn_{\hat{1}}} \frac{\mathrm{d}n_1}{\mathrm{d}\xi} + \left(\frac{\mathrm{d}V}{\mathrm{d}n_2}\right)_{pTn_{\hat{2}}} \frac{\mathrm{d}n_2}{\mathrm{d}\xi} + \ldots = V_1\nu_1 + V_2\nu_2 + \ldots\ .$$

The result can be summarized as follows:

$$\left(\frac{\mathrm{d}V}{\mathrm{d}\xi}\right)_{pT} = \sum \nu_i V_i \equiv \Delta_\mathrm{R} V_\mathrm{m}, \qquad \left(\frac{\mathrm{d}S}{\mathrm{d}\xi}\right)_{pT} = \sum \nu_i S_i \equiv \Delta_\mathrm{R} S_\mathrm{m}\ .$$

Here, the symbol Δ_R is again used to simplify the notation. By further application of the flip rule, we get:

$$\left(\frac{\mathrm{d}\mathcal{A}}{\mathrm{d}p}\right)_{T\xi} = -\left(\frac{\mathrm{d}V}{\mathrm{d}\xi}\right)_{pT} = -\Delta_\mathrm{R} V_\mathrm{m}; \qquad \left(\frac{\mathrm{d}\mathcal{A}}{\mathrm{d}T}\right)_{p\xi} = \left(\frac{\mathrm{d}S}{\mathrm{d}\xi}\right)_{pT} = \Delta_\mathrm{R} S_\mathrm{m}\,.$$

These equations tell us what we could have predicted on the basis of the concept of coupling: If the reaction increases the volume $(\Delta_\mathrm{R} V_\mathrm{m} > 0)$, then the reaction will be hindered when higher external pressure hinders the expansion. In other words, the affinity $\mathcal{A}$ weakens when the external pressure increases. On the other hand, if the reaction increases the entropy ($\Delta_R S_m > 0$), the reaction will be boosted by a higher external temperature. Here the affinity $\mathcal{A}$ strengthens with increase of external temperature.

If we assume the reaction has reached equilibrium ($\mathcal{A} = 0$) and we want to maintain this equilibrium despite a temperature increase, we must simultaneously increase the pressure. Quantitatively, we obtain the following relation between p and T (generalized [CLAUSIUS]-CLAPEYRON Equation, derivation hint: cut back to p, T, ξ):

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mathcal{A}\xi} = -\left(\frac{\mathrm{d}\mathcal{A}}{\mathrm{d}T}\right)_{p\xi} \Bigg/ \left(\frac{\mathrm{d}\mathcal{A}}{\mathrm{d}p}\right)_{T\xi} = \left(\frac{\mathrm{d}S}{\mathrm{d}\xi}\right)_{pT} \Bigg/ \left(\frac{\mathrm{d}V}{\mathrm{d}\xi}\right)_{pT} = \frac{\Delta_R S_m}{\Delta_R V_m} .$$

The term $\Delta_R S_m \cdot \mathrm{d}\xi$ describes the increase in entropy content of the body as the reaction progresses by $\mathrm{d}\xi$ (at constant p and T). This amount should not be confused with the entropy that is input from the surroundings $\acute{S}_m \cdot \mathrm{d}\xi$. If the energy released by the reaction $\mathrm{d}W = -\mathcal{A} \cdot \mathrm{d}\xi$ is burned up producing the entropy $S_p = -\mathrm{d}W/T$ we must subtract it from the increase in entropy content. The total entropy input from the surroundings becomes:

$$\acute{S}_m \cdot \mathrm{d}\xi = \Delta_R S_m \cdot \mathrm{d}\xi - \frac{\mathcal{A} \cdot \mathrm{d}\xi}{T} \qquad \text{or} \qquad \acute{S}_m = \Delta_R S_m - \frac{\mathcal{A}}{T} .$$

$T \cdot \acute{S}_m$ represents the heat$^\bullet$ of reaction that arises from two different sources and is therefore not a characteristic quantity. In earlier times it was interpreted as a measure of the driving force of a chemical reaction. Since the term $T \cdot \Delta_R S_m$ is

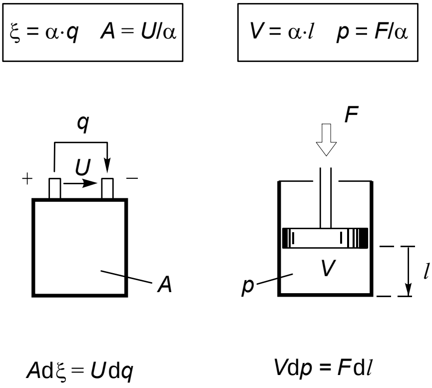


Fig. 4.13: Galvanic cell compared to cylinder with piston

substantially smaller than $\mathcal{A}$, its contribution was overlooked. Since the total reaction heat• is approximately equal to $\mathcal{A}$ scientists tended to ignore the mistake.

While we can arbitrarily set the work coordinates S and V to within certain limits, this is not possible for changes in ξ. A galvanic cell provides an exception whereby the transported charge q has a fixed relationship to the extent of reaction ξ of the internal chemical reaction, similar to the relationship between volume V and piston position l in a gas cylinder (Figure 4.13). The affinity $\mathcal{A}$ is related to the terminal voltage U — just as the cylinder pressure p is related to the force F on the piston — and can be measured easily without regard to p, T and ξ provided that the constant of proportionality α between q and ξ is known.

4.5.3. Phase Transitions

Phase transition means the change of a substance from one phase into another, i.e., the conversion of a single substance. We restrict the scope of our analysis to the influence of pressure and temperature.

For each state of aggregation and each modification of a substance, $\mu(p, T)$ shows different behavior (solid curves in Figure 4.14). The form with the lowest chemical potential, often called "poorest in energy", is the most stable. In the figure, form I is stable below transition temperature T_t, and form II at temperatures above T_t, while form III should not exist. Nevertheless, form III may be created during a chemical reaction if its rate of formation exceeds that of its competitors. It changes more or less rapidly to the stable, "lowest-energy form" as a result of its greater chemical potential.

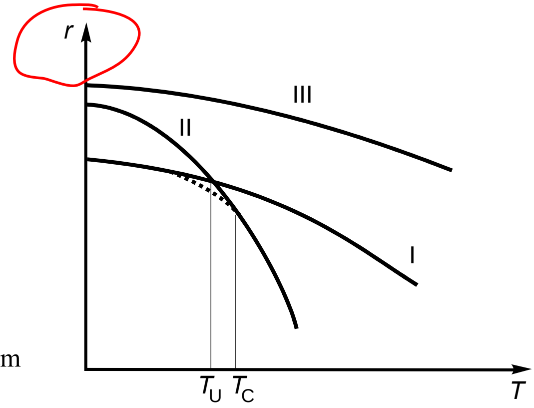


Fig. 4.14: $\mu(p, T)$-Diagram

The location of the transition point at a given pressure is given by the equation

$$\mu_{\mathrm{I}} = \mu_{\mathrm{II}} \, .$$

At this temperature the structure of form I becomes unstable and transforms into II. A step change in properties is associated with this transition. The entropy content increases (dashed curve in left graph of Figure 4.15) and, in general, the vol-ume also increases. During the melting process the change in entropy for a mona-tomic substance is around 10 J/K per mol (Richards' Rule) and the volume change is 3% on average. It requires an amount of entropy of 100 J/K to evaporate 1 mol of a substance at 1 bar pressure (Pictet-Trouton's Rule).

At the transition point T_{t}, the entropy capacity $Ç_{\mathrm{m}} = (\mathrm{d}S_{\mathrm{m}}/\mathrm{d}T)_p$ diverges to infinity (see Figure 4.15, right graph, dashed line). The curves start at zero, or slightly above, and increase $\sim T^2$ (Debye's law). The maximum value for simple solids occurs at approximately $\Theta/4$ where Θ is the Debye characteristic temperature that falls in the range of 100 to 500 K. At higher temperatures the entropy capacity approaches a hyperbolic asymptote that essentially depends only on the number of atoms, and not on its structure or state of bonding (Dulong-Petit and Kopp-Neumann rules).

Since an increase in pressure changes the chemical potential, it can also shift the transition temperature. Starting with an equilibrium, i.e., $\mu_{\mathrm{I}} = \mu_{\mathrm{II}}$, the tem-

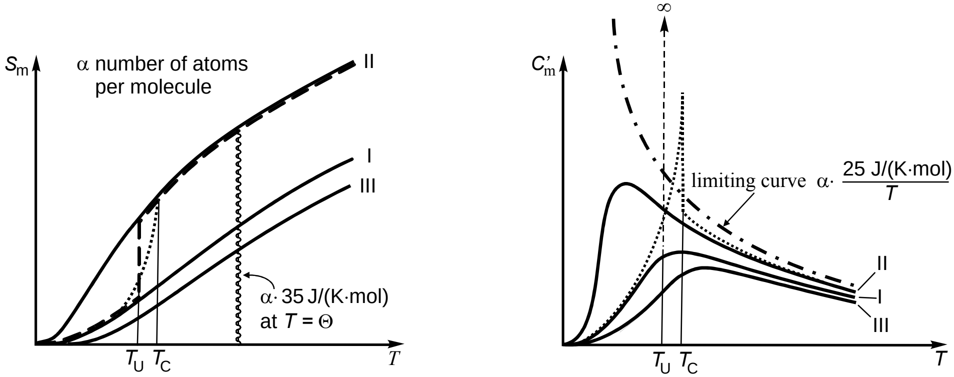


Fig. 4.15: Entropy content (left side) and entropy capacity (right side)

perature must change by $\mathrm{d}T$ to restore equilibrium of the chemical potential after a pressure change of $\mathrm{d}p$. The pressure change causes the chemical potential increase of $V_\mathrm{I} \cdot \mathrm{d}p$ and $V_\mathrm{II} \cdot \mathrm{d}p$. The new equilibrium condition becomes:

$$\mu_\mathrm{I}\ V_\mathrm{I}\ \mathrm{d}p - S_\mathrm{I}\ \mathrm{d}T = \mu_\mathrm{II} + V_\mathrm{II}\ \mathrm{d}p - S_\mathrm{II}\ \mathrm{d}T\,.$$

It follows that $0 = \Delta_\mathrm{t}V_\mathrm{m} \cdot \mathrm{d}p - \Delta_\mathrm{t}S_\mathrm{m} \cdot \mathrm{d}T$ or

$$\frac{\mathrm{d}T_\mathrm{t}}{\mathrm{d}p} = \frac{\Delta_\mathrm{t}V_\mathrm{m}}{\Delta_\mathrm{t}S_\mathrm{m}} \qquad \text{[CLAUSIUS-]CLAYPERON Equation.}$$

4.5.4. λ –Transitions

The transition from one material structure of a substance to another during a rise in temperature does not always occur discontinuously, but can sometimes develop slowly. The S_m-curve in the latter case has no discontinuity but increases steeply until it approaches the vertical, and then at temperature T_C makes a sharp turn to follow the S_m-curve for the second state. The point of inflection is called the CURIE-point of the transition. The $Ç_\mathrm{m}$-curve, obtained by differentiating the S_m-curve, has the shape of the Greek letter λ (note the shape of the dotted curve in the right graph of Figure 4.15). For this reason, the process is called a λ -transition. Such a transition occurs when the two forms I and II have stable intermediate forms with lower chemical potentials than the two basic forms (dotted curves in Figures 4.14 and 4.15).

During a normal transition, for example, the transition from a body-centered cubic to a face-centered cubic lattice, all possible intermediate forms are "higher in energy" and, therefore, less stable. At the transition point the structure jumps from one form into the other.

λ-transitions occur when superstructures disappear, or at the CURIE-point in ferromagnetism. With increasing temperature, the initial strict order of the building blocks at first deteriorates slowly, then more quickly because the increasing disorder weakens the restoring forces. It breaks down completely at the CURIE-point T_C.

4.6. Homogeneous Bodies

With some care, homogeneous bodies can be broken up and put back together again (Figure 4.16) without the expenditure of much work. We can neglect the minimal work required to form the outer surfaces, and ignore the presence of external fields such as the gravitational field, which is only significant for a giant body like the Earth. This property is not self-evident, for instance charged bodies do not have this ability. By increasing the entropy S, the volume V, and the amounts n_i of a homogeneous body consisting of one or more substances A_i, its energy E grows by the same factor a. We can consider the entire body as being constructed of parts, each containing the same amount of energy. This condition is formally expressed by the equation:

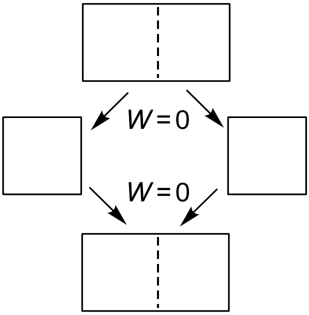


Fig. 4.16: Partitioning a body

$$E\left(aV, aS, an_1, an_2, \ldots\right) = aE\left(V, S, n_1, n_2, \ldots\right).$$

In order to describe the consequences of this relationship, it is advantageous to expand our mathematical tools.

4.6.1. Degree of a Quantity

A function that contains a factor a common to all terms that can be "factored out" to the power g:

$$f\left(ax_1, ax_2 \ldots\right) = a^g \cdot f\left(x_1, x_2, \ldots\right),$$

are called homogeneous functions of degree g. For example, $f(x,y) = x^2 + 3xy + y^2$ is homogeneous of degree 2 (all quadratic terms), and $f(x,y) = 1/x + 1/y$ is homogeneous of degree −1 (because $1/ax + 1/ay = a^{-1}(1/x + 1/y)$). The energy function from the last section is linearly homogeneous ($g = 1$).

Consider an elastic system with work coordinates $x_1, x_2, \dots x_n$ and a set of variables y, z ... that depend on x_i. Although the following discussion deals with purely mathematical relationships, we will use physical terminology in order to make it easier for the mathematical novice to understand later applications. If we assume that for the quantity $y = f(x_1, \dots x_n)$ the function f is homogeneous of degree g, then we will say that y itself has degree g. Since each x_i increases by the factor a if multiplied by a, we have $g = 1$ for x_i.

In addition to $x_1, \dots x_n$ it is useful to introduce the quantities $z_1, \dots z_n$ having the degrees $g_1, \dots g_n$ as independent variables. An arbitrary variable $y = h(x_1, \dots x_n)$ of degree g can be written in the form $y = F(z_1, \dots z_n)$ where F need not be a homogeneous function. But this function F satisfies the following equation:

$$F\left(a^{g_1} z_1, \dots, a^{g_n} z_n\right) = a^g \cdot F\left(z_1, \dots, z_n\right). \tag{+}$$

In order to prove this relation (if one is not interested in the proofs, skip the indented sections below) we express z_i in terms of x_i and consider the fact that the functions f_i and h are homogeneous:

$$F\left(a^{g_1} z_1 \dots a^{g_n} z_n\right) = F\left(f_1\left(ax_1 \dots ax_n\right), \dots, f_n\left(ax_1 \dots ax_n\right)\right)$$
$$= h\left(ax_1 \dots ax_n\right) = a^g \cdot h\left(x_1 \dots x_n\right) = a^g \cdot F\left(z_1 \dots z_n\right).$$

The degree of a quantity composed of several others can be determined immediately with rules similar to those of exponents. If u, v and w have degree s, s and t, then $u + v$, $u \cdot w$ and u/w have degree s, $s + t$ and $s - t$, respectively. Constants have the degree 0 and the derivative $\left(\mathrm{d}y/\mathrm{d}z_i\right)_{z_{\hat{i}}}$ has the degree of the ratio y/z_i.

In order to prove the last statement about $\left(\mathrm{d}y/\mathrm{d}z_i\right)_{z_{\hat{i}}}$, we take the derivative of the above equation (+) with respect to z_i and simultaneously divide both sides by a^{g_i}. By using the shorthand notation F_i for $\left(\mathrm{d}F/\mathrm{d}z_i\right)_{z_{\hat{i}}}$, we get

$$F_i\left(a^{g_1} z_1 \dots a^{g_n} z_n\right) = a^{g-g_i} \cdot F_i\left(z_1 \dots z_n\right).$$

Finally, on replacing z_i by $f_i(x_1 \dots x_n)$, we find that F_i has the degree $g - g_i$ as claimed.

Applied to our homogeneous body, this means that in addition to E, other quantities such as V, S, n_i, m, etc., are "proportional to the size of a section of this body" and are of degree 1. On the other hand, the forces derived from work coordinates $y_i = (\mathrm{d}E/\mathrm{d}x_i)_{x_{\hat{i}}}$ have degree 0, and are "independent of the size of a section".

The last statement is most important, since it means that pressure, temperature and chemical potential depend only on the relationship $V : S : n_1 : n_2 :\ldots$ Even if the section of the body under consideration is reduced almost to a point, and the composition (including entropy) of the surroundings of the section are changed arbitrarily, the values of p, T and μ_i in that section remain fixed as long as the relationship $V : S : n_1 : n_2 :\ldots$ is preserved there. In contrast, the electric potential exhibits completely different behavior, since its value is not determined only by local conditions but is also influenced by distant charges.

Therefore it seems reasonable to ignore the shape and size of a body and to introduce measures of the local composition (including entropy) of a body, and to express p, T and μ_i as functions of these variables. It is common to relate V, S, n_i of a small section, as well as E and other parameters (all of degree 1) to the volume or total amount of all substances $n = \sum n_i$ of this section. In the first case, relating to the volume V, we obtain the entropy density c_S, the energy density c_E ,… and the concentrations ("substance densities") c_i of the individual substances. In the second case, relating to the total amount of all substances n, we get the average (molar) volume $\overline{V}$, the average (molar) entropy $\overline{S}$, ... and the mole fractions x_i of the substances:

$$\left(\frac{V}{V} \equiv 1\right), \quad \frac{S}{V} \equiv c_S, \ \ldots, \quad \frac{n_i}{V} \equiv c_i \ ;$$

$$\frac{V}{n} \equiv \overline{V}, \quad \frac{S}{n} \equiv \overline{S}, \ \ldots, \quad \frac{n_i}{n} \equiv x_i \ .$$

All these quantities are of degree 0. Since the sum of all x_i must be 1, they cannot be selected arbitrarily. The number of independent variables is therefore decreased by one in both cases.

4.6.2. "Dissection" of a Quantity

A variable $y = F(z_1 \ldots z_n)$ of degree g can be decomposed into separate terms in a distinct way, depending on the chosen set of independent variables:

$$g \cdot y = g_1 z_1 \left(\frac{\mathrm{d}y}{\mathrm{d}z_1} \right)_{z_{2,\ldots,n}} + \ldots + g_n z_n \left(\frac{\mathrm{d}y}{\mathrm{d}z_n} \right)_{z_{1,\ldots,n-1}} .$$

We will refer to this operation as a "dissection" of y with respect to z_i. If we choose different independent variables, we can get another "dissection" of the same quantity.

> In order to derive this relationship we take the derivative with respect to a of all terms on both sides of equation (+) by first treating them as functions of a and later setting $a = 1$:
>
> $$\sum g_i z_i \, a^{g_i - 1} \cdot F_i \left(a^{g_1} z_1 \ldots a^{g_n} z_n \right) = g a^{g-1} \cdot F \left(z_1 \ldots z_n \right).$$

As an example let us decompose the volume $V(p, T, n_1, n_2 \ldots)$ of our homogeneous body:

$$V = 0 + 0 + n_1 \left(\frac{\mathrm{d}V}{\mathrm{d}n_1} \right) + n_2 \left(\frac{\mathrm{d}V}{\mathrm{d}n_2} \right) \ldots = \sum n_i V_i .$$

A corresponding result is obtained for the entropy S and, of course, also for energy, mass, etc. by decomposing into the same variables:

$$V = \sum n_i V_i, \quad S = \sum n_i S_i, \quad m = \sum n_i M_i, \ldots \; .$$

These equations indicate nothing more than the fact that the volume, entropy, mass, etc. of bodies can be composed additively from the volume demand, entropy demand, mass demand, etc. of their constituent parts. If a body consists of only a single substance, we have:

$$V = nV_{\mathrm{m}}, \quad S = nS_{\mathrm{m}}, \quad m = nM_{\mathrm{m}}, \ldots \; .$$

These relations were mentioned in section 4.4.1.

An important formula we get by dissecting E with respect to V, S, n_1, n_2 ...:

$$E = V \left(\frac{\mathrm{d}E}{\mathrm{d}V} \right)_{Sn_1n_2..} + S \left(\frac{\mathrm{d}E}{\mathrm{d}S} \right)_{Vn_1n_2..} + n_1 \left(\frac{\mathrm{d}E}{\mathrm{d}n_1} \right)_{VSn_2..} + n_2 \left(\frac{\mathrm{d}E}{\mathrm{d}n_2} \right)_{VSn_1..} + \ldots ,$$

i.e.

$$E = -pV + TS + \mu_1 n_1 + \mu_2 n_2 + \ldots \; .$$

The total energy given by this equation is divided into separate contributions from volume, entropy and different substances. By forming the differential $\mathrm{d}(E - E)$

where the first E is dissected as in the last equation, and the second dE is derived from the main equation, then we obtain the so-called GIBBS-DUHEM relationship:

$$\mathrm{d}(E - E) = -V\mathrm{d}p + S\mathrm{d}T + n_1\mathrm{d}\mu_1 + n_2\mathrm{d}\mu_2 + \ldots = 0\ ,$$

where work coordinates and forces have exchanged roles compared with the main equation.

4.6.3. Reduction of Coefficients

The required number of coefficients for an n-actuator system $(n{+}1)n/2$ is reduced by n if the energy of the system is a linear homogeneous function of the work coordinates. We will not prove this, but illustrate it for a homogeneous body consisting of two substances ($n = 4$). Starting from the main equation

$$\mathrm{d}E = -p\mathrm{d}V + T\mathrm{d}S + \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2,$$

we form derivatives of the main quantities with respect to p, T, n_1, n_2 as independent variables:

$$\begin{array}{ccc|c}
\left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_{Tn_1n_2} & \left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{pn_1n_2} & \left(\frac{\mathrm{d}V}{\mathrm{d}n_1}\right)_{pTn_2} & \left(\frac{\mathrm{d}V}{\mathrm{d}n_2}\right)_{pTn_1} \\
\left(\frac{\mathrm{d}S}{\mathrm{d}p}\right)_{Tn_1n_2} & \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_{pn_1n_2} & \left(\frac{\mathrm{d}S}{\mathrm{d}n_1}\right)_{pTn_2} & \left(\frac{\mathrm{d}S}{\mathrm{d}n_2}\right)_{pTn_1} \\
\left(\frac{\mathrm{d}\mu_1}{\mathrm{d}p}\right)_{Tn_1n_2} & \left(\frac{\mathrm{d}\mu_1}{\mathrm{d}T}\right)_{pn_1n_2} & \left(\frac{\mathrm{d}\mu_1}{\mathrm{d}n_1}\right)_{pTn_2} & \left(\frac{\mathrm{d}\mu_1}{\mathrm{d}n_2}\right)_{pTn_1} \\
\left(\frac{\mathrm{d}\mu_2}{\mathrm{d}p}\right)_{Tn_1n_2} & \left(\frac{\mathrm{d}\mu_2}{\mathrm{d}T}\right)_{pn_1n_2} & \left(\frac{\mathrm{d}\mu_2}{\mathrm{d}n_1}\right)_{pTn_2} & \left(\frac{\mathrm{d}\mu_2}{\mathrm{d}n_2}\right)_{pTn_1}
\end{array}$$

Parameter values below the diagonal can be ignored as a result of the flip rule. Values in the last column are not required since they can be obtained by dissecting V, S, μ_1 and μ_2 with respect to p, T, n_1 and n_2. The resulting equation can be solved for the desired quantities:

$$V = n_1\left(\frac{\mathrm{d}V}{\mathrm{d}n_1}\right)_{pTn_2} + n_2\left(\frac{\mathrm{d}V}{\mathrm{d}n_2}\right)_{pTn_1}\ , \ldots\ ,\ 0 = n_1\left(\frac{\mathrm{d}\mu_1}{\mathrm{d}n_1}\right)_{pTn_2} + n_2\left(\frac{\mathrm{d}\mu_1}{\mathrm{d}n_2}\right)_{pTn_1}\ , \ldots.$$

4.7. Asymptotic Laws for Substances at High Dilution

If all entropy is removed from a body, its temperature T becomes 0. What happens to the chemical potential of a substance if the amount of substance in the body becomes increasingly smaller? It will be shown that changes of the chemical potential are independent of the chosen substance and even independent of the body it is distributed in. It can be described by a general law that can be used for the analysis of dilute gases and solutions.

4.7.1. Chemical Potential at Low Concentration

We know that the chemical potential decreases as the amount of substance distributed in a body is reduced. Initially this drop in chemical potential is irregular but approaches a regular trend with decreasing concentration. If n is reduced by a power of ten, μ drops by a constant amount regardless of the substance under consideration (Figure 4.17). On a logarithmic scale for n the $\mu(n)$ curves approach parallel straight lines, their asymptotes, for larger n. The slope of these lines is directly proportional to temperature, while the intersection point with the μ-axis is influenced by the composition and condition (p, T, etc.) of the body, as well as by the kind of substance distributed in the body. In general, we can describe chemical potentials by:

$$\mu = \mu_0 + RT \cdot \ln \frac{n}{n_0} \ .$$

Here n_0 is an arbitrary reference point and R is a universal constant, characteristic for the behavior of diluted substances with value

$R = 8.314$ J/(K·mol).

Although the parameter μ_0 depends on n, it always remains finite for "finite" systems. "Finite" means the volume does not vanish, and neither the volume nor any amount of substance in the body becomes arbitrarily large.

As a special case of the above we can state that $\mu \to -\infty$ as $n \to 0$ for $T > 0$. This asymptotic rule reminds us of the behavior of entropy as the absolute zero of temperature is approached (see section 2.4). Similar exceptions also apply here. If a substance cannot diffuse within a body, it cannot be extracted from a body, and we can say it is "trapped in" even if the chemical potential outside drops to an arbitrary low value. The internal chemical potential cannot be obtained by measurement — just like temperature in the case of trapped entropy.

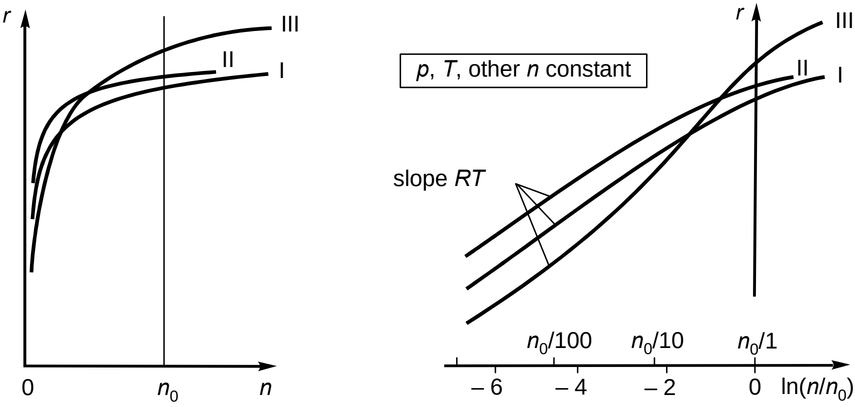


Fig. 4.17: $\mu(n)$ and $\mu(\ln(n/n_0))$

Since derivatives of μ are frequently considered, let us briefly examine them. The most important is the derivative with respect to n for any constraint a = const.:

$$\left(\frac{\mathrm{d}\mu}{\mathrm{d}n}\right)_a = \left(\frac{\mathrm{d}\mu_0}{\mathrm{d}n}\right)_a + \frac{RT}{n} \;.$$

For small n, the first term is negligible compared to the second term which increases greatly with decreasing n. The derivative with respect to T

$$\left(\frac{\mathrm{d}\mu}{\mathrm{d}T}\right)_a = \left(\frac{\mathrm{d}\mu_0}{\mathrm{d}T}\right)_a + R \cdot \ln\frac{n}{n_0} \;,$$

represents the entropy demand S_m of a substance as long as the pressure and amounts of substance are held constant, $a = (p, n_1, n_2 \ldots)$. Due to the second term, S_m grows slowly with increasing dilution, but in the limit it will become infinite. Since μ_0 remains finite under the present conditions, we expect the same behavior for all derivatives. There are cases where $\mathrm{d}\mu_0/\mathrm{d}n$ increases without bound as $n \rightarrow 0$. However, this growth is so slow that it is negligible compared to that of RT/n.

4.7.2. Properties of Dilute Gases

We can now derive a number of properties for the gaseous state of matter from the asymptotic law for the chemical potential discussed above. We will briefly describe a few here. Consider a volume V within which small amounts n_i of one or several substances A_i are uniformly distributed. In other words, we consider a mixture of dilute gases. The main equation can be expressed as:

$$\mathrm{d}E = -p\mathrm{d}V + T\mathrm{d}S + \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2 + \dots\,.$$

If we add a small amount $\mathrm{d}n_i$ of substance i while holding the volume V and the temperature T constant, then the internal pressure p increases by $\mathrm{d}p = (\mathrm{d}p/\mathrm{d}n_i)_{VTn_{\hat{i}}} \cdot \mathrm{d}n_i$. The derivative takes the following constant value:

$$\left(\frac{\mathrm{d}p}{\mathrm{d}n_i}\right)_{VTn_{\hat{i}}} = -\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}V}\right)_{Tn_in_{\hat{i}}} = \sum_j \frac{n_j}{V}\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}n_j}\right)_{pTn_{\hat{j}}} \approx \frac{RT}{V}$$

To derive this result, in the first step the derivative was flipped, and in the second step μ_i was dissected with respect to T, V, n_1, n_2 …

$$0 \cdot \mu_i = V\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}V}\right)_{Tn_in_{\hat{i}}} + n_1\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}n_1}\right)_{VTn_{\hat{1}}} + n_2\left(\frac{\mathrm{d}\mu_i}{\mathrm{d}n_2}\right)_{VTn_{\hat{2}}} + \dots\,.$$

This follows since the body is homogeneous. In order to calculate the derivations, we set $\mu_i = \mu_{i0} + RT\ln(n_i/n_0)$ and differentiate

$$j = i\text{:}\quad \left(\frac{\mathrm{d}\mu_i}{\mathrm{d}n_i}\right)_{VTn_{\hat{i}}} = \left(\frac{\mathrm{d}\mu_{i0}}{\mathrm{d}n_i}\right)_{VTn_{\hat{i}}} + \frac{RT}{n_i}; \qquad j \neq i\text{:}\quad \left(\frac{\mathrm{d}\mu_i}{\mathrm{d}n_j}\right)_{VTn_{\hat{j}}} = \left(\frac{\mathrm{d}\mu_{i0}}{\mathrm{d}n_j}\right)_{VTn_{\hat{j}}}.$$

For small n_j the term RT/n_i is much larger than all other terms and is therefore the only one shown in the earlier equation as $\approx RT/V$.

Let us assume an initially empty room such that the internal pressure is zero. By adding the amounts of substance n_1, n_2 … sequentially, the pressure rises in increments of n_iRT/V and the final pressure becomes $p = (n_1 + n_2 + \dots)\cdot RT/V$. This can be expressed as

$$pV = \underbrace{n}_{n_1 + n_2 + \dots}\cdot RT\,.$$

This equation is the so-called perfect or ideal gas law, where $p_i = n_iRT/V$ is called the partial pressure of each gas. Since R first arose as part of this law, this explains its common name of "universal gas constant". This law is valid only for gases at low density, but is always useful for approximate calculations and is independent of the kind of substance considered. For example, 1 mol of an arbitrary substance requires the constant volume $V_i = (\mathrm{d}V/\mathrm{d}n_i)_{pTn_{\hat{i}}} = RT/p$, of approximately 24 dm^3 under normal room conditions. Figure 3.12 illustrates the *V*(*p*, *T*)-surface.

The information about entropy content is not as complete as that for volume. To obtain a complete picture, we have to consult other sources. We will limit our discussion to a pure substance. From experience we know that the entropy capacities *Ç* for dilute gases, whose molecules consist of only a few atoms, are proportional to $1/T$ for average temperatures, i.e., the heat• capacities *C*, which are greater by the factor *T*, are nearly constant. For monatomic molecules, the molar entropy capacity $Ç_\mathrm{m}$ is given by $^5/_2\,(R/T)$ for small polyatomic molecules (consisting of a few light atoms) it is $^7/_2\,(R/T)$ if the molecules are straight, and $^8/_2\,(R/T)$ if the molecules have bends. $Ç_V$ is always smaller than *Ç* by the amount $n{\cdot}R/T$:

$$Ç - Ç_V = n\frac{R}{T}\ .$$

We can arrive at this result by cutting back to *p*, *T*, *n* and applying the gas law $V = n{\cdot}RT/p$:

$$\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_{pn} - \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_{Vn} = \left(\frac{\mathrm{d}S}{\mathrm{d}p}\right)_{Tn} \cdot \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{Vn} = -\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{pn} \bigg/ \left(\frac{\mathrm{d}V}{\mathrm{d}p}\right)_{Tn} = -\left(\frac{nR}{p}\right)^2 \bigg/ \left(-\frac{nRT}{p^2}\right).$$

If the entropy content relates to a reference point (p_0, T_0), it can be calculated for other *p*- and *T*-values since

$$\mathrm{d}S = \left(\frac{\mathrm{d}S}{\mathrm{d}p}\right)_{Tn} \mathrm{d}p + \left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_{pn} \mathrm{d}T = -\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{pn} \mathrm{d}p + \frac{C}{T}\mathrm{d}T = -\frac{nR}{p}\mathrm{d}p + \frac{C}{T}\mathrm{d}T\ ,$$

and obtain on integration, assuming *C* is constant:

$$S = S_0 - R\ln\frac{p}{p_0} + C\ln\frac{T}{T_0}\ .$$

Figure 3.13 illustrates the *S*(*p*,*T*)-surface.

The energy *E* of dilute gases at a given temperature does not depend on volume or pressure. If we differentiate *E* with respect to *V* (divide by d*V*) at constant *T* and *n*, and substitute $(\mathrm{d}p/\mathrm{d}T)_{Vn} = p/T$ from the gas law, we get:

$$\left(\frac{\mathrm{d}E}{\mathrm{d}V}\right)_{Tn} = T\cdot\left(\frac{\mathrm{d}S}{\mathrm{d}V}\right)_{Tn} - p = T\cdot\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{Vn} - p = 0 \ .$$

Since we know the pressure and temperature coefficients of μ by using V_m and $-S_\mathrm{m}$, we can calculate $\mu(p, T)$ relative to a reference point μ_0. For instance, if we use $V_\mathrm{m} = RT/p$, the variation with pressure is given by the simple expression

$$\mu = \mu_0 + \int_{p_0}^{p} V_\mathrm{m}\mathrm{d}p = \mu_0 + RT\cdot\ln\frac{p}{p_0}\,.$$

4.7.3. Chemical Potentials in Mixtures

Ideally the chemical potential μ of a substance in a homogeneous mixture is characterized by the following behavior:

$$\mu = \overset{\circ}{\mu} + RT\cdot\ln x$$

(x amount fraction (or mole fraction), $\overset{\circ}{\mu}$ chemical potential of a pure substance). Since the amount fraction is proportional to the amount of substance for small x, this does not contradict the asymptotic law for μ. Deviations from this behavior are accounted for by introducing finite correction factors or additional terms:

$$\mu = \overset{\circ}{\mu} + RT\cdot\ln(f\cdot x) \qquad \text{or} \qquad \mu = \overset{\circ}{\mu} + RT\cdot\ln x + \overset{+}{\mu}\,.$$

The expression $f\cdot x$ is called the activity a, which is something like the effective amount fraction of a substance, f is the activity coefficient, and $\overset{+}{\mu}$ is called the excess potential.

The volume and entropy of a substance in a mixture can, as we know, be obtained by differentiation with respect to p and T at fixed composition. Starting with the proper representation of μ and abbreviating the derivatives of $\overset{\circ}{\mu}$ and $\overset{+}{\mu}$ appropriately, we get

$$V_\mathrm{m} = \overset{\circ}{V}_\mathrm{m} + \overset{+}{V}_\mathrm{m}\,, \qquad S_\mathrm{m} = \overset{\circ}{S}_\mathrm{m} - R\cdot\ln x + \overset{+}{S}_\mathrm{m}\,.$$

If we are mixing the substances $A_{(i)}$ with the amounts n_i, then the volume and entropy have the values $\sum n_i\cdot\overset{\circ}{V}_i$ and $\sum n_i\cdot\overset{\circ}{S}_i$, respectively, before mixing, and $\sum n_i \cdot V_i$ and $\sum n_i \cdot S_i$ after mixing. The differences, the "volume of mixing" $\Delta_M V_m$ and the "entropy of mixing" $\Delta_M S_m$ are given by

$$\Delta_M V_m = \sum n_i \overset{\circ}{V}_i, \quad \Delta_M S_m = \sum n_i \overset{\circ}{S}_i - R \cdot \sum n_i \ln x_i .$$

For substances similar to gases at low pressures, or different isotopes of an element, heavy and light water, which follow ideal curves $\mu = \overset{\circ}{\mu} + RT \cdot \ln x$ when mixed, the excess potential $\overset{+}{\mu}$ and also the excess volume $\overset{+}{V}_m$ and excess entropy $\overset{+}{S}_m$, vanish. Their volume does not change due to the mixing process, nor is entropy added or released to the environment. The temperature remains constant as though different parts of the same substance were combined. For this reason such mixtures are called "ideal". In fact, $\Delta_M V_m = 0$, but $\Delta_M S_m \neq 0$ because the positive term $-R \cdot \sum n_i \ln x_i$ does not vanish with $x_i < 1$. The total requirement for entropy has increased and consequently, the mixture should cool down as long as no entropy flows in from the outside. This is not the case, however, because energy is released from the drop in chemical potential of the substances during the mixing process, and the entropy produced exactly compensates for the missing entropy. The work loss W_p is calculated from the released energy caused by the potential drop of all the substances. The entropy S_p that is produced during mixing of the substances is given by W_p/T:

$$W_p = \sum n_i \left(\overset{\circ}{\mu}_i - \mu_i \right) = -\sum n_i RT \ln x_i, \qquad S_p = -R \cdot \sum n_i \ln x_i .$$

Figure 4.18 shows the dependence of the chemical potential on amount fraction x. These curves are especially remarkable in the vicinity of $x = 0$ and $x = 1$. If we examine the behavior of a substance in a strongly diluted mixture, the change in $\overset{+}{\mu}$ becomes insignificant compared with the changes of the term $RT \cdot \ln x$, which approaches negative infinity. We can substitute $\overset{+}{\mu}$ with the constant limit value $\overset{+}{\mu}_0$ at $x = 0$ and write:

$$\mu = \left(\overset{\circ}{\mu} + \overset{+}{\mu}_0 \right) + RT \cdot \ln x \qquad (x \ll 1) .$$

From this relationship we can also make a statement about the function in the vicinity of $x = 1$ due to the special properties of homogeneous substances. To derive this statement, we return to the GIBBS-DUHEM Equation (see section 4.6.2) and restrict ourselves to two substances for simplicity, where F indicates a "foreign" substance:

$$\mathrm{d}(E - E) = -V\mathrm{d}p + S\mathrm{d}T + n\mathrm{d}\mu + n_\mathrm{F}\mathrm{d}\mu_\mathrm{F} = 0\ .$$

Now differentiate with respect to x while holding p and T constant and re-arrange the terms:

$$\left(\frac{\mathrm{d}\mu}{\mathrm{d}x}\right)_{pT} = -\frac{n_F}{n}\left(\frac{\mathrm{d}\mu_\mathrm{F}}{\mathrm{d}x}\right)_{pT} = -\frac{n_\mathrm{F}}{n}\left(\frac{\mathrm{d}\mu_\mathrm{F}}{\mathrm{d}x_\mathrm{F}}\right)_{pT}\left(\frac{\mathrm{d}x_\mathrm{F}}{\mathrm{d}x}\right)_{pT} \approx -x_\mathrm{F}\cdot\frac{RT}{x_\mathrm{F}}\cdot(-1)\ .$$

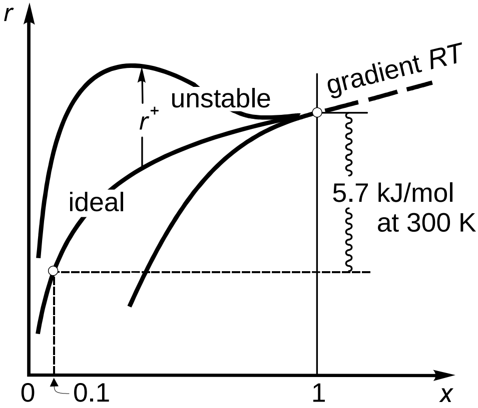


Fig. 4.18: $\mu(x)$ in mixtures

In the second step we expand $(\mathrm{d}\mu_\mathrm{F}/\mathrm{d}x)_{pT}$ by $\mathrm{d}x_F$. In the third step x_F is assumed to be small, so that $n_\mathrm{F}/n \approx x_\mathrm{F}$ and μ_F may be written as $\left(\overset{\circ}{\mu}_\mathrm{F} + \overset{+}{\mu}_{\mathrm{F},0}\right) + RT\ln x_\mathrm{F}$. Finally, we use $x_\mathrm{F} = 1 - x$. The equation indicates that the $\mu(x)$ curves have a slope of RT for $x \approx 1$ or $x_\mathrm{F} \approx 0$. The drop of the chemical potential of a pure substance due to the addition of a small amount x_F of a "foreign" substance is generally expressed by

$$\mu = \overset{\circ}{\mu} - RT x_\mathrm{F} \qquad\qquad (x_\mathrm{F} \ll 1)\,.$$

4.7.4. Osmosis, Boiling and Freezing Points of Dilute Solutions

A common characteristic of the above phenomena is that they are determined essentially by the behavior of the chemical potential in the vicinity of $x = 1$. Since the individual properties of substances are unimportant both in this region and near $x = 0$, there exist some general laws that are essentially independent of the kind of substance.

a) Osmosis

Let us consider a container with amount n of a liquid. If we dissolve a small amount n_F of a foreign substance in it, the chemical potential μ of this liquid drops by $RT \cdot x_F \approx RT \cdot n_F / n$. Now suppose that this container is connected to another container through a barrier permeable only to the solvent (Figure 4.19). The second tank contains only pure liquid that penetrates the barrier and flows into the solution in the first container because of the chemical potential drop. This flow can be stopped by increasing the pressure on the solution to compensate for the drop of the chemical potential:

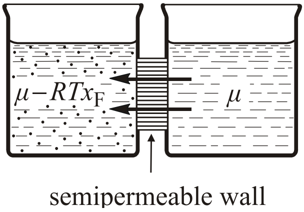


Fig. 4.19: Osmosis

$$-RT \cdot n_F / n + V_m \cdot \Delta p = 0.$$

After multiplying by n and writing $V = n \cdot V_m$ for the volume of the liquid — the small contribution $V_F \cdot n_F$ of the foreign substance is neglected — we get the following expression for the "osmotic pressure" (VAN'T HOFF Equation):

$$\Delta p = n_F \frac{RT}{V} .$$

b) Vapor Pressure Lowering

The pure liquid is initially in equilibrium with its vapor ($'$) at a pressure p, in other words, $\mu = \mu'$. By dissolving a non-volatile foreign substance, the equilibrium is disturbed and the vapor should condense on top of the solution due to its higher chemical potential. The equilibrium can be restored by lowering the pressure by Δp, because the chemical potential μ' of the vapor decreases more rapidly on account of its greater volume demand $V'_m = RT/p$ compared with that of the liquid ($\Delta p < 0!$):

$$\mu - RT x_F + V_m \cdot \Delta p = \mu' + V'_m \cdot \Delta p = \mu' + RT \cdot \Delta p / p .$$

Since the term $V_m \cdot \Delta p$ is negligible compared to $V'_m \cdot \Delta p$, the "vapor pressure lowering" (RAOULT's Law) is given by:

$$\Delta p = -x_F \cdot p\,.$$

c) Changes in Boiling and Freezing Points

If T_b is the temperature at which the liquid boils at 1.013 bar pressure, at which its chemical potential μ is equal to the potential μ' of the vapor, then T_b rises when a foreign substance is dissolved in the liquid. In order to lower the chemical potential of the vapor compared to that of the liquid, the temperature can be raised instead of reducing the pressure (Figure 4.20). The temperature coefficient of μ-values is negative and particularly large in the case of gases:

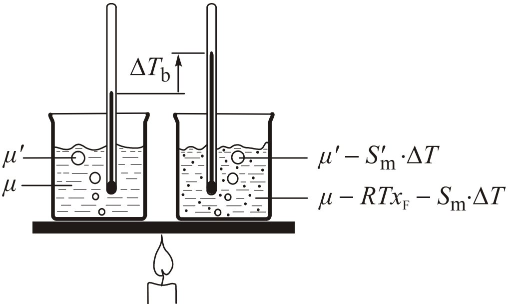


Fig. 4.20: Increasing boiling point

$$\mu - RT x_F - S_m \Delta T = \mu' - S'_m\, \Delta T\,.$$

By solving for the boiling point, we get

$$\Delta T_b = \frac{RT}{\Delta_V S_m} x_F\,.$$

Usually in this equation, the entropy of evaporation $\Delta_V S_m = S'_m - S_m$ is replaced by the evaporation heat• $T{\cdot}\Delta_V S_m$.

Contrary to the boiling point, the freezing point T_f of a solution is lower than that of the pure solvent. A similar approach leads to

$$\Delta T_f = -\frac{RT}{\Delta_F S_m} x_F\,,$$

where $\Delta_F S$ represents the entropy of fusion. For an aqueous solution with concentration $c_F = 1$ mol/dm^3, the boiling point elevation ΔT_b is approximately 0.5 K and the freezing point lowering ΔT_f is about −2 K.

4.7.5. Law of Mass Action

Consider the reaction in a solid, liquid or gaseous solution,

$A + B = C + D$ or more generally $\nu_A A + \nu_B B + \nu_C C \ldots = 0.$

As long as $\Delta_R \mu = \nu_A \mu_A + \nu_B \mu_B + \ldots < 0$, the initial substances are converted. Their amount in the solution decreases together with their chemical potentials, while the corresponding amount of products increases. This reaction stops when $\Delta_R \mu = 0$. The amount fractions at which this condition is reached are easily determined from the "equilibrium condition". Provided that the amount fractions are low, we can express the chemical potentials μ of the involved substances in simplified form:

$$\mu = \left(\overset{\circ}{\mu} + \overset{+}{\mu}_0\right) + RT \ln x$$

to obtain

$$\Delta_R \mu = \Delta_R\left(\overset{\circ}{\mu} + \overset{+}{\mu}_0\right) + RT \cdot \Delta_R \ln x = 0\ .$$

After dividing by RT and taking the anti-logarithm, we get

$$e^{\Delta_R \ln x} = e^{-\Delta_R\left(\overset{\circ}{\mu} + \overset{+}{\mu}_0\right)/RT} = K\ .$$

The parameter K depends on p and T but not on x_i . Evaluating the expression on the left hand side gives the well-known "law of mass action":

$$\frac{x_A \cdot x_B}{x_C \cdot x_D} = K \qquad \text{or more generally} \qquad x^{\nu_1} \cdot x^{\nu_2} \cdot \ldots = K\ .$$

Instead of x_i, partial pressures $p_i = x_i\, p$ are often used in the case of gas mixtures, and concentrations $c_i = x_i\, n/V$ (where $n = \sum n_i$ = total amount of all substances) for solid and liquid mixtures.

4.7.6. Solution Equilibria

At low gas pressures or for small amounts of a substance in a mixture, the chemical potential can be expressed as (see section 4.7.2):

$$\mu = \mu_0 + RT \cdot \ln \frac{p}{p_0} \qquad \text{or} \qquad \mu = \left(\overset{\circ}{\mu} + \overset{+}{\mu}_0\right) + RT \ln x\ .$$

If we increase x or p by the factor α, the chemical potential μ grows in both cases by the amount $RT \ln \alpha$. This allows us to establish several laws and relationships.

a) Solubility of Gases

When a body, solid or liquid, comes into contact with a gas, then the gas diffuses into the body until its chemical potential inside is as high as on the outside. As long as the external pressure and the amount x in the body are small, then these quantities are proportional (HENRY's Law).

$x \sim p.$

If we raise the pressure by α, then x has to increase proportionately to maintain the chemical potential equilibrium. It would be more correct to take into account the pressure dependence of the μ-value for the dissolved gas in the body, but this effect is negligible.

b) Distribution Equilibrium

The amount fractions x and x' of dissolved substances in adjacent bodies (Figure 4.21) behave similarly. In order to establish equilibrium, the small values of x and x' become proportional (NERNST's Law)):

$x \sim x'.$

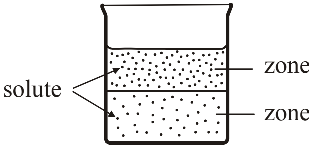


Fig. 4.21: Distribution equilibr
of a substance betwe
adjacent bodies

c) Solubility Product

A substance submerged in a liquid will generally begin to dissolve. The extremely low chemical potential of this substance in the pure solvent rises rapidly. (For $x \to 0$, we know that $\mu = \left(\overset{\circ}{\mu} + \overset{+}{\mu}_0\right) + RT \ln x \to -\infty$.) The process stops when the chemical potential μ of the substance in the solution is equal to that of the solid. If the substance dissociates on dissolution, like salt in water:

$AB = A^+ + B^-$,

then the products of the dissociation together compensate for the dissolution drive of the salt AB: $\mu_{AB} = \mu_A + \mu_B$. If the amount fraction x_A of one product is lowered by α, the amount fraction of the second product x_B has to increase by α in order to maintain the equilibrium — assuming that the concentrations are sufficiently low. The product

$$x_A \cdot x_B = K$$

must remain constant. K is here the so-called "solubility product constant" of the substance *AB*. If for some reason the product $x_A \cdot x_B$ exceeds the value K, i.e., $\mu_A + \mu_B > \mu_{AB}$, the substance AB precipitates from the solution. If a substance dissociates into several ions, then K consists of the corresponding number of amount fractions.

d) Solubility and Temperature

The solubility of a substance is raised with increasing temperature if the chemical potential of the dissolved substance μ decreases faster than that in its pure state μ', and vice versa. This holds when $S_m > S'_m$, because the temperature coefficient of the chemical potential $(d\mu/dT)_{p\ldots} = -S_m$. If the "molar entropy of solution" $\Delta_L S_m = S_m - S'_m$ or the "molar solution heat" $T \cdot \Delta_L S_m$ is positive, the solubility increases with temperature. In this case, entropy is received from the surroundings during dissolution. We obtain the same result if we interpret this process as a chemical reaction $A_{pure} \rightarrow A_{dissolved}$ and assume that the extent of reaction and the entropy change are coupled.

4.8. Effect of External Fields

By considering the influence of external fields on the chemical potential, we can calculate the substance changes caused by these fields.

As an example, consider gas diffusion into the atmosphere. Since the work $W = m \cdot g \cdot h = n \cdot M_m \cdot g \cdot h$ required to raise an amount n of a substance from the ground ($h = 0$) to a height h at constant p and T, the chemical potential μ is greater than μ_0 at ground level by $M_m \cdot g \cdot h$ (see section 4.3.3):

$$\mu = \mu_0 + M_m \cdot g \cdot h \, .$$

Equilibrium exists when the chemical potential ("gravito-chemical potential" would be more precise, see section 4.3.3) has the same value everywhere. In order to compensate for the increased chemical potential $M_{\mathrm{m}} \cdot g \cdot \mathrm{d}h$ due to the increase in height $\mathrm{d}h$, the pressure must drop. As a result, μ changes by $V_{\mathrm{m}} \cdot \mathrm{d}p$, or $(RT/p) \cdot \mathrm{d}p$ for gases:

$$M_{\mathrm{m}} \cdot g\,\mathrm{d}h + \frac{RT}{p}\mathrm{d}p = 0, \qquad \text{or} \qquad \frac{\mathrm{d}p}{p} = -\frac{M_{\mathrm{m}} \cdot g}{RT}\mathrm{d}h\,.$$

After integrating and taking the anti-logarithm, we obtain the "barometric height formula":

$$p = p_0 \cdot \mathrm{e}^{-\frac{M_{\mathrm{m}} \cdot g}{RT}h}\,.$$

A magnetic field H boosts the dissociation of iodine vapour

$$\mathrm{I_2} \rightleftharpoons 2\mathrm{I}\,,$$

since it lowers the chemical potential of the paramagnetic iodine atoms, attracted by the field, relative to the diamagnetic $\mathrm{I_2}$. To calculate this effect, we can start with the main equation $\mathrm{d}E = -p\mathrm{d}V + H\mathrm{d}M + T\mathrm{d}S + \mu_1\mathrm{d}n_1 + \mu_2\mathrm{d}n_2$ of the gas mixture, and then evaluate $(\mathrm{d}\mu_i/\mathrm{d}H)_{pTn_1n_2}$ by using the flip rule, etc.

5. THERMODYNAMICS OF ENTROPY PRODUCING PROCESSES

This section deals with the interactions of entropy flows, electric currents, substance flows, etc. This topic is generally covered under the heading "thermodynamics of irreversible processes". The conceptual and mathematical framework is similar in many respects to the model we know as "elastic coupling". Before we examine general systems, let us introduce a mechanical example.

5.1. Mechanical Example

Consider two adjacent smooth blocks of constant thickness, with a viscous film of lubricant between and below them (Figure 5.1). Both blocks are pulled parallel to each other with forces F and F' at speeds of $v = \mathrm{d}l/\mathrm{d}t$ and $v' = \mathrm{d}l'/\mathrm{d}t$ respectively (where l, l' are work coordinates, t is time). For an elastic body the work performed by the forces is stored as energy (W_S = stored work):

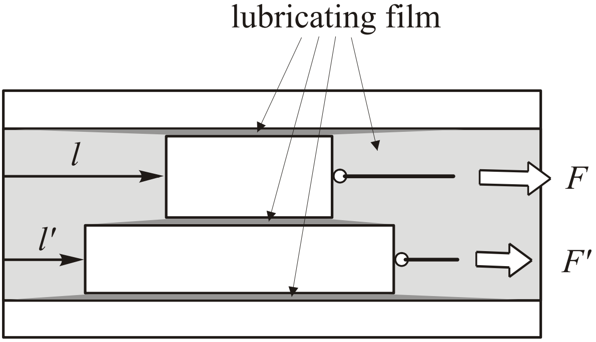


Fig. 5.1: Entropy production by friction

$$\mathrm{d}W_\mathrm{S} = F\mathrm{d}l + F'\mathrm{d}l',$$

and is retrievable by reversing the process. But in our new example the work is used to produce entropy and is burned up permanently (W_p = burned up work):

$$\mathrm{d}W_\mathrm{p} = F\mathrm{d}l + F'\mathrm{d}l'.$$

An important indicator of the lost power is the time derivative of the work given by

$$P_\mathrm{p} = \frac{\mathrm{d}W_\mathrm{p}}{\mathrm{d}t} = Fv + F'v' .$$

Another difference is that the forces do not depend on the positions l, l' but rather on the speeds of both blocks due to coupling:

$$F = F(v,v'); \qquad F' = F'(v,v') .$$

By accelerating the motion by dv, dv', the forces F and F' change by

$$\mathrm{d}F = \left(\frac{\mathrm{d}F}{\mathrm{d}v}\right)_{v'} \mathrm{d}v + \left(\frac{\mathrm{d}F}{\mathrm{d}v'}\right)_{v} \mathrm{d}v' ,$$

$$\mathrm{d}F' = \left(\frac{\mathrm{d}F'}{\mathrm{d}v}\right)_{v'} \mathrm{d}v + \left(\frac{\mathrm{d}F'}{\mathrm{d}v'}\right)_{v} \mathrm{d}v' .$$

The two coefficients, on the lower left and upper right, are caused by coupling as discussed earlier (see section 3.1.4). The term $(\mathrm{d}F'/\mathrm{d}v)_{v'}$ describes the influence of the motion of the first block on the force applied to the second. Similarly, the term $(\mathrm{d}F/\mathrm{d}v')_{v}$ represents the opposite interaction. Earlier we concluded that these two cross-coefficients were equal, based on F and F' as derivatives of E and an application of SCHWARZ's theorem. Such a method cannot be used here since we have no corresponding energy equation involving F, F', v and v'.

Nevertheless, the two coefficients here do have the same value, simply because F and F' are the sum of the forces of friction from the support and from the adjacent block. The first contribution depends on v or v', respectively, and the second one depends on the difference $v - v'$:

$$F = f(v) + g(v - v'), \quad F' = h(v') - g(v - v').$$

By forming the derivatives $(\mathrm{d}F/\mathrm{d}v')_{v}$ and $(\mathrm{d}F'/\mathrm{d}v)_{v'}$ we see that they are equal, so that the mutual coupling between the two blocks is equally strong. Formally, it implies that all meaningful derivatives of F, v, F' and v' can be flipped. A prerequisite for the flip rule is that for a system of $2n$ variables $x_1 \ldots x_n$, $y_1 \ldots y_n$, where

y is a function of x, the following symmetry condition is satisfied (see section 3.2.2):

$$\left(\frac{\mathrm{d}y_i}{\mathrm{d}x_j}\right)_{x_{\hat{j}}} = \left(\frac{\mathrm{d}y_j}{\mathrm{d}x_i}\right)_{x_{\hat{i}}} .$$

If we set $n = 2$ and substitute F, F' for y_1, y_2, and v, v' for x_1, x_2, it becomes evident that this prerequisite is indeed satisfied.

As before we can list various effects observed during the motion of the blocks and identify the values of the corresponding coefficients:

a) Primary effects

The faster a block moves, the greater is the opposing force:

$$\left(\frac{\mathrm{d}F}{\mathrm{d}v}\right)_{v'} > 0, \qquad \left(\frac{\mathrm{d}F'}{\mathrm{d}v'}\right)_{v'} > 0 .$$

b) Coupling effects

If the speed v or the force F is increased, the other block also begins to speed up at a constant force F'. If the speed v' is held constant, the applied force F' decreases:

$$\left(\frac{\mathrm{d}v'}{\mathrm{d}v}\right)_{F'} > 0, \qquad \left(\frac{\mathrm{d}v'}{\mathrm{d}F}\right)_{F'} > 0, \qquad \left(\frac{\mathrm{d}F'}{\mathrm{d}v}\right)_{v'} < 0 \ \ldots .$$

The motions are co-coupled since the acceleration of one block also speeds up the other, and vice versa.

c) Indirect effects.

It is easier to accelerate one block if the other is free to move ($F' = 0$), and it becomes harder if the other block is constrained ($v' = 0$):

$$\left(\frac{\mathrm{d}F}{\mathrm{d}v}\right)_{F'} < \left(\frac{\mathrm{d}F}{\mathrm{d}v}\right)_{v'}, \qquad \left(\frac{\mathrm{d}v}{\mathrm{d}F}\right)_{F'} > \left(\frac{\mathrm{d}v}{\mathrm{d}F}\right)_{v'} .$$

In summary, coupling can be treated formally and conceptually as for an elastic body. This is not a surprise because the underlying structure is quite similar, except that the coordinates x are replaced by the speeds v.

5.2. ONSAGER's Theorem

The above results can be generalized. The lost power P_p of a physical system, i.e., the work burned up per unit time due to entropy production, separates into a sum of products of "speeds", "streams" or "flows" v times the driving "forces" or "strengths" y:

$$P_\mathrm{p} = y_1 v_1 + y_2 v_2 + \ldots + y_n v_n \, .$$

We are already familiar with such a representation from the example of our coupled moving-blocks: $P_\mathrm{p} = F \cdot v + F' \cdot v'$. This sum may consist of a single term in simple cases, for instance, a voltage U driving a current I through an electric resistance: $P_\mathrm{p} = U \cdot I$. Often the motions or currents that cause the energy losses are not independent of each other. They influence each other, so that all y_i become functions of all v_j:

$$y_i = y_i\left(v_1, v_2, \ldots, v_n\right) .$$

or vice-versa. Here we consider only non-degenerate cases for which the v vanish when the driving forces go to zero. In order to obtain a formulation independent of a particular process, we will say that the speeds themselves are coupled.

We call the above representation of lost power the "main equation" of the system with coupled speeds. The variables on the right are called "main quantities", where each term consists of a product of "paired" variables. The concepts of primary and coupled effects are defined in the same way as before. While we could identify the force and work coordinate in an elastic system from its location in the main equation before or after the differential operator d, such a corresponding criterion is absent here because the factors are interchangeable. Usually it is clear how a quantity may be categorized from its context, but sometimes this approach fails and a more precise definition would be useful.

P_p becomes negative if we imagine that time is reversed. The entropy produced must vanish and the burned up work must re-appear if time runs backwards as in a rewinding film. In consequence, only one factor in each term must change sign, because the resulting sign of the product must change. So the forward forces on the blocks maintain the same direction — a spring scale attached to the pulley shows the same deflection even for a rewinding film — while the speeds reverse direction.

The main quantities are divided into two groups based on their behavior during time reversal: with or without a sign change. Those quantities, which do not

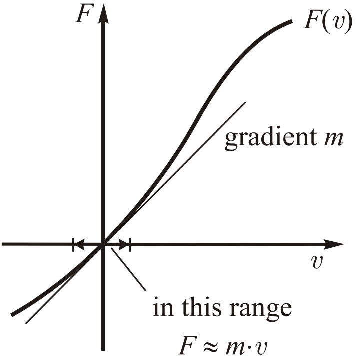


Fig. 5.2: Example for a $F(v)$-curve

change sign are interpreted as "forces" and the others are "speeds". In general this classification is obvious, but for some exceptions the above criterion should be used to make a decision.

An essential property of our earlier main equation is that we can apply the flip rule to derivatives of main quantities. The new main equation possesses the same property based on a theorem developed by ONSAGER, namely that the coupling among speeds is always symmetric:

$$\left(\frac{\mathrm{d}y_i}{\mathrm{d}v_j}\right)_{v_{\hat{j}}} = \left(\frac{\mathrm{d}y_j}{\mathrm{d}v_i}\right)_{v_{\hat{i}}} \qquad (i, j = 1, 2, \ldots, n).$$

Hence the prerequisites for the flip rule are satisfied. However, this theorem is only valid when the system is at rest and all v and y vanish. Since we can determine slopes of curves and planes at this point to help us evaluate the functions in the vicinity (Figure 5.2), this law is valid for the entire region where the slopes are approximately constant.

5.3. Coupling of Electric Currents and Entropy Flows

A current I flows through a piece of wire when a voltage U exists across its ends, and an entropy current J flows through it when a temperature difference ϑ exists between both ends (Figure 5.3).

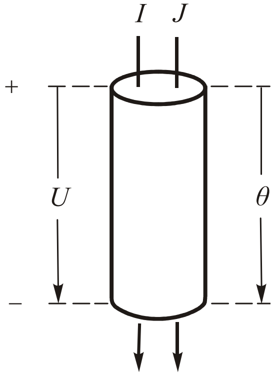


Fig. 5.3: Entropy flow and electricity current in a wire

If the charge dq is moved from potential $\varphi + U$ to the potential φ in the time interval dt, then the potential energy $U \cdot \mathrm{d}q$ is released within the conductor. Simultaneously, the flow of entropy dS from the potential $T + \theta$ to the potential T releases energy $\theta \cdot \mathrm{d}S$. So the total lost work consists of $\mathrm{d}W_\mathrm{p} = U \cdot \mathrm{d}q + \theta \cdot \mathrm{d}S$. The lost power $P_\mathrm{p} = \mathrm{d}W_\mathrm{p} / \mathrm{d}t$ is obtained by differentiating with respect to time (divide by dt):

$$P_\mathrm{p} = U \cdot I + \theta \cdot J \ .$$

This is the main equation of our system where $I = \mathrm{d}q/\mathrm{d}t$ and $J = \mathrm{d}S/\mathrm{d}t$ correspond to the speeds v_i, and U and θ to the forces y_i. The flows are generally coupled. In the previous section it was shown that coupling is equally strong as long as the flows are proportional to U and θ. For the electric current this condition implies that we remain in a region where OHM's law is valid.

Due to this coupling, assumed to be co-coupling although counter-coupling is possible, an electric current always involves an entropy flow, even when no initial temperature difference exists. As a measure of this coupling we can use the "transfer entropy" ε, defined as the quantity of entropy transported per quantity of charge (at $\theta = 0$):

$$\varepsilon \equiv \left(\frac{\mathrm{d}J}{\mathrm{d}I} \right)_\theta \ .$$

The parameter ε depends on the nature and state of the conductor. It vanishes at the absolute zero of temperature because bodies contain no entropy there, and none can be transferred by an electric current. The ε-values for copper and iron at 0° C are $+1.7 \cdot 10^{-6}$ and $-17 \cdot 10^{-6}$ (J/K)/C, respectively. A current of 1 A takes a week to transfer an amount of entropy of 1 J/K (sufficient to melt 1 cm^3 of ice) in a copper wire.

Conversely, the entropy flow pulls along electric charge. If the electric current is stopped, an opposing tension is created by the build-up of charge, whose strength is measured by the value of the parameter $-(\mathrm{d}U/\mathrm{d}\theta)_{I=0}$, the absolute differential thermal voltage (thermoelectric or SEEBECK effect). This coefficient has the same value as ε, as can be shown by using the flip rule. The total voltage $-U$ across a longer piece of wire is obtained by summing all partial voltages $-\mathrm{d}U = \varepsilon\,\mathrm{d}T$:

$$-U = \int_{\text{Start}}^{\text{End}} \varepsilon(T)\,\mathrm{d}T\ .$$

The integration is necessary because ε depends on T, and T cannot be treated as constant for larger temperature differences between the ends. The fact that ε and the total thermal voltage $-U$ differs for each material is utilized for the design of thermoelectric devices (Figure 5.4) which measure the difference in thermoelectric voltage between two conductors. It should be noted that connecting wires can generate thermoelectric voltages and entropy currents if they do not have uniform temperature.

If the current of entropy is suppressed ($J = 0$) in a piece of wire (length l, cross-section A), then the transport of charge is made more difficult because the resistance rises. The increase ΔR relative to the value $R = (\mathrm{d}U/\mathrm{d}I)_\theta$ with unhin-

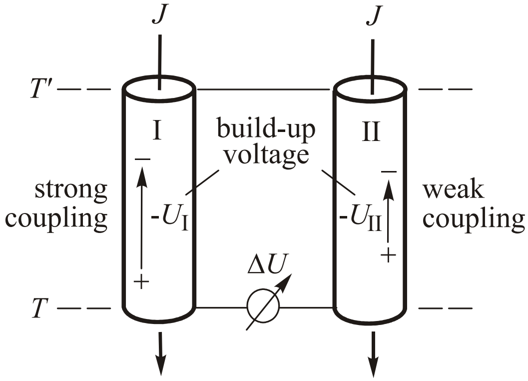


Fig. 5.4: Thermocouple

dered entropy flow ($\theta = 0$) can be calculated according to the familiar approach (cut back to θ, I):

$$\Delta R = \left(\frac{\mathrm{d}U}{\mathrm{d}I}\right)_J - \left(\frac{\mathrm{d}U}{\mathrm{d}I}\right)_\theta = \left(\frac{\mathrm{d}U}{\mathrm{d}\theta}\right)_I \cdot \left(\frac{\mathrm{d}\theta}{\mathrm{d}I}\right)_J = \left(\frac{\mathrm{d}J}{\mathrm{d}I}\right)_\theta^2 \Big/ \left(\frac{\mathrm{d}J}{\mathrm{d}\theta}\right)_I = \frac{\varepsilon^2}{G}\,.$$

$G = (\mathrm{d}J/\mathrm{d}\theta)_I$ represents the entropy conductance in the absence of electric currents ($I = 0$). What is usually tabulated is not R or G but the resistivity ρ ($R = \rho{\cdot}l/A$) and the heat• conductivity λ which is greater by a factor T than the entropy conductivity Λ (where $G = \Lambda{\cdot}A/l$ and $\lambda = T{\cdot}\Lambda$). For a piece of iron wire at 0° C ($\rho = 8.6{\cdot}10^{-8}\ \Omega$ m, $\Lambda = 0.30$ W/K^2 m), the relative difference $\Delta R/R = 1.1\ \%$. This thermal indirect effect is quite significant.

Thermal conductivity Λ and electric conductivity $\sigma = 1/\rho$ are proportional to each other for metals, and in general are independent of the nature, composition and temperature (!) of the metal:

$\Lambda \sim \sigma$ (WIEDEMANN-FRANZ Rule).

If an electric current I flows through the contact area between two conductors, where the first (′) has weak coupling and the second (″) strong coupling, then the location of the joint cools down because more entropy flows away than is received (PELTIER effect). If the current is reversed, the joint heats up (Figure 5.5).

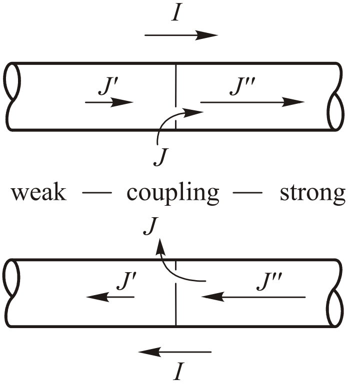


Fig. 5.5: PELTIER effect

In the first case, at constant temperature, the entropy received from the outside is given by the difference of the entropy flows transported by the electric current:

$$J = J'' - J' = (\varepsilon'' - \varepsilon')I\,.$$

A rigorous treatment of thermoelectric phenomena must consider the fact that transferred charges in a wire are bound to electrons, and their potential is determined not only by φ but also influenced by the chemical milieu.

5.4. More Examples

A number of other cases exist where currents of different quantities are coupled. When water is passed through a body with fine pores, an electric potential difference can form between the entry and exit points. Conversely, when a current is passed through a moist body, it causes water to start dripping ("electro-osmosis"). For a mathematical description we refer to the arrangement illustrated in Figure 5.06. When an amount of water dn penetrates the wall, energy $\Delta\mu \cdot \mathrm{d}n$ is released where $\Delta\mu$ is the difference of the chemical potential across the wall. The lost or burned up power P_p is given by $P_\mathrm{p} = \Delta\mu \cdot J_n$ where $J_n = \mathrm{d}n/\mathrm{d}t$ represents the flow of substance. In order to determine the total lost power the electrical losses $U \cdot I$ have to be included, so the main equation becomes:

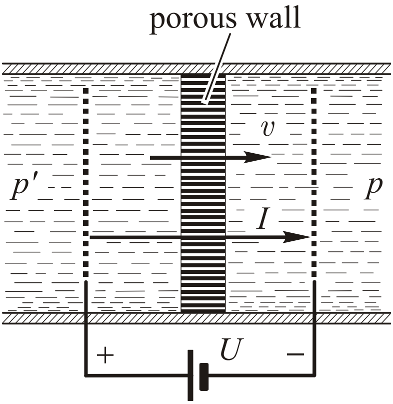


Fig. 5.6: Electro-osmosis

$$P_\mathrm{p} = \Delta\mu \cdot J_n + U \cdot I.$$

The calculation of individual coefficients is possible from this equation as usual. Since $\Delta\mu = V_\mathrm{m} \cdot \Delta p$ (see section 4.3.3), the volume of water penetrating the wall per unit time can be described by $J_V = V_\mathrm{m} \cdot J_n$. We can interpret the flow of water J_V as a volume current across a pressure drop:

$$P_v = \Delta p \cdot J_V + U \cdot I.$$

The coupling between substance and entropy flow can be observed from the example in Figure 5.7. Due to the escaping entropy produced by the electric heater inside the porous ceramic cell, the air flows in the opposite direction through the pores (KNUDSEN effect). If the attached tube is sealed off — it is sufficient to place the tube deeper into the water — then the air pressure inside the cell builds up until the small excess pressure stops the flow of substance. The main equation for the process in the cell walls can be expressed as

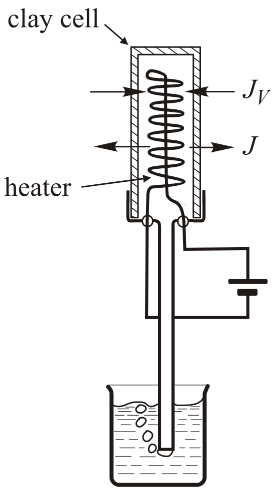


Fig. 5.7: KNUDSEN effect

$$P_\mathrm{p} = \Delta T \cdot J + \Delta\mu_1 \cdot J_1 + \Delta\mu_2 \cdot J_2 + \ \dots \ ,$$

where air is treated as a gas mixture. By means of the coupling concept, we can readily predict and evaluate the possible effects.

The application of the above lines of thought and mathematical procedures to related phenomena such as thermal diffusion, membrane potentials, negative osmosis, etc. should no longer cause insurmountable difficulties, I hope.

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