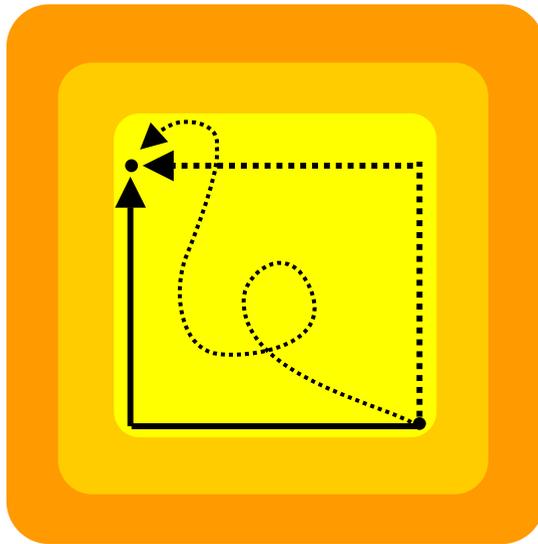


Georg Job

A New Concept of Thermodynamics

Entropy as Heat

Draft, last update: 2006-07-11



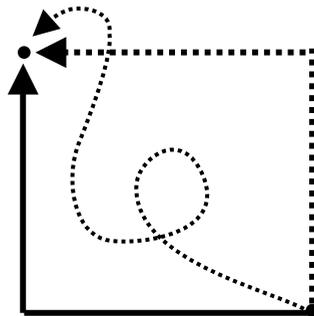
Eduard-Job-Foundation for Thermo- and Matterdynamics

English Translation of
G. Job: “Neudarstellung der Wärmelehre”,
Akademische Verlagsgesellschaft
Frankfurt am Main, 1972

Georg Job

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Entropy as Heat



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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" shows a contradiction between theory and intuition. Whereas in everyday experience heat is considered to be something that may be produced in an oven, keeps a room warm 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 lost 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 a substance. 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. 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 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 parameters.

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 describes real measurements of heat, the flow and generation of heat, energy conversions 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 conversion 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 indirect calculation from other measurable quantities. In order to make these definitions more precise, we first present 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 common perceptions about heat? One can observe different conceptual levels:

- 1st Level: Heat, like cold, is a property of a body. It is produced by friction or fire. When the heat source is eliminated, the heat gradually disappears. 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 de-

stroyed 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 perceived as something with intensity or as hotness. 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 and consider the last and most advanced conceptual level. In summary, heat exists in every body to a greater or lesser degree, it can be transferred to or extracted from a body and 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 generation:

Figure 2.1 shows examples of processes in which heat appears to be generated. From experience we know that heat is only produced by "consuming a certain amount of fuel (fire), force (friction), electric power, etc."

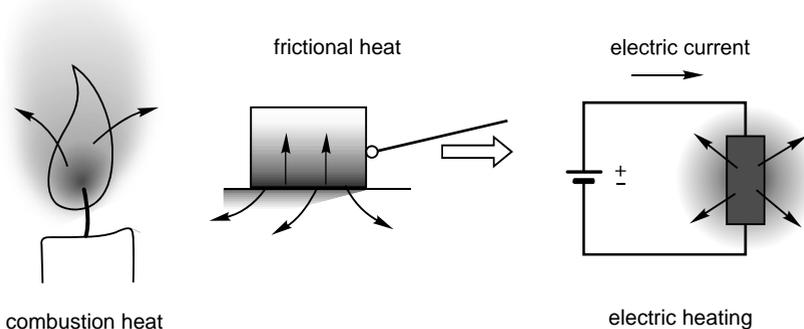


Fig.2.1: Heat generation.

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.

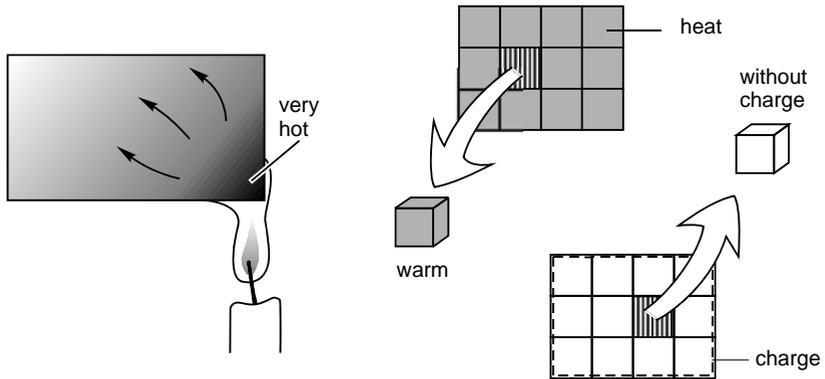


Fig. 2.2: Heat distribution

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.

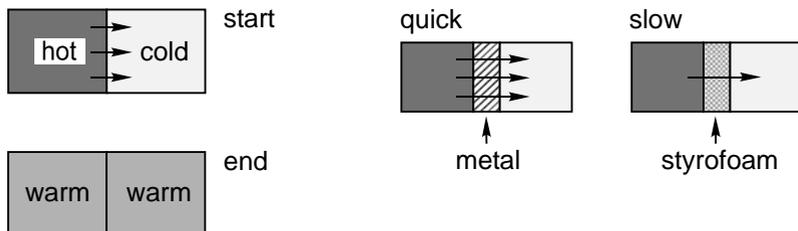


Fig. 2.3: Heat transfer

d) Weight of heat:

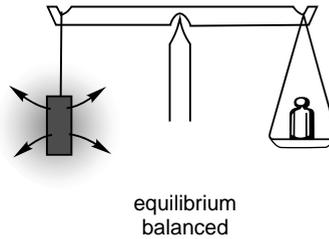


Fig. 2.4: Weight of heat

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

e) Expansion and heat exchange:

The temperature of a rubber band in a constant temperature environment depends on its extension. On extension the rubber band warms up and heat is then transferred to the surroundings until the excess temperature disappears (Fig 2.5). When the tension is lowered, the rubber band cools down and heat flows into it from its surroundings.

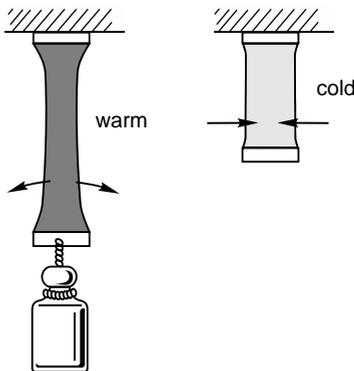


Fig. 2.5: Elongation of an elastic band

The temperature in a gas filled syringe drops when the pressure is reduced and rises when the pressure is increased (Fig 2.6) If this syringe is not thermally insulated, then equilibrium is reached with its environment just as in the rubber band experiment. Solid and liquid bodies behave in a similar manner but the observed effects are less pronounced.

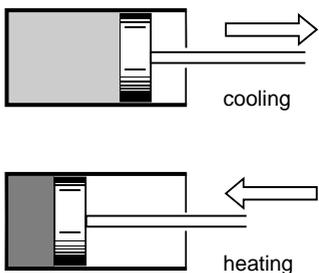


Fig. 2.6: Gas in a cylinder

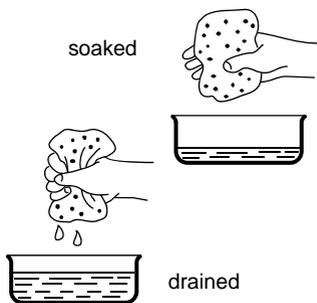


Fig. 2.7: The sponge model

The analogy with a sponge (Fig. 2.7) demonstrates visually how to understand the "absorption" or "expulsion" of heat in the gas syringe or any other body. We will examine this behavior more closely later.

f) Effects of heat:

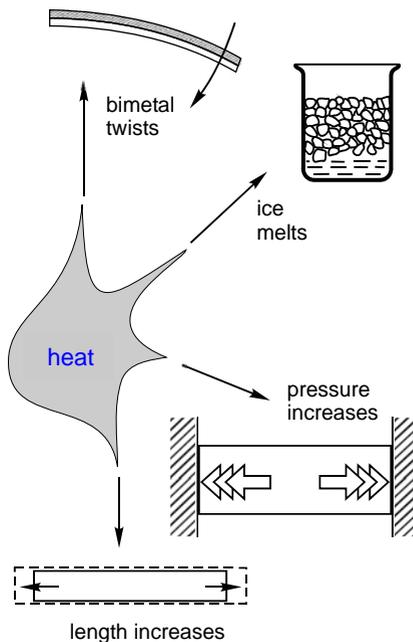


Fig. 2.8: Side effects of heat

The most important effect of heat transfer is a rise in temperature. However, numerous other secondary effects may be observed (Fig 2.8). For example, a metal rod expands, a bimetallic strip bends, iron loses magnetism, the voltage of a hydrogen-oxygen fuel cell decreases, 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 transfer, a rise in temperature, does not occur. When heat is removed, the effects disappear: the metal rod contracts, the bimetallic strip straightens, iron becomes magnetic, 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. In order to develop a theory, based on these observations, which can be experimentally tested, we need to define a measure of heat* and of the magnitude of its effects. Before defining such a measure, 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. No-one 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.

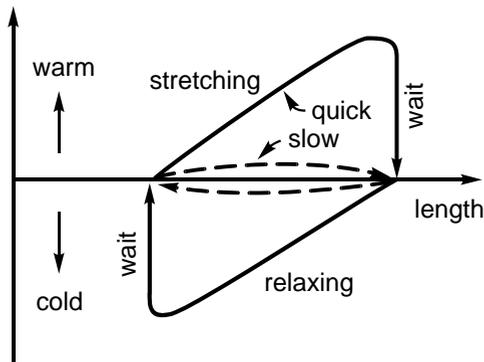


Fig. 2.9: Stretching and relaxing of a rubber band

In order to quantify an amount of heat*, we can consider the following method for 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).

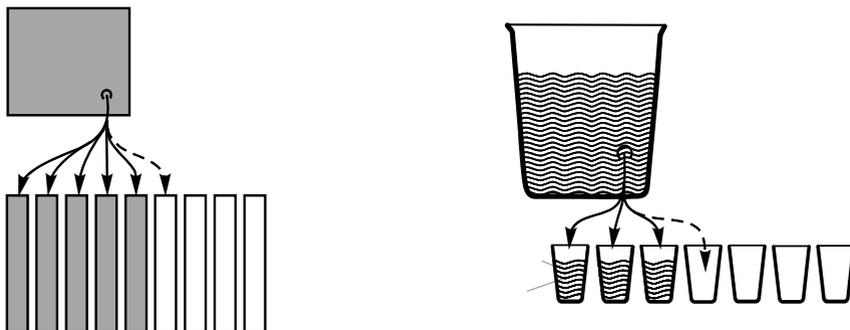


Fig. 2.10: Portioning of heat (left) like water (right)

Another method is to melt ice cubes of equal volume. 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 liquid water as a unit 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.

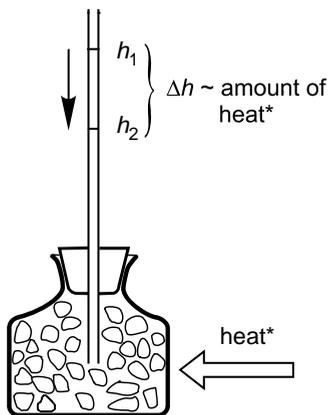


Fig. 2.11: Ice calorimeter

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, just as a sponge can be used to deliver water from one container to another. A gas syringe can be viewed as a practical application of this idea. It is thermally insulated, has a heat* valve installed on its front (Fig. 2.12) and can be brought into contact with various objects under investigation. In principle, other objects can also be used e.g. the rubber band.

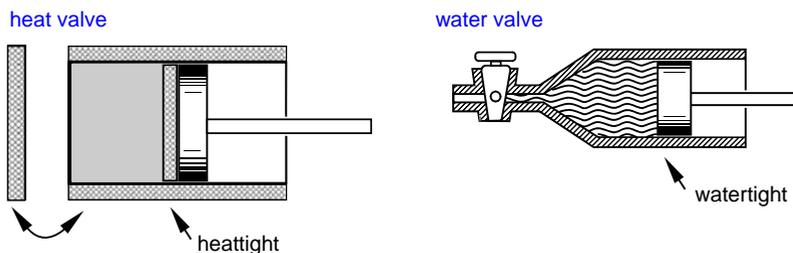


Fig. 2.12: A heat syringe works like a water syringe

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 gas 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.
- We remove the syringe from the bottle and bring it into contact with the rod. During the transport from bottle to rod we keep the valve closed to avoid heat losses.
- We force heat* into the rod until it expands to the desired length.
- We deliver the remaining heat* to the ice water bottle. During the transport from rod to bottle the heat* valve is again closed.
- The surplus heat* is returned to the calorimeter. As a result, the water level in the capillary tube drops and the gas syringe returns to its initial position.

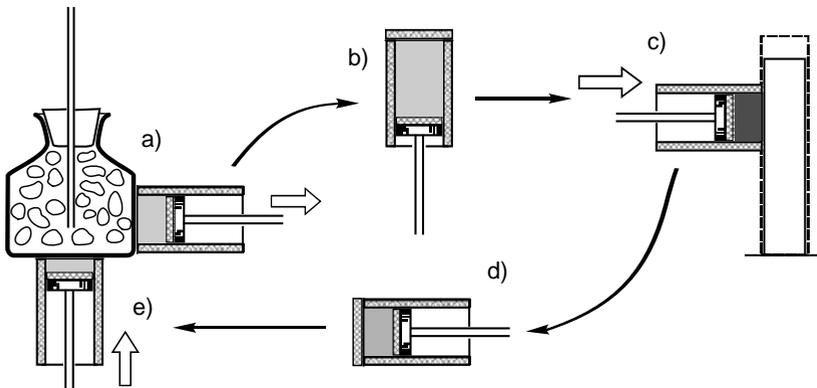


Fig. 2.13: Measuring Heat*

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 created internally. Unwanted transfer of heat* to or from the environment can be prevented through good insulation and internal heat* generation 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 generating heat*. However, steps b) and d) pose some difficulties. If we bring the gas 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 gas probe causing the gas to expand. As mentioned above, we cannot allow spontaneous changes to occur in the measurement procedure. Before we bring the gas probe 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 gas probe. 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 gas probe 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 gas probe 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 2.5.2) 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 test results are predictable.

2.2. Work and Temperature

Work is required to transfer heat* as in moving a piston or stretching a rubber band, 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 dm 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

$$dW = \Delta h \cdot g \cdot dm$$

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 dm in container II is said to have a potential energy greater by dW relative to container I.

$$dE_{II} - dE_I = dW.$$

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

Let us now consider the corresponding heat* transfer process. For example, it takes work to "lift" the quantity of heat* dS from a cold (I) to a hot (II) body by means of a gas probe. If carefully done, the associated work dW is retrievable because the process is basically reversible. We can assign a potential energy dE_{II} to the heat* dS in body II that is greater than the corresponding amount dE_I in body I by

$$dE_{II} - dE_I = dW.$$

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

$$dE_{II} - dE_I = dW.$$

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 dW is independent of the path and method used (gas probe, rubber band, etc.) similar to the case of raising water or moving an electri-

cal charge (Fig. 2.14). 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.

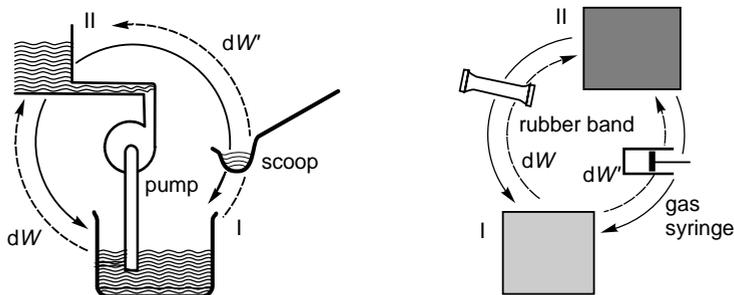


Fig. 2.14: Potential energy and energy conservation in heat* transfer.

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 amount dM (of substance, charge, mass, heat*, etc.) at this location, divided by this amount:

$$\psi = \frac{dE}{dm}.$$

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 dM from one location to another -- divided by dM :

$$\Delta\psi = \frac{dW}{dm}.$$

Although $\Delta\psi$ can be determined, ψ cannot. While for small dM the potential energy is proportional to the amount dM , 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*, 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: $dW = dm \cdot g \cdot \Delta h$ work to raise dm in a gravitational field

$$\frac{dW}{dm} = \Delta(g \cdot h), \quad g \cdot \Delta h \text{ gravitational potential.}$$

- b) Static Electricity: dW work to move charge dQ in an electric field

$$\frac{dW}{dQ} = \Delta\varphi, \quad \varphi \text{ electric potential.}$$

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

$$\frac{dW}{dS} = \Delta T, \quad T \text{ thermal potential.}$$

The last Equation defines a potential function for heat* denoted by T . The value of this potential can only be determined relative 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

$$dE = T \cdot dS.$$

By dividing 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. This is not the case for the electric potential. The potential of an electrically charged body is determined by measuring the work performed in bringing up a test charge dQ to it from infinity (Fig. 2.15). Since the initial charge is distributed over a larger surface when the body is partitioned, the field and the work necessary decrease.

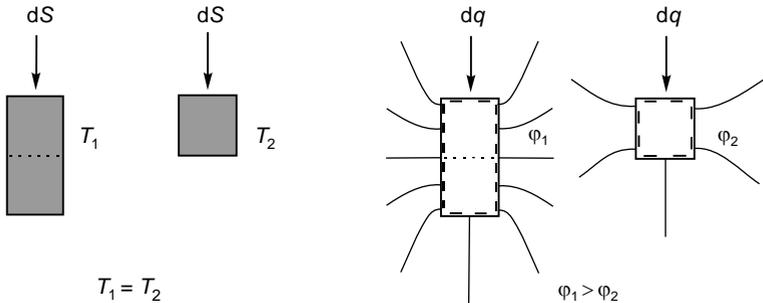


Fig. 2.15: Comparison of charge and heat*

2.2.3. Thermal Tension

Let us consider a body that is heated by small increments of heat* dS by means of a gas probe. 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" t . This phenomenon is well understood for the transfer of water from one container at a 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 $dW_0 = -p_0 dV$. 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 $dW_1 = +p_1 dV$ is performed. The total work is therefore given by

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

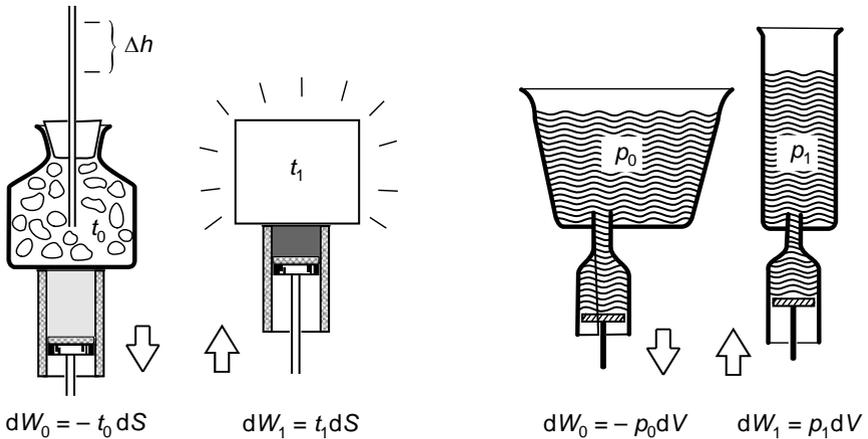


Fig. 2.16: Thermal tension and heat* transfer

Similarly, the work for the transfer of heat* (Fig. 2.16, left side) consists of the two parts $dW_0 = -t_0 dS$ and $dW_1 = +t_1 dS$ 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

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

so that the heat* potential can be interpreted as a thermal tension:

$$T = t.$$

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 of 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).

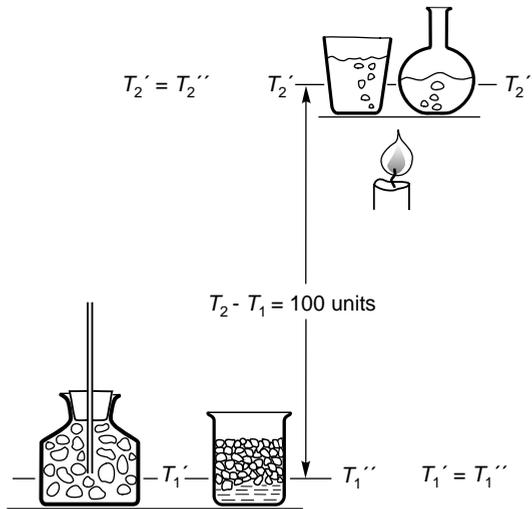


Fig. 2.17: Temperature as thermal tension

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!):

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

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).

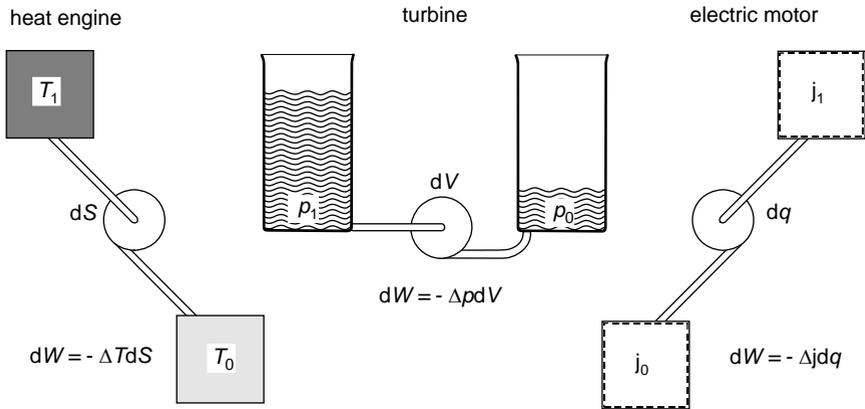


Fig. 2.18: Heat* engine, water wheel, and electric motor

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* dS , charge dQ and water volume dV , the required work is

$$dW = T \cdot dS \quad \text{thermal work,}$$

$$dW = \varphi \cdot dQ \quad \text{electric work,}$$

$$dW = p \cdot dV \quad \text{mechanical work.}$$

Thermal work should not be confused with the work required for "lifting" heat* (for example with a gas probe) 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 is not proportional to the heat* content of a body (Fig. 2.19), the ice water bottle providing an extreme example. On heating, its temperature remains constant provided that ice is present.

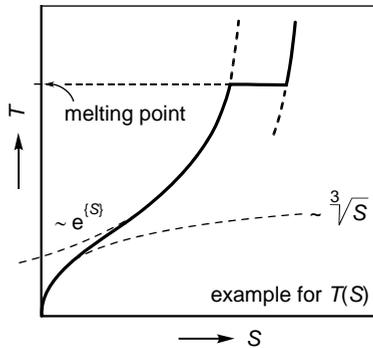


Fig. 2.19: Temperature T as a function of heat* content S

In order to describe the thermal behavior of a body, generally, T is not discussed as a function of S but instead of it the heat* capacity ζ is considered, i.e., the amount of heat* required to raise the thermal tension by one unit:

$$\zeta = \frac{dS}{dT}.$$

The electrical capacitance of a charged body is defined analogously :

$$C = \frac{dQ}{d\varphi}.$$

The heat* capacity 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* was transferred. For example, a body that is free to expand can receive more heat* than one that is constrained.

2.3. Heat* Generation

This section deals with some conditions for and consequences of heat* generation 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 generated because the rubber band remains as cold or warm at the end as it was at the beginning.

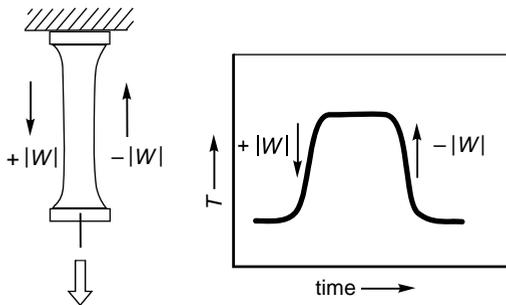


Fig. 2.20: Stretching of a rubber band

- 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 re-

turned 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 generated, and the expended work is used up.

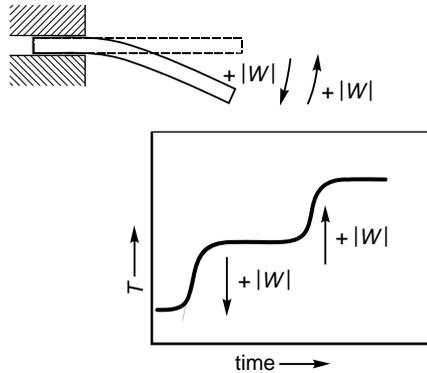


Fig. 2.21: Bending iron

We now want to generalize these results and express them quantitatively. If a small amount of heat* S_p is to be produced in a body, this can only happen by using up energy to overcome its thermal tension T . When we release the resulting heat* and return the body to its initial state, the amount of thermal work emitted, $|W| = T \cdot S_p$, 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: The zero point of the thermal potential cannot be arbitrarily chosen, in contrast to that for electric potential. Temperature can be determined in an absolute sense. From experience we know that heat* is only generated when work is expended, never when work is gained. From $W_p > 0$ and $S_p > 0$ it follows as a consequence, $T > 0$. There are no negative temperatures.

One additional observation is necessary: The heat* content S of a body can increase both by an amount S_c imported from an external source and by an amount S_p produced inside the body:

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

2.3.2. Prerequisites for Heat* Generation

We have shown that energy is required for heat* generation and this seems to be the only condition. 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 electrical resistor, by stirring a liquid or by friction in a bearing. Conversely, one can suspect that heat* is always generated when the required energy is available. The following examples provide some justification for this statement.

- When a rolling vehicle slows down, its kinetic energy is released. This energy can be converted to potential energy when it rolls uphill. There is no, or more accurately, only little heat* generated. This possibility is eliminated when the vehicle rolls on level ground when the total energy is used for heat* generation.
- Chemical energy in a galvanic cell is converted to electrical work. If the whole work 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 electrical work is used for generating heat* and none is conserved as potential energy.

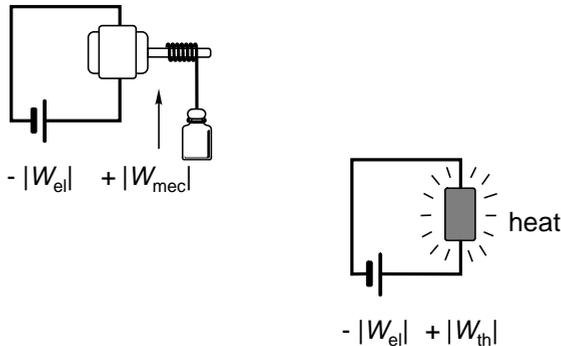


Fig. 2.22: Heat* generation by an electric current

- Work stored on compression of a gas is released when the gas is allowed to expand. If this work is used to drive a small motor, the gas, as expected, will cool down. If the pressurized gas is simply vented from its container without

utilizing its work potential, the gas temperature changes very little. Under these circumstances the generated heat* effectively cancels the temperature drop. A small motor driven by compressed air clearly demonstrates this behavior: When the motor idles, the vented air is warm and when the motor is loaded, the vented air becomes cooler.

In summary we can state that heat* is generated 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* generation and hence complies with energy conservation. In the second case, by contrast, the missing energy has to be supplied externally.

Not every process which 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-generating 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 or dissipation 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 generate heat locally via a chemical reaction (fire, gas burner) or with an electrical 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.

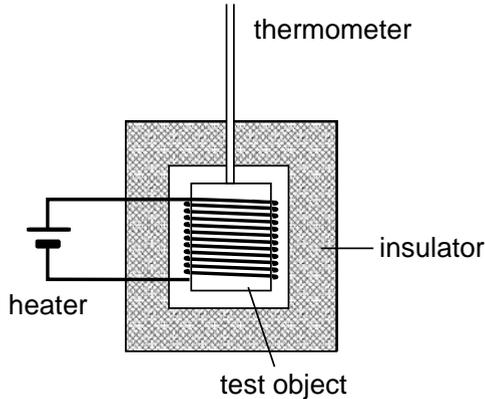


Fig. 2.23: Measuring heat* capacities

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 electrical work expended, dW_p , divided by the measured temperature T , yields the increase dS in the heat* content S . The ratio of dS to the observed temperature rise dT represents the heat* capacity C and we obtain S by integrating the heat* capacity.

$$C = \frac{dS}{dT} = \frac{1}{T} \cdot \frac{dW_p}{dT} \qquad S = S_0 + \int_{T_0}^T C \cdot dT$$

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 $(T_1 - T_0) S$ is released (Fig. 2.24). Where does the energy go? Since it cannot be stored anywhere, it must be used for heat* generation. This heat* S_p , generated 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:

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

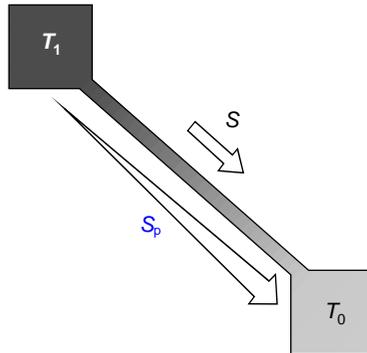


Fig. 2.24: Heat* conduction

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 had excluded this process because it is not reversible. We have now shown that this exclusion is justified.

The thermal work performed on the colder body is given by

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

This work is equivalent to the amount, $S \cdot T_1$, released by the warmer body. 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 some cases.

The energy W_p is the work lost along the conduction path. If we replace the conduction path by a heat* engine, then this amount of energy would be the gained work. Here this energy is not used but wasted and devalued. At the same time, the amount of "thermal charge" is increased.

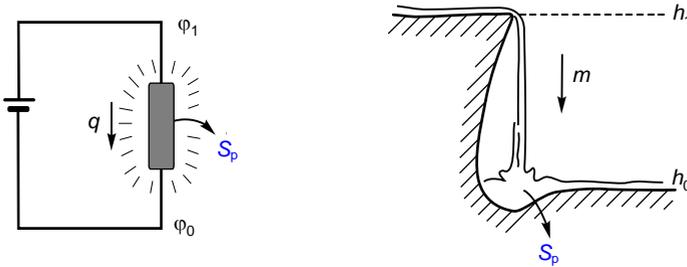


Fig. 2.25: Other cases of potential drop and heat* production

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

$$W_p = (\varphi_1 - \varphi_0) \cdot Q, \quad S_p = \frac{W_p}{T_0} \quad (\text{electric resistor}),$$

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

In all these processes, two steps can be distinguished:

potential drop and heat* generation.

In the case of heat* conduction this distinction is obscured because the quantities which flow and which are generated 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:

$$T \rightarrow 0 \text{ as } S \rightarrow 0 \quad (\text{more precisely: } T \rightarrow 0 \text{ when } S \text{ is sufficiently small}).$$

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, the products of the chemical reaction and the chemical agents used 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 – the procedures are described in Chapter 4 – that ΔS vanishes at very low temperatures. This result and other empirical facts support the obvious assumption that bodies at zero absolute temperature contain no heat*:

$$S \rightarrow 0 \text{ as } T \rightarrow 0 .$$

These two relations formulated here are not satisfied in some singular cases. 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 never approach infinity. The above discussion can be summarized as follows:

$$T \rightarrow 0 \text{ if and only if } S \rightarrow 0 \text{ for finite systems.}$$

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* were locked or frozen into the body if it was cooled too quickly. In the case of glass, it is the heat* required to melt it (the heat* of fusion). 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*. Such parts of heat* are literally locked 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 retain 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

Those familiar with other approaches to thermodynamics need to know how the new and the traditional conceptual approaches are related. 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 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 thermodynamics. A comparison will yield the corresponding concepts of each approach.

We mentioned earlier that heat* can be equated with entropy. Both quantities can be identified strictly from the following comparison. Our procedure for heat* transfer from one body to another is nothing other than 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 gas probe from an ice water bottle. During this process the entropy decrease $-\Delta S_1$ of the first body (ice calorimeter) equals the entropy in-

crease 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 amount of freezing water m in a heat* measurement process is proportional to the entropy loss of the calorimeter $-\Delta S_1$. In addition, m is by definition a measure of the increase in heat* ΔS_2^* of the body under investigation:

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

If we set the proportionality constant between ΔS_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:

$$S = S^* .$$

Those familiar with the abstract introduction of entropy as an integral over the reversibly added reduced heat*, dQ_{rev}/T , 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 that always increases when state changes actually occur in a closed system. Since it is an extensive or substance-like quantity, one can assign a density function 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 which total amount always increases. Since $dS = dQ_{\text{rev}}/T$, the effects of an entropy increase are qualitatively equivalent to a heat* input. Each increment dS , for either reversible or irreversible processes, can be attributed to some dQ_{rev} . Since we cannot tell whether the heat effects are due to entropy or the energy dQ_{rev} received by a body, there is no reason why we should not interpret the quantity S , rather than Q , as heat.

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 subsequently emitted completely as thermal work $|W^*| = T^* \cdot S_p^*$. Conservation of energy requires that

$$W_p = |W^*| = T^* \cdot S_p^* .$$

Expressed in traditional terminology, the work W_p is performed 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 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 $W_p + Q = 0$ and $S_p + Q/T = 0$ or

$$W_p = |Q| = T \cdot S_p .$$

Comparing both equations for W_p shows that heat^{*} in its traditional sense, Q , and thermal work, W^* , as well as thermodynamic temperature, T , and heat^{*} potential, T^* , are equal since $S = S^*$:

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

As a result, our heat^{*} capacity $\zeta^* = dS^*/dT^* = dS/dT = \zeta$, which should be called "entropy capacity" in traditional language, differs from the commonly used heat^{*} capacity $C = dQ/dT$ by the factor T because $T \cdot dS = dQ$. Again, in our terminology, C is referred to as "thermal work capacity" and is related to ζ by

$$C = T \cdot \zeta .$$

Except for the sake of this comparison, there is no reason to introduce a quantity C for our new interpretation. Similarly, there is no need to introduce a variable ζ in the traditional view. In all cases, we can state that

$$\zeta = \zeta^* \quad \text{and} \quad C = C^* .$$

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 contradictions of the energy interpretation of heat with practical observation 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 criticize that heat transfer is treated as a composite procedure, may consider energy flow instead of entropy flow and, in this way, retain familiar 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:

- 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.
- Work can be stored in one form or another and can be retrieved. It cannot be created nor destroyed.

b) Entropy Law:

- The entropy of a system is a state function. Its change is due to the sum of all heat* inputs to the system received from its surroundings in a reversible way, divided by the absolute temperature. The entropy of an isolated system can increase but never decrease during all internal processes.
- 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:

- The entropy of a system in equilibrium vanishes as its temperature approaches absolute zero.
- Absolutely cold bodies contain no heat* unless some of it is locked in.

d) Heat Engines:

- 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: $W/Q_{in} = \Delta T/T_{in}$.

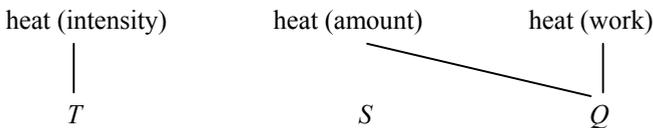
- The useful work of an lossless heat* engine is the product of the thermal potential drop, ΔT , and the amount S of the transferred heat*: $W = \Delta T \cdot S$.

The new interpretation treats work – or rather work storage – and energy as synonymous 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) is analogous to saying: "It is impossible to establish a perfect vacuum".

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, the immediacy of its statements and 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, the word "force" conveys ideas and characteristics to an unbiased layman 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 current theories of thermodynamics there are three quantities – temperature T , entropy S and the energetic (work-like) quantity Q – that can be described by the word "heat".



After assigning the name "amount of heat" to the energetic variable Q and with it all connotations connected with this word, it became difficult to explain the quan-

tity S . This variable was introduced only formally and remained abstract. This is best summarized by the extreme example of the insertion of a right foot into a left trouser leg (Fig. 2.26). Just as in such an awkward situation, theory became fixed by declaring the equality of heat and work as the First Law of thermodynamics. Subsequently, this law became the cornerstone of a large theoretical framework.

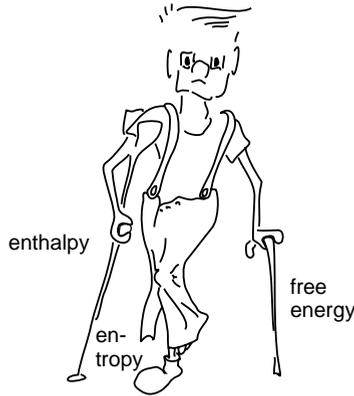


Fig. 2.26: The misfortune of thermodynamics

It is compelling to find the reasons for this misfortune of thermodynamics that led to a contradiction between theory and intuition and 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*

Since ancient times, 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 generation through friction. Here heat can be created and can disappear. No distinction was made between intensity (temperature) and quantity (amount of heat), as in every-day language used today.

* detailed discussion in G.Job,Sudhoffs Archiv 53 (1970) 378

Later, during the 18th century, under the influence of the evolution of chemistry, scholars tended to interpret heat as a kind of substance, which could neither generated nor annihilated like a chemical element. As a result, the first quantitative statements could be made and the transport of heat, as well as the behavior of temperature during the mixing of materials, 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 caused by friction but released by the ground-up material. According to this material 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, 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 (lat. *perpetuum mobile*) on the basis of the material theory of heat. In essence, he used two assumptions:

- a) Work cannot be created.
- b) Heat is not producible and not destroyable.

Building on CARNOT's ideas, E. CLAPEYRON introduced the relationship between steam pressure and heat of evaporation that became known as the Clausius-Clapeyron Equation because R. CLAUSIUS 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 generated heat by using work and in this way, seemed to indicate a connection between these two quantities. B. THOMPSON, H. DAVY (about 1800) and especially J. P. JOULE (after 1840) had shown by careful experiments that heat may be produced. Furthermore, JOULE observed the same heating effect with his calorimeter when he expended a definite amount of work regardless of the method used. When R. MAYER, J. P. JOULE and H. v. HELMHOLTZ, by as-

suming that heat and work are interconvertible, succeeded for the first time in applying the principle of conservation of energy, formerly used only for mechanical processes, to all of physics, confusion spread. 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. CLAUDIUS 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 material 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 neither producible nor destructible~~ *cannot flow from a lower to a higher temperature by itself.*

Although this theory was further developed by THOMPSON in parallel with CLAUDIUS, 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 the natural phenomena to the laws of energy conversion was the ultimate goal of physical research. It is understandable that in such an environment the CLAUDIUS-THOMPSON theory of thermodynamics was treated as a model 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 ex-

perience. 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 material theory just as CLAUSIUS did.