

# THE PRINCIPLE OF EQUIVALENCE OF HEAT AND WORK and THE FIRST PRINCIPLE OF THERMODYNAMICS

...  
*A very elementary theory*

## 1. *The nature of heat*

According to kinetic theory, absolute temperature is a measure of the average translational kinetic energy of the molecules. It follows that every physical system has **internal energy**, understood as sum of the energies of all its molecules. This form of energy is disordered, because molecules, especially in fluids, move in a chaotic way (**random walk**), without any correlation between the respective movements.

Now suppose that two bodies at different temperatures are placed in contact. After a finite interval of time, they will reach the same temperature (if they are isolated with respect to the external environment and therefore can only exchange heat between them); we say that the warmer body has transferred heat to the colder. But we know that absolute temperature is a measure of average molecular kinetic energy, therefore we can describe this process as *a transfer of internal energy* occurring at the molecular scale. Therefore **heat is a kind of energy**.

According to the correct language of Physics, you can't say "*heat of a body*" or similar expressions of common use; indeed a physical system has only internal energy. You can correctly talk about heat only as thermal energy exchanged between physical systems, or absorbed / transferred from / into a body or physical system. In conclusion: we can define heat as **a disordered form of energy in transit at the molecular level from a physical system to another**.

## 2. *Heat and dissipative processes*

The problem of the nature of heat is closely related to that of energy. From Mechanics we know that energy is basically kinetic energy of a particle,  $K = \frac{1}{2}mv^2$  ( $m$  is mass,  $v$  is velocity). Besides we know that forces can be classified as "*conservative*" or "*non-conservative*"; in the first case, the sum of kinetic and potential energy is conserved. This means that kinetic energy of a particle system - while undergoing changes over time - isn't irreversibly lost, but it can be recovered as potential energy, a quantity depending on position. This is the *classical Law of Conservation of Mechanical Energy*. Transformations from a form of energy to another take place continuously, so that motion is conserved for an infinite time. Classical instances of conservative systems are: the motion of the planets, oscillatory motion (pendulum, springs, etc...) *in absence of passive resistances*, which actually cause energy dissipation.

Non-conservative forces are dissipative forces, or friction. A dissipative force acting over a particle can be described as a *force constantly directed against velocity* and therefore *opposite to movement*. Such a force does a negative work, therefore we can define a dissipative force as a force doing negative work during all the movement. Hence *the kinetic energy dissipated is not converted in potential energy*, and *energy dissipation is irreversible* since it could no longer be restored.

As an evident example of dissipative process examine the braking of a vehicle. Analyze the phases of this process.

1. At the beginning, a vehicle has kinetic energy. This energy is “ordered”, in the sense that - ideally at least – all parts of the vehicle are characterized by systematic, coherent motions, as an ensemble of rigid bodies;
2. Brakes slow down motion and stop the car. During this phase, the initial kinetic energy is destroyed; where does it go? If you, having stopped the car, touch the disc brakes, note they are very hot. This suggests that, during braking, they have absorbed the kinetic energy of the car and converted it in internal energy, which is disorderly distributed among the molecules. Therefore you can interpret the first part of the dissipative process as *conversion of an ordered form of energy* (that is, kinetic energy) to a *disordered one* (internal energy of a physical system, or *thermal energy*), because the ordered and systematic motion of the molecules has been transformed in a chaotic, disordered one.
3. The increasing internal energy of brakes and tires manifests itself as increasing temperature. Thereafter heat will flow from brakes and tires to the surrounding air, until, after some time, they are cooled to ambient temperature.
4. Neglecting a possible variation of external temperature and supposing that temperature of brakes and ambient air are equal when starting the process, the final temperature of brakes will coincide with the initial one (this is true also for others thermodynamics variables such as volume and pressure, which is constantly the atmospheric). When the initial thermodynamic conditions (state variables) of a physical system – in this case, the brakes and the tires - coincide with the final ones, we have by definition a ***cyclic process***. Hence we have analyzed a dissipative thermodynamic cycle.

Before going over, we have to examine some lexical aspects. In Mechanics we say “brakes do a negative work to stop a car”. In Thermodynamics we can say more correctly that *brakes absorb energy* or work, or *a work has been done on brakes and tires* (now, “work” means “transfer of mechanical energy”). In general, it’s said that *a work is done on a system* when mechanical energy is transferred to it. If the process is a cycle, we speak of *cyclic work* done on a system. Moreover, we define “*thermostat*” a physical system, such as the external environment during a short time, whose temperature doesn’t change even while absorbing heat.

### 3. ***Principle of equivalence of heat and work***

Now, think again to the dissipative cycle analyzed before. The final result of the process is *the conversion of mechanical energy to thermal energy and heat transfer to external environment*. At this point, we have to determine the ratio between the work transferred to a physical system (mechanical energy dissipated into it) and the amount of heat transferred from the system to a thermostat *during a cyclic process*.

We can experimentally demonstrate ( *principle of equivalence of heat and work* ) that **during a cyclic process the ratio between the work done on a physical system and the amount of heat transferred from it to a thermostat is a constant, the value of which does not depend on the particular system or cyclic process we are considering, depending only on the measurement units employed.** We can express this law by the equation

$$\frac{W}{Q} = J \quad [1]$$

in which  $W$  is work,  $Q$  heat and  $J$  a constant named “**mechanical equivalent of heat**”. Its value is  $\approx 4.186 \frac{J}{cal}$  ( “J” is the symbol for “joule”, unit of measure of work, and  $cal$  is the one for “[little or small] calorie”, the old unit of measure of heat; but, just as a consequence of the principle of equivalence, nowadays it is correct to express heat directly in joules).

From the formula [1] we obtain

$$W = J \cdot Q$$

which implies the equivalence  $1 \text{ cal} = 4.186 \text{ J}$ . Very important is also the “**heat equivalent of work**” (symbol “ $A$ ”), that is the number of calories equivalent to 1 joule.  $A$  is the reciprocal of  $J$  and its value is  $\approx \frac{1}{4.186} = 0.2389 \frac{cal}{J}$ , so we obtain

$$Q = A \cdot W$$

This equation means that the dissipation of one unit of work ( 1 J ) produces 0.2389 cal, *by assuming that the initial and final state of the system are the same.*

#### 4. *Joule’s experiment*

The principle of equivalence of heat and work is an *experimental law*, clearly enunciated the first time by the English scientist *James Prescott Joule* ( 1818 – 1889) in 1843 as result of a famous experiment. Generally, the experiments which verify the principle of equivalence employ devices which convert mechanical energy into heat by friction. Joule converted gravitational energy to heat. His method consisted in exploiting the kinetic energy developed during the fall of two weights for a certain height. If the height of fall  $z$  is known, we can calculate the initial potential energy of two

equal masses, i.e.  $2 m g z$  (  $g$  is acceleration of gravity  $\approx 9.81 \frac{m}{s^2}$  ). The fall transforms the

potential energy in kinetic energy; therefore  $2 m g z$  is the total mechanical energy. He used this energy to rotate a shaft with many small paddles inside a certain amount of water (in detail: each weight is suspended at one end of a rope partially wrapped around a pulley fixed at the top of the shaft. The other end of the rope is fixed to the pulley, so during the fall the two weights unroll the rope, setting in rotation the pulley and the shaft). Also the internal surface of the receptacle is fitted with paddles placed in the spaces between those fixed on the shaft. This recipient, in turn, is immersed in a mixture of ice and water which is a thermostat at  $0^\circ\text{C}$ , so the whole device is initially at  $0^\circ\text{C}$ . The rotation of the paddles of the shaft is transferred to water. The contact between paddles and water acts as friction and converts kinetic energy in *thermal energy* by transforming the initial ordered and systematic motion of the molecules in a random, non- systematic motion. Water heats up and transfers heat to the thermostat, so a little amount of ice melts while temperature does not change. At the end of the experiment the shaft is still and the water is at  $0^\circ\text{C}$ , which was the initial state of the system. Hence all the mechanical energy has been converted in heat, which is transferred to the thermostat. The amount of heat is measured by the product of the latent heat of fusion of ice (ca 80 cal/g) and the mass of melted ice, which we can measure evaluating the variation of volume of the mixture: in fact, density of ice is smaller than density of water, i.e. a certain mass of ice has a larger volume than the same mass of water. So if a given amount of ice melts, we can measure the decrement of volume of the mixture to evaluate the mass of melted ice.

One may observe that it should be easier to measure the heat developed during the whole process simply by measuring the increase of temperature. Of course it’s possible, but measures of temperature are often inaccurate especially when increase of temperature is small as in this case.

## 5. First Principle of Thermodynamics

Although we are discuss only *dissipative cycles*, **the equivalence of heat and work applies to every cyclic process** – heat engines function by converting heat into work during an indefinite series of cycles. But what about non-cyclic transformations?

The principle of equivalence describes the nature of heat by extending the concept of energy to include thermal energy. Hence, according to it, at molecular scale energy loss really does not happen and we are led to think that all physical processes conserve the energy intending it in a more general sense. Therefore the equivalence between heat and work is the basis of a *general principle of energy conservation*, according to which the sum of all the forms of energy involved in any physical phenomenon does remain constant over time.

It needs to complete the meaning of this equivalence, since the integral conversion between heat and work described by  $W = J Q$  takes place only in cyclic processes, while in a general thermodynamic transformation the final state can be different from the initial one. Hence we have to formulate a general equation to include the principle of equivalence in the case of a thermodynamic cycle and consider eventual variations of internal energy during non-cyclic transformations such as isotherms, isobars, etc...Indeed, *every instance of energy conversion involves three terms: heat, work and internal energy* ; interpret heat and work as transfers of energy from or into a physical system, the energy of which must change coherently with the conservation of total energy. When heating a gas at constant volume its internal energy increases and work is zero; the same occurs when compressing a gas adiabatically (i.e., in absence of heat exchanges with other physical systems), as we recognize by rising of temperature. At the contrary, a thermodynamic system doesn't acquire energy by converting wholly heat and work one into other, and therefore its internal energy does not change (more exactly: it can vary during the process, but the initial and final energies must be equal). It implies *internal energy is a state function*, i.e. a physical quantity depending only on *state variables* that are: pressure, volume, temperature and number of moles. By definition, a *state function* depends only on the physical state of a system.

It is reasonable (and coherent with experience) to conjecture that *a variation of internal energy is equal to the difference between heat and work*. Imagine heating a physical system – for instance, a gas under constant pressure. You observe two phenomena: rise of temperature and volume increase. The first is a manifestation of a positive variation of internal energy; the second of work done by the system on the external environment. Energy conservation implies, in this and all similar cases, that heat not converted into work is absorbed as internal energy. The equation of conservation of energy (mechanical and thermal) is

$$Q = \Delta U + W$$

in which  $Q$  is heat (in energy units),  $U$  the internal energy and  $\Delta U$  its variation, that is difference between its “final” value  $U_2$  and the “initial” one  $U_1$ ,  $W$  is work.

This equation represents the *First Principle of Thermodynamics* when employing homogeneous units of measure (only joules or only calories). Otherwise you must multiply  $Q$  by  $J$  if use joule, or  $W$  by  $A$  if use calories.

Note that all these quantities can be positive, zero or negative; for convention,  $Q > 0$  if the system absorbs heat, and  $W > 0$  if the system does a work on another system: this happens when heating a gas at a constant pressure; the gas expands by moving the walls of the container and does a positive work. If a body transfers heat to the surroundings,  $Q$  is negative. When compressing a gas, work is negative. *Adiabatic compression* ( $Q = 0$ ) implies  $\Delta U = -W$ , that implies  $\Delta U > 0$ : in fact, we observe that gas temperature rises. *Adiabatic expansion* implies  $\Delta U < 0$ , because the gas employs the own molecular energy to do work and therefore cools.

Other notable non-cyclic transformations are:

*Reversible isobar* : pressure is constant. Work is equal to  $P \cdot \Delta V$  (by definition work is the product of force and distance,  $F \cdot s$ .  $P$  is the ratio between normal force  $F$  acting on a surface and area of the surface  $A$ ,  $F \cdot s = P \cdot s \cdot A$ . The product  $s \cdot A$  is the variation of volume  $\Delta V$ ), hence the first law becomes

$$Q = \Delta U + P \cdot \Delta V$$

*Isochoric* (or *isometric*, *isovolumetric*) *process*: transformation at constant volume. Work is zero and  $Q = \Delta U$ .

*Reversible isothermal*: the temperature of the system doesn't vary and the process can be inverted. In the case of an ideal gas (the internal energy of which is only kinetic, because ideally molecules don't interact one another)  $\Delta U = 0$ , and  $Q = W$ .

*Adiabatic expansion of a gas without performing external work*: diffusion of a thermally insulated gas implies both heat and work are equal to zero, therefore also  $\Delta U$  is zero. In the case of an ideal gas, this process is isothermal since  $U$  is a function only of temperature.

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Turin, August 2009 by Ezio Fornero

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