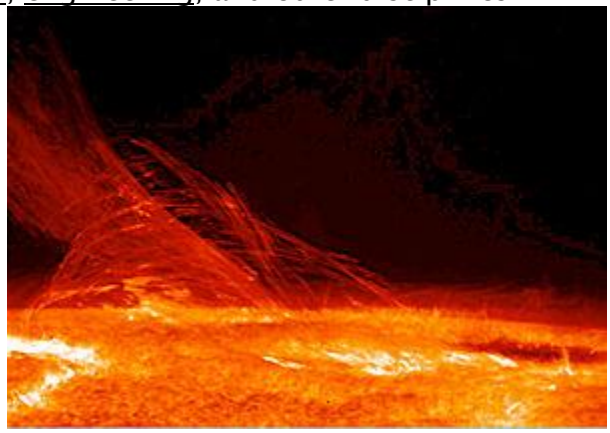
# Quantum Mechanics_heating

In physics, **heating** is transfer of energy, from a hotter body to a colder one, other than by work or transfer of matter. It occurs spontaneously whenever a suitable physical pathway exists between the bodies.[1][2][3][4][5][6] The pathway can be direct, as in conduction and radiation, or indirect, as in convective circulation.[7][8][9] Heating is a dissipative process. Heat is not a state function of a system.

Kinetic theory explains transfers of energy as heat as macroscopic manifestations of the motions and interactions of microscopic constituents such as moleculesand photons.

The quantity of energy transferred as heat is a scalar expressed in an energy unit such as the joule (J) (SI), with a sign that is customarily positive when a transfer adds to the energy of a system. It can be measured by calorimetry,[10] or determined by calculations based on other quantities, relying on the first law of thermodynamics. In calorimetry, latent heat changes a system's state without temperature change, while sensible heat changes its temperature, leaving some other state variable(s) unchanged; the terms latent and sensible are correlative.

Heat is a central concept in thermodynamics and statistical mechanics, and is also important in chemistry, engineering, and other disciplines.



The Sun and Earth form an ongoing example of a heating process. Some of the Sun's thermal radiation strikes and heats the Earth. Compared to the Sun, Earth has a much lower temperature and so sends far less thermal radiation back to the Sun. The heat of this process can be quantified by the net amount, and direction (Sun to Earth), of energy it transferred in a given period of time.

## History

Physicist James Clerk Maxwell, in his 1871 classic *Theory of Heat*, was one of many who began to build on the already established idea that heat has something to do with matter in motion. This was the same idea put forth by Benjamin Thompson in 1798, who said he was only following up on the work of many others. One of Maxwell's recommended books was *Heat as a Mode of Motion*, byJohn Tyndall. Maxwell outlined four stipulations for the definition of heat:

- It is *something which may be transferred from one body to another*, according to the second law of thermodynamics.
- It is a *measurable quantity*, and so can be treated mathematically.
- It *cannot be treated as a material substance*, because it may be transformed into something that is not a material substance, e.g., mechanical work.
- Heat is *one of the forms of energy*.[11]

From empirically based ideas of heat, and from other empirical observations, the notions of internal energy and of entropy can be derived, so as to lead to the recognition of the first and second laws of thermodynamics.[12] This was the way of the historical pioneers of thermodynamics.[13][14]

## Transfers of energy as heat between two bodies

Referring to conduction, Partington writes: "If a hot body is brought in conducting contact with a cold body, the temperature of the hot body falls and that of the cold body rises, and it is said that a *quantity of heat* has passed from the hot body to the cold body."[15]

Referring to radiation, Maxwell writes: "In Radiation, the hotter body loses heat, and the colder body receives heat by means of a process occurring in some intervening medium which does not itself thereby become hot."[16]

Maxwell writes that convection as such "is not a purely thermal phenomenon".[17]In thermodynamics, convection in general is regarded as transport of internal energy. If, however, the convection is enclosed and circulatory, then it may be regarded as transferring energy as heat between source and destination bodies, because it transfers only energy and not matter from the source to the destination body.[9]

## Practical operating devices that harness transfers of energy as heat

In accordance with the first law for closed systems, energy transferred solely as heat enters one body and leaves another, changing the internal energies of each. Transfer,

between bodies, of energy as work is a complementary way of changing internal energies. Though it is not logically rigorous from the viewpoint of strict physical concepts, a common form of words that expresses this is to say that heat and work are interconvertible.

### Heat engine

In classical thermodynamics, a commonly considered model is the heat engine. It consists of four bodies: the working body, the hot reservoir, the cold reservoir, and the work reservoir. A cyclic process leaves the working body in an unchanged state, and is envisaged as being repeated indefinitely often. Work transfers between the working body and the work reservoir are envisaged as reversible, and thus only one work reservoir is needed. But two thermal reservoirs are needed, because transfer of energy as heat is irreversible. A single cycle sees energy taken by the working body from the hot reservoir and sent to the two other reservoirs, the work reservoir and the cold reservoir. The hot reservoir always and only supplies energy and the cold reservoir always and only receives energy. The second law of thermodynamics requires that no cycle can occur in which no energy is received by the cold reservoir. Heat engines achieve higher efficiency when the difference between initial and final temperature is greater.

### Heat pump

Another commonly considered model is the heat pump or refrigerator. Again there are four bodies: the working body, the hot reservoir, the cold reservoir, and the work reservoir. A single cycle sees energy taken in by the working body from the cold reservoir. Then the work reservoir does work on the working body, adding more to its internal energy. The hot working body passes heat to the hot reservoir, but still remains hot. Then the working body is made cool by allowing it to expand without doing work on another body. It is now cool enough to be passed to contact the cold reservoir to start another cycle. The device has transported energy from a colder to a hotter reservoir, in a convective circulation, but this is not regarded as being by an inanimate agency, because the work reservoir is depleted by an amount of energy that is eventually deposited in the hot reservoir, and the work is supplied by thermodynamic operations, not just by simple thermodynamic processes. Accordingly, the cycle is still in accord with the second law of thermodynamics. The efficiency of a

heat pump is best when the temperature difference between the hot and cold reservoirs is least.

### Macroscopic view of quantity of energy transferred as heat

According to Planck, there are three main conceptual approaches to heat. One is the microscopic or kinetic theory approach. Also there are two macroscopic approaches. One is the approach through the law of conservation of energy taken as prior to thermodynamics, with a mechanical analysis of processes, for example in the work of Helmholtz. This mechanical view is taken as currently customary in this article. The other macroscopic approach is the thermodynamic one, which admits heat as a primitive concept, which contributes, by scientific induction[18]to knowledge of the law of conservation of energy.[19]

Bailyn also distinguishes the two macroscopic approaches as the mechanical and the thermodynamic.[20] The thermodynamic view was taken by the founders of thermodynamics in the nineteenth century. It regards quantity of energy transferred as heat as a primitive concept coherent with a primitive concept of temperature, measured primarily by calorimetry. A calorimeter is a body in the surroundings of the system, with its own temperature and internal energy; when it is connected to the system by a path for heat transfer, changes in it measure heat transfer. The mechanical view was pioneered by Helmholtz and developed and used in the twentieth century, largely through the influence of Max Born.[21]It regards quantity of heat transferred as heat as a derived concept, defined for closed systems as quantity of heat transferred by mechanisms other than work transfer, the latter being regarded as primitive for thermodynamics, defined by macroscopic mechanics. According to Born, the transfer of internal energy between open systems that accompanies transfer of matter "cannot be reduced to mechanics".[22] It follows that there is no well-founded definition of quantities of energy transferred as heat or as work associated with transfer of matter.

Nevertheless, for the thermodynamical description of non-equilibrium processes, it is desired to consider the effect of a temperature gradient established by the surroundings across the system of interest when there is no physical barrier or wall between system and surroundings, that is to say, when they are open with respect to one another. The impossibility of a mechanical definition in terms of work for this circumstance does not alter the physical fact that a temperature gradient causes a

diffusive flux of internal energy, a process that, in the thermodynamic view, might be proposed as a candidate concept for transfer of energy as heat.

In this circumstance, it may expected that there may also be active other drivers of diffusive flux of internal energy, such as gradient of chemical potential which drives transfer of matter, and gradient of electric potential which drives electric current and iontophoresis; such effects usually interact with diffusive flux of internal energy driven by temperature gradient, and such interactions are known as cross-effects.[23]

If cross-effects that result in diffusive transfer of internal energy were also labeled as heat transfers, they would sometimes violate the rule that pure heat transfer occurs only down a temperature gradient, never up one. They would also contradict the principle that all heat transfer is of one and the same kind, a principle founded on the idea of heat conduction between closed systems. One might to try to think narrowly of heat flux driven purely by temperature gradient as a conceptual component of diffusive internal energy flux, in the thermodynamic view, the concept resting specifically on careful calculations based on detailed knowledge of the processes and being indirectly assessed. In these circumstances, if perchance it happens that no transfer of matter is actualized, and there are no cross-effects, then the thermodynamic concept and the mechanical concept coincide, as if one were dealing with closed systems. But when there is transfer of matter, the exact laws by which temperature gradient drives diffusive flux of internal energy, rather than being exactly knowable, mostly need to be assumed, and in many cases are practically unverifiable. Consequently, when there is transfer of matter, the calculation of the pure 'heat flux' component of the diffusive flux of internal energy rests on practically unverifiable assumptions.[24][quotations 1][25] This is a reason to think of heat as a specialized concept that relates primarily and precisely to closed systems, and applicable only in a very restricted way to open systems.

In many writings in this context, the term "heat flux" is used when what is meant is therefore more accurately called diffusive flux of internal energy; such usage of the term "heat flux" is a residue of older and now obsolete language usage that allowed that a body may have a "heat content".[26]

### Microscopic view of heat

In the Kinetic theory, heat is explained in terms of the microscopic motions and interactions of constituent particles, such as electrons, atoms, and molecules.[27]Heat

transfer arises from temperature gradients or differences, through the diffuse exchange of microscopic kinetic and potential particle energy, by particle collisions and other interactions. An early and vague expression of this was made by Francis Bacon.[28][29] Precise and detailed versions of it were developed in the nineteenth century.[30]

In statistical mechanics, for a closed system (no transfer of matter), heat is the energy transfer associated with a disordered, microscopic action on the system, associated with jumps in occupation numbers of the energy levels of the system, without change in the values of the energy levels themselves.[31] It is possible for macroscopic thermodynamic work to alter the occupation numbers without change in the values of the system energy levels themselves, but what distinguishes transfer as heat is that the transfer is entirely due to disordered, microscopic action, including radiative transfer. A mathematical definition can be formulated for small increments of quasi-static adiabatic work in terms of the statistical distribution of an ensemble of microstates.

### Notation and units

As a form of energy heat has the unit joule (J) in the International System of Units(SI). However, in many applied fields in engineering the British thermal unit (BTU) and the calorie are often used. The standard unit for the rate of heat transferred is the watt (W), defined as joules per second.

The total amount of energy transferred as heat is conventionally written as $Q$ for algebraic purposes. Heat released by a system into its surroundings is by convention a negative quantity ($Q < 0$); when a system absorbs heat from its surroundings, it is positive ($Q > 0$). Heat transfer rate, or heat flow per unit time, is denoted by $\dot{Q}$. This should not be confused with a time derivative of a function of state (which can also be written with the dot notation) since heat is not a function of state.[32] Heat flux is defined as rate of heat transfer per unit cross-sectional area, resulting in the unit *watts per square metre*.

### Estimation of quantity of heat

Quantity of heat transferred can measured by calorimetry, or determined through calculations based on other quantities.

Calorimetry is the empirical basis of the idea of quantity of heat transferred in a process. The transferred heat is measured by changes in a body of known properties,

for example, temperature rise, change in volume or length, or phase change, such as melting of ice.[33][34]

A calculation of quantity of heat transferred can rely on a hypothetical quantity of energy transferred as adiabatic work and on the first law of thermodynamics. Such calculation is the primary approach of many theoretical studies of quantity of heat transferred.[35][36][37]

### Internal energy and enthalpy

For a closed system (a system from which no matter can enter or exit), one version of the first law of thermodynamics states that the change in internal energy $\Delta U$ of the system is equal to the amount of heat $Q$ supplied to the system minus the amount of work $W$ done by system on its surroundings. The foregoing sign convention for work is used in the present article, but an alternate sign convention, followed by IUPAC, for work, is to consider the work performed on the system by its surroundings as positive. This is the convention adopted by many modern textbooks of physical chemistry, such as those by Peter Atkins and Ira Levine, but many textbooks on physics define work as work done by the system.

$$\Delta U = Q - W \ .$$

This formula can be re-written so as to express a definition of quantity of energy transferred as heat, based purely on the concept of adiabatic work, if it is supposed that $\Delta U$ is defined and measured solely by processes of adiabatic work:

$$Q = \Delta U + W.$$

The work done by the system includes boundary work (when the system increases its volume against an external force, such as that exerted by a piston) and other work (e.g. shaft work performed by a compressor fan), which is called isochoric work:

$$Q = \Delta U + W_{\text{boundary}} + W_{\text{isochoric}}.$$

In this Section we will neglect the "other-" or isochoric work contribution.

The internal energy, $U$, is a state function. In cyclical processes, such as the operation of a heat engine, state functions of the working substance return to their initial values upon completion of a cycle.

The differential, or infinitesimal increment, for the internal energy in an infinitesimal process is an exact differential $\mathrm{d}U$. The symbol for exact differentialsis the lowercase letter d.

In contrast, neither of the infinitesimal increments $\delta Q$ nor $\delta W$ in an infinitesimal process represents the state of the system. Thus, infinitesimal increments of heat and

work are inexact differentials. The lowercase Greek letter delta, δ, is the symbol for inexact differentials. The integral of any inexact differential over the time it takes for a system to leave and return to the same thermodynamic state does not necessarily equal zero.

As recounted below, in the section headed Entropy, the second law of thermodynamics observes that if heat is supplied to a system in which no irreversible processes take place and which has a well-defined temperature *T*, the increment of heat δ*Q* and the temperature *T* form the exact differential

$$\mathrm{d}S = \frac{\delta Q}{T},$$

and that *S*, the entropy of the working body, is a function of state. Likewise, with a well-defined pressure, *P*, behind the moving boundary, the work differential, δ*W*, and the pressure, *P*, combine to form the exact differential

$$\mathrm{d}V = \frac{\delta W}{P},$$

with *V* the volume of the system, which is a state variable. In general, for homogeneous systems,

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V.$$

Associated with this differential equation is that the internal energy may be considered to be a function *U*(*S*,*V*) of its natural variables *S* and *V*. The internal energy representation of the fundamental thermodynamic relation is written

$$U = U(S, V).$$ [38][39]

If *V* is constant

$$T\mathrm{d}S = \mathrm{d}U \qquad (V \text{ constant})$$

and if *P* is constant

$$T\mathrm{d}S = \mathrm{d}H \qquad (P \text{ constant})$$

with *H* the enthalpy defined by

$$H = U + PV.$$

The enthalpy may be considered to be a function *H*(*S*,*P*) of its natural variables *S* and *P*. The enthalpy representation of the fundamental thermodynamic relation is written

$$H = H(S, P).$$ [39][40]

The internal energy representation and the enthalpy representation are partial Legendre transforms of one another. They contain the same physical information, written in different ways. Like the internal energy, the enthalpy stated as a function of

its natural variables is a thermodynamic potential and contains all thermodynamic information about a body.[40][41]

**Heat added to a body at constant pressure**

If a quantity $Q$ of heat is added to a body while it does expansion work $W$ on its surroundings, one has

$$\Delta H = \Delta U + \Delta(PV)\,.$$

If this is constrained to happen at constant pressure with $\Delta P = 0$, the expansion work $W$ done by the body is given by $W = P\,\Delta V$, recalling the first law of thermodynamics, one has

$$\Delta U = Q - W = Q - P\,\Delta V \text{ and } \Delta(PV) = P\,\Delta V\,.$$

Consequently, by substitution one has

$$\begin{aligned}\Delta H &= Q - P\,\Delta V + P\,\Delta V \\ &= Q \qquad\qquad \text{at constant pressure.}\end{aligned}$$

In this scenario, the increase in enthalpy is equal to the quantity of heat added to the system. Since many processes do take place at constant pressure, or approximately at atmospheric pressure, the enthalpy is therefore sometimes given the misleading name of 'heat content'.[42] It is sometimes also called the heat function.[43]

In terms of the natural variables $S$ and $P$ of the state function $H$, this process of change of state from state 1 to state 2 can be expressed as

$$\begin{aligned}\Delta H &= \int_{S_1}^{S_2} \left(\frac{\partial H}{\partial S}\right)_P \mathrm{d}S + \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_S \mathrm{d}P \\ &= \int_{S_1}^{S_2} \left(\frac{\partial H}{\partial S}\right)_P \mathrm{d}S \qquad \text{at constant pressure.}\end{aligned}$$

It is known that the temperature $T(S, P)$ is identically stated by

$$\left(\frac{\partial H}{\partial S}\right)_P \equiv T(S,P)\,.$$

Consequently

$$\Delta H = \int_{S_1}^{S_2} T(S,P)\mathrm{d}S \qquad \text{at constant pressure.}$$

In this case, the integral specifies a quantity of heat transferred at constant pressure.

**Entropy**

Main article: Entropy

Rudolf Clausius

In 1856, German physicist Rudolf Clausius, referring to closed systems, in which transfer of matter does not occur, defined the *second fundamental theorem* (thesecond law of thermodynamics) in the mechanical theory of heat(thermodynamics): "if two transformations which, without necessitating any other permanent change, can mutually replace one another, be called equivalent, then the generations of the quantity of heat *Q* from work at the temperature *T*, has the*equivalence-value*:"[44][45]

$$\frac{Q}{T}.$$

In 1865, he came to define the Entropy symbolized by *S*, such that, due to the supply of the amount of heat *Q* at temperature *T* the entropy of the system is increased by

$$\Delta S = \frac{Q}{T} \qquad (1)$$

In a transfer of energy as heat without work being done, there are changes of entropy in both the surroundings which lose heat and the system which gains it. The increase, $\Delta S$, of entropy in the system may be considered to consist of two parts, an increment, $\Delta S'$ that matches, or 'compensates', the change, $-\Delta S'$, of entropy in the surroundings, and a further increment, $\Delta S''$ that may be considered to be 'generated' or 'produced' in the system, and is said therefore to be 'uncompensated'. Thus

$$\Delta S = \Delta S' + \Delta S''.$$

This may also be written

$$\Delta S_{\text{system}} = \Delta S_{\text{compensated}} + \Delta S_{\text{uncompensated}} \quad \text{with} \quad \Delta S_{\text{compensated}} = -\Delta S_{\text{surroundings}}.$$

The total change of entropy in the system and surroundings is thus

$$\Delta S_{\text{overall}} = \Delta S' + \Delta S'' - \Delta S' = \Delta S''.$$

This may also be written

$$\Delta S_{\text{overall}} = \Delta S_{\text{compensated}} + \Delta S_{\text{uncompensated}} + \Delta S_{\text{surroundings}} = \Delta S_{\text{uncompensated}}.$$

It is then said that an amount of entropy $\Delta S$ has been transferred from the surroundings to the system. Because entropy is not a conserved quantity, this is an exception to the general way of speaking, in which an amount transferred is of a conserved quantity.

The second law of thermodynamics observes that in a natural transfer of energy as heat, in which the temperature of the system is different from that of the surroundings, it is always so that

$$\Delta S_{\text{overall}} > 0.$$

For purposes of mathematical analysis of transfers, one thinks of fictive processes that are called 'reversible', with the temperature $T$ of the system being hardly less than that of the surroundings, and the transfer taking place at an imperceptibly slow speed.

Following the definition above in formula (1), for such a fictive 'reversible' process, a quantity of transferred heat $\delta Q$ (an inexact differential) is analyzed as a quantity $T\,\mathrm{d}S$, with $\mathrm{d}S$ (an exact differential):

$$T\,\mathrm{d}S = \delta Q.$$

This equality is only valid for a fictive transfer in which there is no production of entropy, that is to say, in which there is no uncompensated entropy.

If, in contrast, the process is natural, and can really occur, with irreversibility, then there is entropy production, with $\mathrm{d}S_{\text{uncompensated}} > 0$. The quantity $T\mathrm{d}S_{\text{uncompensated}}$ was termed by Clausius the "uncompensated heat", though that does not accord with present-day terminology. Then one has

$$T\,\mathrm{d}S = \delta Q + T\,\mathrm{d}S_{\text{uncompensated}} > \delta Q.$$

This leads to the statement

$$T\,\mathrm{d}S \geq \delta Q \quad (\text{second law})\,.$$

which is the second law of thermodynamics for closed systems.

In non-equilibrium thermodynamics that approximates by assuming the hypothesis of local thermodynamic equilibrium, there is a special notation for this. The transfer of energy as heat is assumed to take place across an infinitesimal temperature difference, so that the system element and its surroundings have near enough the same temperature $T$. Then one writes

$$\mathrm{d}S = \mathrm{d}S_{\mathrm{e}} + \mathrm{d}S_{\mathrm{i}}\,,$$

where by definition

$$\delta Q = T\,\mathrm{d}S_{\mathrm{e}} \quad \text{and} \quad \mathrm{d}S_{\mathrm{i}} \equiv \mathrm{d}S_{\text{uncompensated}}.$$

The second law for a natural process asserts that

$\mathrm{d}S_\mathrm{i} > 0$.[46][47][48][49]

## Latent and sensible heat

Joseph Black

In an 1847 lecture entitled *On Matter, Living Force, and Heat*, James Prescott Joule characterized the terms latent heat and sensible heat as components of heat each affecting distinct physical phenomena, namely the potential and kinetic energy of particles, respectively.[50][quotations 2] He described latent energy as the energy possessed via a distancing of particles where attraction was over a greater distance, i.e. a form of potential energy, and the sensible heat as an energy involving the motion of particles or what was known as a *living force*. At the time of Joule kinetic energy either held 'invisibly' internally or held 'visibly' externally was known as a *living force*.

Latent heat is the heat released or absorbed by a chemical substance or athermodynamic system during a change of state that occurs without a change in temperature. Such a process may be a phase transition, such as the melting of ice or the boiling of water.[51][52] The term was introduced around 1750 by Joseph Black as derived from the Latin *latere* (*to lie hidden*), characterizing its effect as not being directly measurable with a thermometer.

Sensible heat, in contrast to latent heat, is the heat transferred to a thermodynamic system that has as its sole effect a change of temperature.[53]

Both latent heat and sensible heat transfers increase the internal energy of the system to which they are transferred.

Consequences of Black's distinction between sensible and latent heat are examined in the Wikipedia article on calorimetry.

## Specific heat

Specific heat, also called specific heat capacity, is defined as the amount of energy that has to be transferred to or from one unit of mass (kilogram) or amount of substance (mole) to change the system temperature by one degree. Specific heat is a

physical property, which means that it depends on the substance under consideration and its state as specified by its properties.

The specific heats of monatomic gases (e.g., helium) are nearly constant with temperature. Diatomic gases such as hydrogen display some temperature dependence, and triatomic gases (e.g., carbon dioxide) still more.

### Relation between heat, hotness, and temperature

According to Baierlein, a system's hotness is its tendency to transfer energy as heat. All physical systems are capable of heating or cooling others.[54] This does not require that they have thermodynamic temperatures. With reference to hotness, the comparative terms hotter and colder are defined by the rule that heat flows from the hotter body to the colder.[55][56][57] If a physical system is very rapidly or irregularly changing, for example by turbulence, it may be impossible to characterize it by a temperature, but still there can be transfer of energy as heat between it and another system. If a system has a physical state that is regular enough, and persists long enough to allow it to reach thermal equilibrium with a specified thermometer, then it has a temperature according to that thermometer. An empirical thermometer registers degree of hotness for such a system. Such a temperature is called empirical.[58][59][60] Physical systems that are too turbulent to have temperatures may still differ in hotness. A physical system that passes heat to another physical system is said to be the hotter of the two. More is required for the system to have a thermodynamic temperature. Its behavior must be so regular that its empirical temperature is the same for all suitably calibrated and scaled thermometers, and then its hotness is said to lie on the one-dimensional hotness manifold. This is part of the reason why heat is defined following Carathéodory and Born, solely as occurring other than by work or transfer of matter; temperature is advisedly and deliberately not mentioned in this now widely accepted definition. This is also the reason why the zeroth law of thermodynamics is stated explicitly. If three physical systems, *A*, *B*, and *C* are each not in their own states of internal thermodynamic equilibrium, it is possible that, with suitable physical connections being made between them, *A* can heat *B* and *B* can heat *C* and *C* can heat *A*. In non-equilibrium situations, cycles of flow are possible. It is the special and uniquely distinguishing characteristic of internal thermodynamic equilibrium that this possibility is not open to thermodynamic systems (as distinguished amongst physical systems) which are in their own states of internal

thermodynamic equilibrium; this is the reason why the zeroth law of thermodynamics needs explicit statement. That is to say, the relation 'is not colder than' between general non-equilibrium physical systems is not transitive, whereas, in contrast, the relation 'has no lower a temperature than' between thermodynamic systems in their own states of internal thermodynamic equilibrium is transitive. It follows from this that the relation 'is in thermal equilibrium with' is transitive, which is one way of stating the zeroth law. With the relation between temperature and entropy, these facts reflect the fact that it has not been possible to define non-equilibrium entropy in a clearly satisfactory way.[61]

**Rigorous definition of quantity of energy transferred as heat**

It is sometimes convenient to have a rigorous definition of quantity of energy transferred as heat. Such a definition is customarily based on the work ofCarathéodory (1909), referring to processes in a closed system, as follows.[35][62][63][64][65][66]

The internal energy $U_X$ of a body in an arbitrary state $X$ can be determined by amounts of work adiabatically performed by the body on its surrounds when it starts from a reference state $O$, allowing that sometimes the amount of work is calculated by assuming that some adiabatic process is virtually though not actually reversible. Adiabatic work is defined in terms of adiabatic walls, which allow the frictionless performance of work but no other transfer, of energy or matter. In particular they do not allow the passage of energy as heat. According to Carathéodory (1909), passage of energy as heat is allowed, by walls which are postulated to be "permeable only to heat".

For the definition of quantity of energy transferred as heat, it is customarily envisaged that an arbitrary state of interest $Y$ is reached from state $O$ by a process with two components, one adiabatic and the other not adiabatic. For convenience one may say that the adiabatic component was the sum of work done by the body through volume change through movement of the walls while the non-adiabatic wall was temporarily rendered adiabatic, and of isochoric adiabatic work. Then the non-adiabatic component is a process of energy transfer through the wall that passes only heat, newly made accessible for the purpose of this transfer, from the surroundings to the body. The change in internal energy to reach the state $Y$ from the state $O$ is the difference of the two amounts of energy transferred.

Although Carathéodory himself did not state such a definition, following his work it is customary in theoretical studies to define the quantity of energy transferred as heat, $Q$, to the body from its surroundings, in the combined process of change to state $Y$ from the state $O$, as the change in internal energy, $\Delta U_Y$, minus the amount of work, $W$, done by the body on its surrounds by the adiabatic process, so that $Q = \Delta U_Y - W$.

In this definition, for the sake of conceptal rigour, the quantity of energy transferred as heat is not specified directly in terms of the non-adiabatic process. It is defined through knowledge of precisely two variables, the change of internal energy and the amount of adiabatic work done, for the combined process of change from the reference state $O$ to the arbitrary state $Y$. It is important that this does not explicitly involve the amount of energy transferred in the non-adiabatic component of the combined process. It is assumed here that the amount of energy required to pass from state $O$ to state $Y$, the change of internal energy, is known, independently of the combined process, by a determination through a purely adiabatic process, like that for the determination of the internal energy of state $X$above. The rigour that is prized in this definition is that there is one and only one kind of energy transfer admitted as fundamental: energy transferred as work. Energy transfer as heat is considered as a derived quantity. The uniqueness of work in this scheme is considered to guarantee rigor and purity of conception. The conceptual purity of this definition, based on the concept of energy transferred as work as an ideal notion, relies on the idea that some frictionless and otherwise non-dissipative processes of energy transfer can be realized in physical actuality. The second law of thermodynamics, on the other hand, assures us that such processes are not found in nature.

**Heat, temperature, and thermal equilibrium regarded as jointly primitive notions**

Before the rigorous mathematical definition of heat based on Carathéodory's 1909 paper, recounted just above, historically, heat, temperature, and thermal equilibrium were presented in thermodynamics textbooks as jointly primitive notions.[67] Carathéodory introduced his 1909 paper thus: "The proposition that the discipline of thermodynamics can be justified without recourse to any hypothesis that cannot be verified experimentally must be regarded as one of the most noteworthy results of the research in thermodynamics that was accomplished during the last century." Referring to the "point of view adopted by most authors who were active in the last fifty years", Carathéodory wrote: "There exists a physical quantity called heat

that is not identical with the mechanical quantities (mass, force, pressure, etc.) and whose variations can be determined by calorimetric measurements." James Serrin introduces an account of the theory of thermodynamics thus: "In the following section, we shall use the classical notions of *heat*, *work*, and *hotness* as primitive elements, ... That heat is an appropriate and natural primitive for thermodynamics was already accepted by Carnot. Its continued validity as a primitive element of thermodynamical structure is due to the fact that it synthesizes an essential physical concept, as well as to its successful use in recent work to unify different constitutive theories."[68][69] This traditional kind of presentation of the basis of thermodynamics includes ideas that may be summarized by the statement that heat transfer is purely due to spatial non-uniformity of temperature, and is by conduction and radiation, from hotter to colder bodies. It is sometimes proposed that this traditional kind of presentation necessarily rests on "circular reasoning"; against this proposal, there stands the rigorously logical mathematical development of the theory presented by Truesdell and Bharatha (1977).[70]

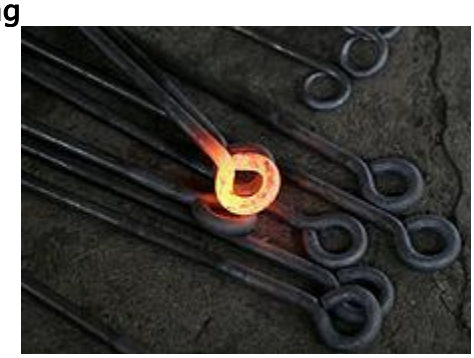
This alternative approach to the definition of quantity of energy transferred as heat differs in logical structure from that of Carathéodory, recounted just above.

This alternative approach admits calorimetry as a primary or direct way to measure quantity of energy transferred as heat. It relies on temperature as one of its primitive concepts, and used in calorimetry.[71] It is presupposed that enough processes exist physically to allow measurement of differences in internal energies. Such processes are not restricted to adiabatic transfers of energy as work. They include calorimetry, which is the commonest practical way of finding internal energy differences.[72] The needed temperature can be either empirical or absolute thermodynamic.

In contrast, the Carathéodory way recounted just above does not use calorimetry or temperature in its primary definition of quantity of energy transferred as heat. The Carathédory way regards calorimetry only as a secondary or indirect way of measuring quantity of energy transferred as heat. As recounted in more detail just above, the Carathéodory way regards quantity of energy transferred as heat in a process as primarily or directly defined as a residual quantity. It is calculated from the difference of the internal energies of the initial and final states of the system, and from the actual work done by the system during the process. That internal energy difference is supposed to have been measured in advance through processes of purely adiabatic

transfer of energy as work, processes that take the system between the initial and final states. By the Carathéodory way it is presupposed as known from experiment that there actually physically exist enough such adiabatic processes, so that there need be no recourse to calorimetry for measurement of quantity of energy transferred as heat. This presupposition is essential but is explicitly labeled neither as a law of thermodynamics nor as an axiom of the Carathéodory way. In fact, the actual physical existence of such adiabatic processes is indeed mostly supposition, and those supposed processes have in most cases not been actually verified empirically to exist.[73]

**Heat transfer in engineering**



A red-hot iron rod from which heat transfer to the surrounding environment will be primarily through radiation.

The discipline of heat transfer, typically considered an aspect of mechanical engineering and chemical engineering, deals with specific applied methods by which thermal energy in a system is generated, or converted, or transferred to another system. Although the definition of heat implicitly means the transfer of energy, the term *heat transfer* encompasses this traditional usage in many engineering disciplines and laymen language.

*Heat transfer* includes the mechanisms of heat conduction, thermal radiation, andmass transfer.

In engineering, the term *convective heat transfer* is used to describe the combined effects of conduction and fluid flow. From the thermodynamic point of view, heat flows into a fluid by diffusion to increase its energy, the fluid then transfers (advects) this increased internal energy (not heat) from one location to another, and this is then followed by a second thermal interaction which transfers heat to a second body or system, again by diffusion. This entire process is often regarded as an additional

mechanism of heat transfer, although technically, "heat transfer" and thus heating and cooling occurs only on either end of such a conductive flow, but not as a result of flow. Thus, conduction can be said to "transfer" heat only as a net result of the process, but may not do so at every time within the complicated convective process.

Although distinct physical laws may describe the behavior of each of these methods, real systems often exhibit a complicated combination which are often described by a variety of complex mathematical methods.

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