Thermodynamics



**Thermodynamics** is a branch of [physics](https://en.wikipedia.org/wiki/Physics) that deals with [heat](https://en.wikipedia.org/wiki/Heat) and [temperature](https://en.wikipedia.org/wiki/Temperature), and their relation to [energy](https://en.wikipedia.org/wiki/Energy), [work](https://en.wikipedia.org/wiki/Work_%28thermodynamics%29), [radiation](https://en.wikipedia.org/wiki/Radiation), and properties of [matter](https://en.wikipedia.org/wiki/Matter). The behavior of these quantities is governed by the four [laws of thermodynamics](https://en.wikipedia.org/wiki/Laws_of_thermodynamics) which convey a quantitative description using measurable macroscopic [physical quantities](https://en.wikipedia.org/wiki/Physical_quantity), but may be explained in terms of [microscopic](https://en.wikipedia.org/wiki/Microscopic) constituents by [statistical mechanics](https://en.wikipedia.org/wiki/Statistical_mechanics). Thermodynamics applies to a wide variety of topics in [science](https://en.wikipedia.org/wiki/Science) and [engineering](https://en.wikipedia.org/wiki/Engineering), especially [physical chemistry](https://en.wikipedia.org/wiki/Physical_chemistry), [chemical engineering](https://en.wikipedia.org/wiki/Chemical_engineering) and [mechanical engineering](https://en.wikipedia.org/wiki/Mechanical_engineering), but also in fields as complex as [meteorology](https://en.wikipedia.org/wiki/Meteorology).

Historically, thermodynamics developed out of a desire to increase the [efficiency](https://en.wikipedia.org/wiki/Thermodynamic_efficiency) of early [steam engines](https://en.wikipedia.org/wiki/Steam_engine), particularly through the work of French physicist [Nicolas Léonard Sadi Carnot](https://en.wikipedia.org/wiki/Nicolas_L%C3%A9onard_Sadi_Carnot) (1824) who believed that engine efficiency was the key that could help France win the [Napoleonic Wars](https://en.wikipedia.org/wiki/Napoleonic_Wars).[[1]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-1) Scots-Irish physicist [Lord Kelvin](https://en.wikipedia.org/wiki/William_Thomson%2C_1st_Baron_Kelvin) was the first to formulate a concise definition of thermodynamics in 1854[[2]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-kelvin1854-2) which stated, "Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency."

The initial application of thermodynamics to [mechanical heat engines](https://en.wikipedia.org/wiki/Mechanical_heat_engine) was quickly extended to the study of chemical compounds and chemical reactions. [Chemical thermodynamics](https://en.wikipedia.org/wiki/Chemical_thermodynamics) studies the nature of the role of [entropy](https://en.wikipedia.org/wiki/Entropy) in the process of [chemical reactions](https://en.wikipedia.org/wiki/Chemical_reaction) and has provided the bulk of expansion and knowledge of the field.[[3]](https://en.wikipedia.org/wiki/Thermodynamics%22%20%5Cl%20%22cite_note-Gibbs_1876-3)[[4]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Duhem_1886-4)[[5]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Lewis_Randall_1923-5)[[6]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Guggenheim_1933-6)[[7]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Guggenheim_1949/1967-7)[[8]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-8)[[9]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Fermi-9)[[10]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Perrot-10)[[11]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-11) Other formulations of thermodynamics emerged. [Statistical thermodynamics](https://en.wikipedia.org/wiki/Statistical_thermodynamics), or statistical mechanics, concerns itself with [statistical](https://en.wikipedia.org/wiki/Statistics) predictions of the collective motion of particles from their microscopic behavior. In 1909, [Constantin Carathéodory](https://en.wikipedia.org/wiki/Constantin_Carath%C3%A9odory) presented a purely mathematical approach in an [axiomatic](https://en.wikipedia.org/wiki/Axiomatic) formulation, a description often referred to as *geometrical thermodynamics*.



Introduction

A description of any thermodynamic system employs the four [laws of thermodynamics](https://en.wikipedia.org/wiki/Laws_of_thermodynamics) that form an axiomatic basis. The first law specifies that energy can be exchanged between physical systems as [heat](https://en.wikipedia.org/wiki/Heat) and [work](https://en.wikipedia.org/wiki/Mechanical_work).[[12]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-12) The second law defines the existence of a quantity called [entropy](https://en.wikipedia.org/wiki/Entropy), that describes the direction, thermodynamically, that a system can evolve and quantifies the state of order of a system and that can be used to quantify the useful work that can be extracted from the system.[[13]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-13)

In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of the thermodynamic [*system*](https://en.wikipedia.org/wiki/System_%28thermodynamics%29) and its [*surroundings*](https://en.wikipedia.org/wiki/Surroundings_%28thermodynamics%29). A system is composed of particles, whose average motions define its properties, and those properties are in turn related to one another through [equations of state](https://en.wikipedia.org/wiki/Equation_of_state). Properties can be combined to express [internal energy](https://en.wikipedia.org/wiki/Internal_energy) and [thermodynamic potentials](https://en.wikipedia.org/wiki/Thermodynamic_potential), which are useful for determining conditions for [equilibrium](https://en.wikipedia.org/wiki/Dynamic_equilibrium) and [spontaneous processes](https://en.wikipedia.org/wiki/Spontaneous_process).

With these tools, thermodynamics can be used to describe how systems respond to changes in their environment. This can be applied to a wide variety of topics in [science](https://en.wikipedia.org/wiki/Science) and [engineering](https://en.wikipedia.org/wiki/Engineering), such as [engines](https://en.wikipedia.org/wiki/Engine), [phase transitions](https://en.wikipedia.org/wiki/Phase_transition), [chemical reactions](https://en.wikipedia.org/wiki/Chemical_reaction), [transport phenomena](https://en.wikipedia.org/wiki/Transport_phenomena), and even [black holes](https://en.wikipedia.org/wiki/Black_hole). The results of thermodynamics are essential for other fields of [physics](https://en.wikipedia.org/wiki/Physics) and for [chemistry](https://en.wikipedia.org/wiki/Chemistry), [chemical engineering](https://en.wikipedia.org/wiki/Chemical_engineering), [corrosion engineering](https://en.wikipedia.org/wiki/Corrosion_engineering), [aerospace engineering](https://en.wikipedia.org/wiki/Aerospace_engineering), [mechanical engineering](https://en.wikipedia.org/wiki/Mechanical_engineering), [cell biology](https://en.wikipedia.org/wiki/Cell_biology), [biomedical engineering](https://en.wikipedia.org/wiki/Biomedical_engineering), [materials science](https://en.wikipedia.org/wiki/Materials_science), and [economics](https://en.wikipedia.org/wiki/Economics), to name a few.[[14]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-14)[[15]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-15)

This article is focused mainly on classical thermodynamics which primarily studies systems in [thermodynamic equilibrium](https://en.wikipedia.org/wiki/Thermodynamic_equilibrium). [Non-equilibrium thermodynamics](https://en.wikipedia.org/wiki/Non-equilibrium_thermodynamics) is often treated as an extension of the classical treatment, but statistical mechanics has brought many advances to that field.



The [thermodynamicists](https://en.wikipedia.org/wiki/Thermodynamicist%22%20%5Co%20%22Thermodynamicist) representative of the original eight founding schools of thermodynamics. The schools with the most-lasting effect in founding the modern versions of thermodynamics are the Berlin school, particularly as established in [Rudolf Clausius](https://en.wikipedia.org/wiki/Rudolf_Clausius)’s 1865 textbook *The Mechanical Theory of Heat*, the Vienna school, with the [statistical mechanics](https://en.wikipedia.org/wiki/Statistical_mechanics) of [Ludwig Boltzmann](https://en.wikipedia.org/wiki/Ludwig_Boltzmann), and the Gibbsian school at Yale University, American engineer [Willard Gibbs](https://en.wikipedia.org/wiki/Willard_Gibbs)' 1876 [*On the Equilibrium of Heterogeneous Substances*](https://en.wikipedia.org/wiki/On_the_Equilibrium_of_Heterogeneous_Substances) launching [chemical thermodynamics](https://en.wikipedia.org/wiki/Chemical_thermodynamics).[[16]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-autogenerated1-16)

History

The [history of thermodynamics](https://en.wikipedia.org/wiki/History_of_thermodynamics) as a scientific discipline generally begins with [Otto von Guericke](https://en.wikipedia.org/wiki/Otto_von_Guericke) who, in 1650, built and designed the world's first [vacuum pump](https://en.wikipedia.org/wiki/Vacuum_pump) and demonstrated a [vacuum](https://en.wikipedia.org/wiki/Vacuum) using his [Magdeburg hemispheres](https://en.wikipedia.org/wiki/Magdeburg_hemispheres). Guericke was driven to make a vacuum in order to disprove [Aristotle](https://en.wikipedia.org/wiki/Aristotle)'s long-held supposition that 'nature abhors a vacuum'. Shortly after Guericke, the English physicist and chemist [Robert Boyle](https://en.wikipedia.org/wiki/Robert_Boyle) had learned of Guericke's designs and, in 1656, in coordination with English scientist [Robert Hooke](https://en.wikipedia.org/wiki/Robert_Hooke), built an air pump.[[17]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-17) Using this pump, Boyle and Hooke noticed a correlation between [pressure](https://en.wikipedia.org/wiki/Pressure), [temperature](https://en.wikipedia.org/wiki/Temperature), and [volume](https://en.wikipedia.org/wiki/Volume_%28thermodynamics%29). In time, [Boyle's Law](https://en.wikipedia.org/wiki/Boyle%27s_Law) was formulated, which states that pressure and volume are [inversely proportional](https://en.wikipedia.org/wiki/Inverse_proportion). Then, in 1679, based on these concepts, an associate of Boyle's named [Denis Papin](https://en.wikipedia.org/wiki/Denis_Papin) built a [steam digester](https://en.wikipedia.org/wiki/Steam_digester), which was a closed vessel with a tightly fitting lid that confined steam until a high pressure was generated.

Later designs implemented a steam release valve that kept the machine from exploding. By watching the valve rhythmically move up and down, Papin conceived of the idea of a [piston](https://en.wikipedia.org/wiki/Piston) and a cylinder engine. He did not, however, follow through with his design. Nevertheless, in 1697, based on Papin's designs, engineer [Thomas Savery](https://en.wikipedia.org/wiki/Thomas_Savery) built the first engine, followed by [Thomas Newcomen](https://en.wikipedia.org/wiki/Thomas_Newcomen) in 1712. Although these early engines were crude and inefficient, they attracted the attention of the leading scientists of the time.

The fundamental concepts of [heat capacity](https://en.wikipedia.org/wiki/Heat_capacity) and [latent heat](https://en.wikipedia.org/wiki/Latent_heat), which were necessary for the development of thermodynamics, were developed by Professor [Joseph Black](https://en.wikipedia.org/wiki/Joseph_Black) at the University of Glasgow, where [James Watt](https://en.wikipedia.org/wiki/James_Watt) was employed as an instrument maker. Black and Watt performed experiments together, but it was Watt who conceived the idea of the [external condenser](https://en.wikipedia.org/wiki/Watt_steam_engine#Separate_condenser) which resulted in a large increase in [steam engine](https://en.wikipedia.org/wiki/Steam_engine) efficiency.[[18]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-18) Drawing on all the previous work led [Sadi Carnot](https://en.wikipedia.org/wiki/Nicolas_L%C3%A9onard_Sadi_Carnot%22%20%5Co%20%22Nicolas%20L%C3%A9onard%20Sadi%20Carnot), the "father of thermodynamics", to publish [*Reflections on the Motive Power of Fire*](https://en.wikipedia.org/wiki/Reflections_on_the_Motive_Power_of_Fire) (1824), a discourse on heat, power, energy and engine efficiency. The book outlined the basic energetic relations between the [Carnot engine](https://en.wikipedia.org/wiki/Carnot_engine), the [Carnot cycle](https://en.wikipedia.org/wiki/Carnot_cycle), and **motive power**. It marked the start of thermodynamics as a modern science.[[10]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Perrot-10)

The first thermodynamic textbook was written in 1859 by [William Rankine](https://en.wikipedia.org/wiki/William_John_Macquorn_Rankine), originally trained as a physicist and a civil and mechanical engineering professor at the [University of Glasgow](https://en.wikipedia.org/wiki/University_of_Glasgow).[[19]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-19) The first and second laws of thermodynamics emerged simultaneously in the 1850s, primarily out of the works of [William Rankine](https://en.wikipedia.org/wiki/William_John_Macquorn_Rankine), [Rudolf Clausius](https://en.wikipedia.org/wiki/Rudolf_Clausius), and [William Thomson](https://en.wikipedia.org/wiki/William_Thomson%2C_1st_Baron_Kelvin) (Lord Kelvin).[[20]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-NKS_note_b-20)

The foundations of statistical thermodynamics were set out by physicists such as [James Clerk Maxwell](https://en.wikipedia.org/wiki/James_Clerk_Maxwell), [Ludwig Boltzmann](https://en.wikipedia.org/wiki/Ludwig_Boltzmann), [Max Planck](https://en.wikipedia.org/wiki/Max_Planck), [Rudolf Clausius](https://en.wikipedia.org/wiki/Rudolf_Clausius) and [J. Willard Gibbs](https://en.wikipedia.org/wiki/Josiah_Willard_Gibbs).

During the years 1873–76 the American mathematical physicist [Josiah Willard Gibbs](https://en.wikipedia.org/wiki/Josiah_Willard_Gibbs) published a series of three papers, the most famous being [*On the Equilibrium of Heterogeneous Substances*](https://en.wikipedia.org/wiki/On_the_Equilibrium_of_Heterogeneous_Substances),[[3]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-Gibbs_1876-3) in which he showed how [thermodynamic processes](https://en.wikipedia.org/wiki/Thermodynamic_processes), including [chemical reactions](https://en.wikipedia.org/wiki/Chemical_reaction), could be graphically analyzed, by studying the [energy](https://en.wikipedia.org/wiki/Energy), [entropy](https://en.wikipedia.org/wiki/Entropy), [volume](https://en.wikipedia.org/wiki/Volume_%28thermodynamics%29), [temperature](https://en.wikipedia.org/wiki/Temperature) and [pressure](https://en.wikipedia.org/wiki/Pressure) of the [thermodynamic system](https://en.wikipedia.org/wiki/Thermodynamic_system) in such a manner, one can determine if a process would occur spontaneously. Also [Pierre Duhem](https://en.wikipedia.org/wiki/Pierre_Duhem) in the 19th century wrote about chemical thermodynamics. During the early 20th century, chemists such as [Gilbert N. Lewis](https://en.wikipedia.org/wiki/Gilbert_N._Lewis), [Merle Randall](https://en.wikipedia.org/wiki/Merle_Randall), and [E. A. Guggenheim](https://en.wikipedia.org/wiki/E._A._Guggenheim) applied the mathematical methods of Gibbs to the analysis of chemical processes.

Etymology

The etymology of *thermodynamics* has an intricate history. It was first spelled in a hyphenated form as an adjective (*thermo-dynamic*) and from 1854 to 1868 as the noun *thermo-dynamics* to represent the science of generalized heat engines.

American [biophysicist](https://en.wikipedia.org/wiki/Biophysics) Donald Haynie claims that *thermodynamics* was coined in 1840 from the [Greek](https://en.wikipedia.org/wiki/Greek_language) root [θέρμη](https://en.wiktionary.org/wiki/%CE%B8%CE%AD%CF%81%CE%BC%CE%B7%22%20%5Co%20%22wikt%3A%CE%B8%CE%AD%CF%81%CE%BC%CE%B7) *therme,* meaning “heat”, and *dynamis,* meaning “power”

Pierre Perrot claims that the term *thermodynamics* was coined by [James Joule](https://en.wikipedia.org/wiki/James_Joule) in 1858 to designate the science of relations between heat and power, however, Joule never used that term, but used instead the term *perfect thermo-dynamic engine* in reference to Thomson's 1849 phraseology.

By 1858, *thermo-dynamics*, as a functional term, was used in [William Thomson](https://en.wikipedia.org/wiki/William_Thomson%2C_1st_Baron_Kelvin)'s paper "An Account of Carnot's Theory of the Motive Power of Heat."

Branches of thermodynamics

The study of thermodynamical systems has developed into several related branches, each using a different fundamental model as a theoretical or experimental basis, or applying the principles to varying types of systems.

**Classical thermodynamics**

Classical thermodynamics is the description of the states of thermodynamic systems at near-equilibrium, that uses macroscopic, measurable properties. It is used to model exchanges of energy, work and heat based on the [laws of thermodynamics](https://en.wikipedia.org/wiki/Laws_of_thermodynamics). The qualifier *classical* reflects the fact that it represents the first level of understanding of the subject as it developed in the 19th century and describes the changes of a system in terms of macroscopic empirical (large scale, and measurable) parameters. A microscopic interpretation of these concepts was later provided by the development of *statistical mechanics*.

**Statistical mechanics**

[Statistical mechanics](https://en.wikipedia.org/wiki/Statistical_mechanics), also called statistical thermodynamics, emerged with the development of atomic and molecular theories in the late 19th century and early 20th century, and supplemented classical thermodynamics with an interpretation of the microscopic interactions between individual particles or quantum-mechanical states. This field relates the microscopic properties of individual atoms and molecules to the macroscopic, bulk properties of materials that can be observed on the human scale, thereby explaining classical thermodynamics as a natural result of statistics, classical mechanics, and [quantum theory](https://en.wikipedia.org/wiki/Quantum_mechanics) at the microscopic level.

**Chemical thermodynamics**[[edit](https://en.wikipedia.org/w/index.php?title=Thermodynamics&action=edit&section=7" \o "Edit section: Chemical thermodynamics)]

[Chemical thermodynamics](https://en.wikipedia.org/wiki/Chemical_thermodynamics) is the study of the interrelation of [energy](https://en.wikipedia.org/wiki/Energy) with [chemical reactions](https://en.wikipedia.org/wiki/Chemical_reactions) or with a physical change of [state](https://en.wikipedia.org/wiki/Thermodynamic_state) within the confines of the [laws of thermodynamics](https://en.wikipedia.org/wiki/Laws_of_thermodynamics).

**Equilibrium thermodynamics**

[Equilibrium thermodynamics](https://en.wikipedia.org/wiki/Equilibrium_thermodynamics) is the study of transfers of matter and energy in systems or bodies that, by agencies in their surroundings, can be driven from one state of thermodynamic equilibrium to another. The term 'thermodynamic equilibrium' indicates a state of balance, in which all macroscopic flows are zero; in the case of the simplest systems or bodies, their intensive properties are homogeneous, and their pressures are perpendicular to their boundaries. In an equilibrium state there are no unbalanced potentials, or driving forces, between macroscopically distinct parts of the system. A central aim in equilibrium thermodynamics is: given a system in a well-defined initial equilibrium state, and given its surroundings, and given its constitutive walls, to calculate what will be the final equilibrium state of the system after a specified thermodynamic operation has changed its walls or surroundings.

[Non-equilibrium thermodynamics](https://en.wikipedia.org/wiki/Non-equilibrium_thermodynamics) is a branch of thermodynamics that deals with systems that are not in [thermodynamic equilibrium](https://en.wikipedia.org/wiki/Thermodynamic_equilibrium). Most systems found in nature are not in thermodynamic equilibrium because they are not in stationary states, and are continuously and discontinuously subject to flux of matter and energy to and from other systems. The thermodynamic study of non-equilibrium systems requires more general concepts than are dealt with by equilibrium thermodynamics. Many natural systems still today remain beyond the scope of currently known macroscopic thermodynamic methods.

Laws of thermodynamics

*Main article:*[*Laws of thermodynamics*](https://en.wikipedia.org/wiki/Laws_of_thermodynamics)

Thermodynamics is principally based on a set of four laws which are universally valid when applied to systems that fall within the constraints implied by each. In the various theoretical descriptions of thermodynamics these laws may be expressed in seemingly differing forms, but the most prominent formulations are the following.

**Zeroth Law**

The [zeroth law of thermodynamics](https://en.wikipedia.org/wiki/Zeroth_law_of_thermodynamics) states: *If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other.*

This statement implies that thermal equilibrium is an [equivalence relation](https://en.wikipedia.org/wiki/Equivalence_relation) on the set of [thermodynamic systems](https://en.wikipedia.org/wiki/Thermodynamic_system) under consideration. Systems are said to be in equilibrium if the small, random exchanges between them (e.g. [Brownian motion](https://en.wikipedia.org/wiki/Brownian_motion)) do not lead to a net change in energy. This law is tacitly assumed in every measurement of temperature. Thus, if one seeks to decide whether two bodies are at the same [temperature](https://en.wikipedia.org/wiki/Temperature), it is not necessary to bring them into contact and measure any changes of their observable properties in time.[[25]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-25) The law provides an empirical definition of temperature, and justification for the construction of practical thermometers.

The zeroth law was not initially recognized as a separate law of thermodynamics, as its basis in thermodynamical equilibrium was implied in the other laws. The first, second, and third laws had been explicitly stated already, and found common acceptance in the physics community before the importance of the zeroth law for the definition of temperature was realized. As it was impractical to renumber the other laws, it was named the *zeroth law*.

**First Law**

The [first law of thermodynamics](https://en.wikipedia.org/wiki/First_law_of_thermodynamics) states: *In a process without transfer of matter, the change in*[*internal energy*](https://en.wikipedia.org/wiki/Internal_energy)*,* Δ*U, of a*[*thermodynamic system*](https://en.wikipedia.org/wiki/Thermodynamic_system)*is equal to the energy gained as heat,* *Q, less the thermodynamic work,* *W, done by the system on its surroundings*

{\displaystyle \Delta U=Q-W}.

For processes that include transfer of matter, a further statement is needed: *With due account of the respective fiducial reference states of the systems, when two systems, which may be of different chemical compositions, initially separated only by an impermeable wall, and otherwise isolated, are combined into a new system by the thermodynamic operation of removal of the wall, then*

{\displaystyle U\_{0}=U\_{1}+U\_{2}},

*where* *U*0 *denotes the internal energy of the combined system, and* *U*1 *and* *U*2 *denote the internal energies of the respective separated systems.*

Adapted for thermodynamics, this law is an expression of the principle of [conservation of energy](https://en.wikipedia.org/wiki/Conservation_of_energy), which states that energy can be transformed (changed from one form to another), but cannot be created or destroyed.[[27]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-28)

Internal energy is a principal property of the [thermodynamic state](https://en.wikipedia.org/wiki/Thermodynamic_state), while heat and work are modes of energy transfer by which a process may change this state. A change of internal energy of a system may be achieved by any combination of heat added or removed and work performed on or by the system. As a [function of state](https://en.wikipedia.org/wiki/State_function), the internal energy does not depend on the manner, or on the path through intermediate steps, by which the system arrived at its state.

**Second Law**

The [second law of thermodynamics](https://en.wikipedia.org/wiki/Second_law_of_thermodynamics) states: *Heat cannot spontaneously flow from a colder location to a hotter location.*[[20]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-NKS_note_b-20)

This law is an expression of the universal principle of decay observable in nature. The second law is an observation of the fact that over time, differences in temperature, pressure, and chemical potential tend to even out in a physical system that is isolated from the outside world. [Entropy](https://en.wikipedia.org/wiki/Entropy) is a measure of how much this process has progressed. The entropy of an isolated system which is not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium. However, principles guiding systems that are far from equilibrium are still debatable. One of such principles is the [maximum entropy production](https://en.wikipedia.org/wiki/Entropy_production) principle.[[28]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-29)[[29]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-30) It states that non-equilibrium systems behave such a way as to maximize its entropy production.[[30]](https://en.wikipedia.org/wiki/Thermodynamics#cite_note-31)

In classical thermodynamics, the second law is a basic postulate applicable to any system involving heat energy transfer; in statistical thermodynamics, the second law is a consequence of the assumed randomness of molecular chaos. There are many versions of the second law, but they all have the same effect, which is to explain the phenomenon of [irreversibility](https://en.wikipedia.org/wiki/Irreversibility) in nature.

**Third Law**

The [third law of thermodynamics](https://en.wikipedia.org/wiki/Third_law_of_thermodynamics) states: *As the temperature of a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.*

This law of thermodynamics is a statistical law of nature regarding entropy and the impossibility of reaching [absolute zero](https://en.wikipedia.org/wiki/Absolute_zero) of temperature. This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is the absolute entropy. Alternate definitions include "the entropy of all systems and of all states of a system is smallest at absolute zero," or equivalently "it is impossible to reach the absolute zero of temperature by any finite number of processes".

Absolute zero, at which all activity would stop if it were possible to achieve, is −273.15 °C (degrees Celsius), or −459.67 °F (degrees Fahrenheit), or 0 K (kelvin), or 0° R (degrees [Rankine](https://en.wikipedia.org/wiki/Rankine_scale)).

System models[[edit](https://en.wikipedia.org/w/index.php?title=Thermodynamics&action=edit&section=14" \o "Edit section: System models)]



A diagram of a generic thermodynamic system

An important concept in thermodynamics is the [thermodynamic system](https://en.wikipedia.org/wiki/Thermodynamic_system), which is a precisely defined region of the universe under study. Everything in the universe except the system is called the [*surroundings*](https://en.wikipedia.org/wiki/Environment_%28systems%29). A system is separated from the remainder of the universe by a [*boundary*](https://en.wikipedia.org/wiki/Boundary_%28thermodynamic%29) which may be a physical boundary or notional, but which by convention defines a finite volume. Exchanges of [work](https://en.wikipedia.org/wiki/Work_%28thermodynamics%29), [heat](https://en.wikipedia.org/wiki/Heat), or [matter](https://en.wikipedia.org/wiki/Matter) between the system and the surroundings take place across this boundary.

In practice, the boundary of a system is simply an imaginary dotted line drawn around a volume within which is going to be a change in the [internal energy](https://en.wikipedia.org/wiki/Internal_energy) of that volume. Anything that passes across the boundary that effects a change in the internal energy of the system needs to be accounted for in the energy balance equation. The volume can be the region surrounding a single atom resonating energy, such as [Max Planck](https://en.wikipedia.org/wiki/Max_Planck) defined in 1900; it can be a body of steam or air in a [steam engine](https://en.wikipedia.org/wiki/Steam_engine), such as [Sadi Carnot](https://en.wikipedia.org/wiki/Nicolas_L%C3%A9onard_Sadi_Carnot%22%20%5Co%20%22Nicolas%20L%C3%A9onard%20Sadi%20Carnot) defined in 1824; it can be the body of a [tropical cyclone](https://en.wikipedia.org/wiki/Tropical_cyclone), such as [Kerry Emanuel](https://en.wikipedia.org/wiki/Kerry_Emanuel) theorized in 1986 in the field of [atmospheric thermodynamics](https://en.wikipedia.org/wiki/Atmospheric_thermodynamics); it could also be just one [nuclide](https://en.wikipedia.org/wiki/Nuclide) (i.e. a system of [quarks](https://en.wikipedia.org/wiki/Quark)) as hypothesized in [quantum thermodynamics](https://en.wikipedia.org/wiki/Quantum_thermodynamics), or the [event horizon](https://en.wikipedia.org/wiki/Event_horizon) of a [black hole](https://en.wikipedia.org/wiki/Black_hole_thermodynamics).

Boundaries are of four types: fixed, movable, real, and imaginary. For example, in an engine, a fixed boundary means the piston is locked at its position, within which a constant volume process might occur. If the piston is allowed to move that boundary is movable while the cylinder and cylinder head boundaries are fixed. For closed systems, boundaries are real while for open systems boundaries are often imaginary. In the case of a jet engine, a fixed imaginary boundary might be assumed at the intake of the engine, fixed boundaries along the surface of the case and a second fixed imaginary boundary across the exhaust nozzle.

Generally, thermodynamics distinguishes three classes of systems, defined in terms of what is allowed to cross their boundaries:

|  |
| --- |
| **Interactions of thermodynamic systems** |
| **Type of system** | [**Mass flow**](https://en.wikipedia.org/wiki/Mass_flow) | [**Work**](https://en.wikipedia.org/wiki/Work_%28thermodynamics%29) | [**Heat**](https://en.wikipedia.org/wiki/Heat) |
| [Open](https://en.wikipedia.org/wiki/Thermodynamic_system#Open_system) | Green tick | Green tick | Green tick |
| [Closed](https://en.wikipedia.org/wiki/Thermodynamic_system#Closed_system) | Red X | Green tick | Green tick |
| [Thermally isolated](https://en.wikipedia.org/wiki/Thermally_isolated_system) | Red X | Green tick | Red X |
| [Mechanically isolated](https://en.wikipedia.org/wiki/Mechanically_isolated_system) | Red X | Red X | Green tick |
| [Isolated](https://en.wikipedia.org/wiki/Isolated_system) | Red X | Red X | Red X |

As time passes in an isolated system, internal differences of pressures, densities, and temperatures tend to even out. A system in which all equalizing processes have gone to completion is said to be in a [state](https://en.wikipedia.org/wiki/State_%28thermodynamic%29) of [thermodynamic equilibrium](https://en.wikipedia.org/wiki/Thermodynamic_equilibrium).

Once in thermodynamic equilibrium, a system's properties are, by definition, unchanging in time. Systems in equilibrium are much simpler and easier to understand than are systems which are not in equilibrium. Often, when analysing a dynamic thermodynamic process, the simplifying assumption is made that each intermediate state in the process is at equilibrium, producing thermodynamic processes which develop so slowly as to allow each intermediate step to be an equilibrium state and are said to be [reversible processes](https://en.wikipedia.org/wiki/Reversible_process_%28thermodynamics%29).

States and processes[[edit](https://en.wikipedia.org/w/index.php?title=Thermodynamics&action=edit&section=15" \o "Edit section: States and processes)]

When a system is at equilibrium under a given set of conditions, it is said to be in a definite [thermodynamic state](https://en.wikipedia.org/wiki/Thermodynamic_state). The state of the system can be described by a number of [state quantities](https://en.wikipedia.org/wiki/State_function) that do not depend on the process by which the system arrived at its state. They are called [intensive variables](https://en.wikipedia.org/wiki/Intensive_variable) or [extensive variables](https://en.wikipedia.org/wiki/Extensive_variable) according to how they change when the size of the system changes. The properties of the system can be described by an [equation of state](https://en.wikipedia.org/wiki/Equation_of_state) which specifies the relationship between these variables. State may be thought of as the instantaneous quantitative description of a system with a set number of variables held constant.

A [thermodynamic process](https://en.wikipedia.org/wiki/Thermodynamic_process) may be defined as the energetic evolution of a thermodynamic system proceeding from an initial state to a final state. It can be described by [process quantities](https://en.wikipedia.org/wiki/Process_function). Typically, each thermodynamic process is distinguished from other processes in energetic character according to what parameters, such as temperature, pressure, or volume, etc., are held fixed; Furthermore, it is useful to group these processes into pairs, in which each variable held constant is one member of a [conjugate](https://en.wikipedia.org/wiki/Conjugate_variables_%28thermodynamics%29) pair.

Several commonly studied thermodynamic processes are:

* [Adiabatic process](https://en.wikipedia.org/wiki/Adiabatic_process): occurs without loss or gain of energy by [heat](https://en.wikipedia.org/wiki/Heat)
* [Isenthalpic process](https://en.wikipedia.org/wiki/Isenthalpic_process): occurs at a constant [enthalpy](https://en.wikipedia.org/wiki/Enthalpy)
* [Isentropic process](https://en.wikipedia.org/wiki/Isentropic_process): a reversible adiabatic process, occurs at a constant [entropy](https://en.wikipedia.org/wiki/Entropy)
* [Isobaric process](https://en.wikipedia.org/wiki/Isobaric_process): occurs at constant [pressure](https://en.wikipedia.org/wiki/Pressure)
* [Isochoric process](https://en.wikipedia.org/wiki/Isochoric_process): occurs at constant [volume](https://en.wikipedia.org/wiki/Volume_%28thermodynamics%29) (also called isometric/isovolumetric)
* [Isothermal process](https://en.wikipedia.org/wiki/Isothermal_process): occurs at a constant [temperature](https://en.wikipedia.org/wiki/Temperature)
* [Steady state process](https://en.wikipedia.org/wiki/Steady_state): occurs without a change in the [internal energy](https://en.wikipedia.org/wiki/Internal_energy)

Instrumentation[[edit](https://en.wikipedia.org/w/index.php?title=Thermodynamics&action=edit&section=16" \o "Edit section: Instrumentation)]

There are two types of [thermodynamic instruments](https://en.wikipedia.org/wiki/Thermodynamic_instruments), the **meter** and the **reservoir**. A thermodynamic meter is any device which measures any parameter of a [thermodynamic system](https://en.wikipedia.org/wiki/Thermodynamic_system). In some cases, the thermodynamic parameter is actually defined in terms of an idealized measuring instrument. For example, the [zeroth law](https://en.wikipedia.org/wiki/Zeroth_law_of_thermodynamics) states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. This principle, as noted by [James Maxwell](https://en.wikipedia.org/wiki/James_Clerk_Maxwell) in 1872, asserts that it is possible to measure temperature. An idealized [thermometer](https://en.wikipedia.org/wiki/Thermometer) is a sample of an ideal gas at constant pressure. From the [ideal gas law](https://en.wikipedia.org/wiki/Ideal_gas_law) *pV=nRT*, the volume of such a sample can be used as an indicator of temperature; in this manner it defines temperature. Although pressure is defined mechanically, a pressure-measuring device, called a [barometer](https://en.wikipedia.org/wiki/Barometer) may also be constructed from a sample of an ideal gas held at a constant temperature. A [calorimeter](https://en.wikipedia.org/wiki/Calorimeter) is a device which is used to measure and define the internal energy of a system.

A thermodynamic reservoir is a system which is so large that its state parameters are not appreciably altered when it is brought into contact with the system of interest. When the reservoir is brought into contact with the system, the system is brought into equilibrium with the reservoir. For example, a pressure reservoir is a system at a particular pressure, which imposes that pressure upon the system to which it is mechanically connected. The Earth's atmosphere is often used as a pressure reservoir. If ocean water is used to cool a power plant, the ocean is often a temperature reservoir in the analysis of the power plant cycle.

Conjugate variables

*Main article:*[*Conjugate variables*](https://en.wikipedia.org/wiki/Conjugate_variables_%28thermodynamics%29)

The central concept of thermodynamics is that of [energy](https://en.wikipedia.org/wiki/Energy), the ability to do [work](https://en.wikipedia.org/wiki/Work_%28thermodynamics%29). By the [First Law](https://en.wikipedia.org/wiki/First_law_of_thermodynamics), the total energy of a system and its surroundings is conserved. Energy may be transferred into a system by heating, compression, or addition of matter, and extracted from a system by cooling, expansion, or extraction of matter. In [mechanics](https://en.wikipedia.org/wiki/Mechanics), for example, energy transfer equals the product of the force applied to a body and the resulting displacement.

[Conjugate variables](https://en.wikipedia.org/wiki/Conjugate_variables_%28thermodynamics%29) are pairs of thermodynamic concepts, with the first being akin to a "force" applied to some [thermodynamic system](https://en.wikipedia.org/wiki/Thermodynamic_system), the second being akin to the resulting "displacement," and the product of the two equaling the amount of energy transferred. The common conjugate variables are:

* [Pressure](https://en.wikipedia.org/wiki/Pressure)-[volume](https://en.wikipedia.org/wiki/Volume_%28thermodynamics%29) (the [mechanical](https://en.wikipedia.org/wiki/Mechanics) parameters);
* [Temperature](https://en.wikipedia.org/wiki/Temperature)-[entropy](https://en.wikipedia.org/wiki/Entropy) (thermal parameters);
* [Chemical potential](https://en.wikipedia.org/wiki/Chemical_potential)-[particle number](https://en.wikipedia.org/wiki/Particle_number) (material parameters).

Potentials

[Thermodynamic potentials](https://en.wikipedia.org/wiki/Thermodynamic_potential) are different quantitative measures of the stored energy in a system. Potentials are used to measure the energy changes in systems as they evolve from an initial state to a final state. The potential used depends on the constraints of the system, such as constant temperature or pressure. For example, the Helmholtz and Gibbs energies are the energies available in a system to do useful work when the temperature and volume or the pressure and temperature are fixed, respectively.