Laws of Thermodynamics

The four laws of Thermodynamics summarize the most important facts of thermodynamics. They define fundamental physical quantities such as temperature, energy and entropy, in order to describe thermodynamic systems. They also describe the transfer of energy as heat and work in thermodynamic processes.

♦ The Zeroth law of thermodynamics recognizes that if two systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other, thus supporting the notion of temperature and heat.

♦ The first law of thermodynamics distinguishes between two kinds of physical process, namely energy transfer as work and energy transfer as heat.

♦ The second law of thermodynamics distinguishes between reversible and irreversible physical processes.

♦ The third law of thermodynamics concerns the entropy of a perfect crystal at absolute zero temperature, and implies that it is impossible to cool a system to exactly absolute zero, or equivalently that perpetual motion machines of the third kind are impossible.

Zeroth Law:

If system A and system B are individually in thermal equilibrium with system C, then system A is in thermal equilibrium with system B - i.e. If two systems are in thermal equilibrium with a third, they are in thermal equilibrium with each other.

First Law:

It may be expressed by several forms of the fundamental thermo-dynamic relation.

Increase in internal energy of a system = heat supplied to the system + work done on the system

For a thermodynamic cycle, the net heat supplied to the system equals the network done by the system.

These statements entail that the internal energy obeys the principle of conservation of energy i.e.

“Energy can be neither created nor destroyed. It can only change forms. In any process in an isolated system, the total energy remains the same.”

Second Law:

The second law of thermodynamics assets the existence of a quantity called the entropy of a system and it state that

When two isolated systems in separate but nearby regions of space, each in thermodynamic equilibrium in itself (but not necessarily in equilibrium with each other at first) are at sometime flowed to interact, breaking the isolation that separates the two systems, allowing them to exchange matter or energy, they will eventually reach mutual thermodynamic equilibrium. The sum of the entropies of the initial, isolated systems is less than or equal to the entropy of the final combination of exchanging systems. In the process of reaching a new thermodynamic equilibrium, total entropy has increased, or at least has not decreased.

The second law refers to a wide variety of processes, J reversible and irreversible. Its main import is to tell about irreversibility.

Third Law:

"The entropy of a perfect crystal at absolute zero is exactly equal to zero".

The third law is also stated in a form that includes non-crystal systems, such as glasses:

As temperature approaches absolute zero, the entropy of a system approaches a minimum.

The minimum, not necessarily zero, is called the residual entropy of the system.

Thermodynamic System:

A thermodynamic system is a precisely defined macroscopic region of the universe, often called a physical system, that is studied using the principles of thermodynamics.

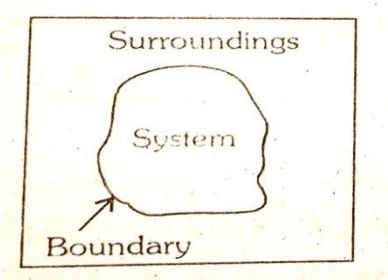
All space in the universe outside the thermodynamic system is known as the surroundings, the environment, or a reservoir. A system is separated from its surroundings by a boundary which may be notional or real, but which by convention delimits a finite volume.

Exchanges of work, heat or matter between the systems and the surroundings may take place across this boundary. Thermodynamic systems are often classified by specifying the nature of the exchanges that are allowed to occur across its boundary.

A thermodynamic system is characterized and defined by a set of thermodynamic parameters associated with the system. The parameters are experimentally measurable macroscopic properties such as volume, pressure, temperature, electric field and others.

The set of thermodynamic parameters necessary to uniquely define a system is called the thermodynamic state of a system. The state of a system is expressed as a functional relationship, the equation of state, between its parameters. A system is in thermodynamic equilibrium when the state of the system does not change with time.

In 1824, Sadi Carnot described a thermodynamic system as the working substance under study.



As thermodynamics is fundamentally concerned with the flow and balance of energy and matter, systems arc distinguished depending on the kinds of interaction they undergo and the types of energy they exchange with the surrounded environment.

Isolated systems are completely isolated from environment. They do not exchange heat, work or with their environment. An example is a complied rigid container, such as a completely insulated gas cylinder.

Closed systems are able to exchange energy (heat and work) but nor matter with their environment. A greenhouse is an example of a closed system exchanging heat but not work with its environment.

Whether a system exchanges heat, work or both is usually thought of as a property of its boundary.

Open systems may exchange any form of energy as well as matter with their environment. A boundary allowing matter exchange is called permeable. The ocean would oc an example of an open system.

Interactions of thermodynamics systems.

Type of System	Mass flow	Work	Heat
Open	✓	✓	✓
Closed	×	✓	✓
Isolated	×	×	×

In practice, a system can never be absolutely isolated from its environment, because there is always atleast some slight coupling such as gravitational attraction. In analyzing a system in steady state, the energy into the system is equal to the energy leaving the system.

Boundary:

A system boundary is a real or imaginary two- dimensional closed surface that encloses or demarcates the volume or region that a thermodynamic system occupies, across which quantities such as heat, mass or work can flow.

In short, a thermodynamic boundary is a geometry division between a system and its surroundings

Boundaries can also be fixed (e.g. a constant volume reactor) or moveable (e.g. a piston). For example, in an engine, a fixed boundary means the piston is locked a; its position, as such a constant volume process occurs

In that same engine, a moveable boundary allows the piston to move in and out. Boundaries may be real or imaginary. For closed systems, boundaries are real while for open system boundaries are often imaginary. For theoretical purposes, a boundary may be declared to be adiabatic, isothermal, diathermias, insulating, permeable or semi permeable, but actual. Physical materials that provide such idealized properties are not always readily available.

Anything that passes across the boundary that effects a change in the internal energy needs to be accounted for in the energy balance equation.

Surroundings:

The system is the part of the universe being studied, white the surroundings is the remainder of the universe that lies outside the boundaries of the system. It is also known as the environment, and the reservoir. Depending on the type of system, it may interact with the system by exchanging mass, energy (including heat and work), momentum, electric charge or other conserved properties. The environment is ignored in analysis of the system, except in regards to these interactions.