Work in thermodynamic processes

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For thermodynamic work, appropriately chosen externally measured quantities are exactly matched by values of or contributions to changes in macroscopic internal state variables of the system, which always occur in conjugate pairs, for example pressure and volume[1] or magnetic flux density and magnetization.[3]

In the International System of Units (SI), work is measured in joules (symbol J). The rate at which work is performed is power, measured in joules per second, and denoted with the unit watt (W).

Work, i.e. "weight lifted through a height", was originally defined in 1824 by Sadi Carnot in his famous paper Reflections on the Motive Power of Fire, where he used the term motive power for work. Specifically, according to Carnot:

We use here motive power to express the useful effect that a motor is capable of producing. This effect can always be likened to the elevation of a weight to a certain height. It has, as we know, as a measure, the product of the weight multiplied by the height to which it is raised.

In 1845, the English physicist James Joule wrote a paper On the mechanical equivalent of heat for the British Association meeting in Cambridge.[6] In this paper, he reported his best-known experiment, in which the mechanical power released through the action of a "weight falling through a height" was used to turn a paddle-wheel in an insulated barrel of water.

A fundamental guiding principle of thermodynamics is the conservation of energy. The total energy of a system is the sum of its internal energy, of its potential energy as a whole system in an external force field, such as gravity, and of its kinetic energy as a whole system in motion. Thermodynamics has special concern with transfers of energy, from a body of matter, such as, for example a cylinder of steam, to the surroundings of the body, by mechanisms through which the body exerts macroscopic forces on its surroundings so as to lift a weight there; such mechanisms are the ones that are said to mediate thermodynamic work.

Energy can also be transferred to or from a system through transfer of matter. The possibility of such transfer defines the system as an open system, as opposed to a closed system. By definition, such transfer is neither as work nor as heat.

Changes in the potential energy of a body as a whole with respect to forces in its surroundings, and in the kinetic energy of the body moving as a whole with respect to its surroundings, are by definition excluded from the body''s cardinal energy (examples are internal energy and enthalpy).

In contrast, the conversion of heat into work in a heat engine can never exceed the Carnot efficiency, as a consequence of the second law of thermodynamics. Such energy conversion, through work done relatively rapidly, in a practical heat engine, by a thermodynamic system on its surroundings, cannot be idealized, not even nearly, as reversible.

Thermodynamic work done by a thermodynamic system on its surroundings is defined so as to comply with this principle. Historically, thermodynamics was about how a thermodynamic system could do work on its surroundings.

Work done on, and work done by, a thermodynamic system need to be distinguished, through consideration of their precise mechanisms. Work done on a thermodynamic system, by devices or systems in the surroundings, is performed by actions such as compression, and includes shaft work, stirring, and rubbing. Such work done by compression is thermodynamic work as here defined. But shaft work, stirring, and rubbing are not thermodynamic work as here defined, in that they do not change the volume of the system against its resisting pressure. Work without change of volume is known as isochoric work, for example when an agency, in the surroundings of the system, drives a frictional action on the surface or in the interior of the system.

The amount of energy transferred as work is measured through quantities defined externally to the system of interest, and thus belonging to its surroundings. In an important sign convention, preferred in chemistry, work that adds to the internal energy of the system is counted as positive. On the other hand, for historical reasons, an oft-encountered sign convention, preferred in physics, is to consider work done by the system on its surroundings as positive.