

# The second law of thermodynamics

matter and energy, and especially of temperature. It can be formulated in a variety of interesting and important ways.

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This statement of the law recognizes that in classical

The second law refers to a wide variety of processes, reversible and irreversible. All natural processes are irreversible. Reversible processes are a convenient theoretical fiction and do not occur in nature.

A prime example of irreversibility is in the transfer of heat by conduction or radiation. It was known long before the discovery of the notion of entropy that when two bodies initially of different temperatures come into thermal connection, then heat always flows from the hotter body to the colder one.

According to the second law of thermodynamics an element of heat transferred,  $\delta Q$ , is the product of the temperature ( $T$ ) with the increment ( $dS$ ) of the system's conjugate variable, its entropy ( $S$ ).

$$\delta Q = T dS .$$

a thermodynamic system may be arranged, commonly understood as a measure of disorder. According to the second law of thermodynamics the entropy of an isolated system never decreases; such a system will spontaneously evolve toward thermodynamic equilibrium, the configuration with maximum entropy. Systems that are not isolated may decrease in entropy, provided they increase the entropy of their environment by at least that same amount. Since entropy is a state function is a measure of the number of specific ways in which

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$$\Delta S = \int \frac{dQ_{\text{rev}}}{T}$$

decrease in entropy of the system.) The above definition is sometimes called the macroscopic definition of entropy because it can be used without regard to any microscopic description of the contents of a system. The concept of entropy has been found to be generally useful and has several other formulations. Entropy was discovered when it was noticed to be a quantity that behaves as a function of state, as a consequence of the second law of thermodynamics.

Entropy is an extensive property Entropy is an extensive property. It has the dimension Entropy is an extensive property. It has the dimension of energy Entropy is an extensive property. It has the dimension of energy divided by temperature Entropy is an extensive property. It has the dimension of energy divided by temperature, which has a unit of joules Entropy is an extensive property. It has the dimension of energy divided by temperature, which has a unit of joules per kelvin ( $\text{J K}^{-1}$ ) in the International System of Units (or  $\text{kg m}^2 \text{s}^{-2} \text{K}^{-1}$  in basic units). But the entropy of a pure substance is usually given as an intensive property in basic units). But the entropy of a pure substance is usually given

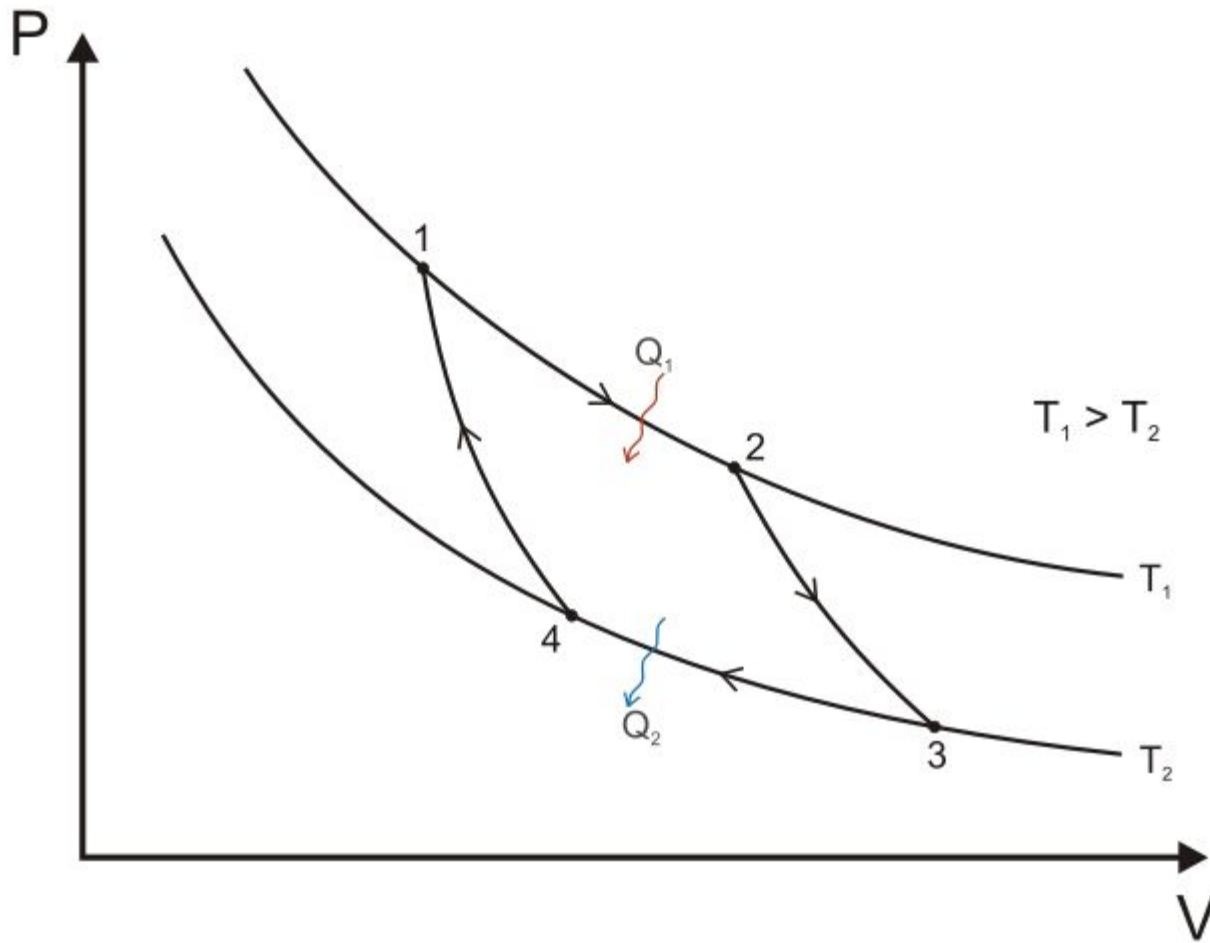
using either statistical mechanics) was defined later, using either statistical mechanics or the third law of thermodynamics.

In the modern microscopic interpretation of entropy in statistical mechanics, entropy is the amount of additional information needed to specify the exact physical state of a system, given its thermodynamic specification. Understanding the role of thermodynamic entropy in various processes requires an understanding of how and why that information changes as the system evolves from its initial to its final condition. It is often said that entropy is an expression of the disorder, or randomness. In the modern microscopic interpretation of entropy in statistical mechanics, entropy is the amount of additional information needed to specify the exact physical state of a system, given its thermodynamic specification. Understanding the role of thermodynamic entropy in various processes requires an understanding of how and why that information changes as the system evolves from its initial to its final condition. It is often said that entropy is an expression of the disorder, or randomness of a system, or of our lack of information about it. The second law is

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Every single thermodynamic system exists in a particular state. When a system is taken through a series of different states and finally returned to its initial state, a thermodynamic cycle is said to have occurred. In the process of going through this cycle, the system may perform work on its surroundings, thereby acting as a [heat engine](#)

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A Carnot cycle illustrated on a [PV diagram](#) to illustrate the work done.



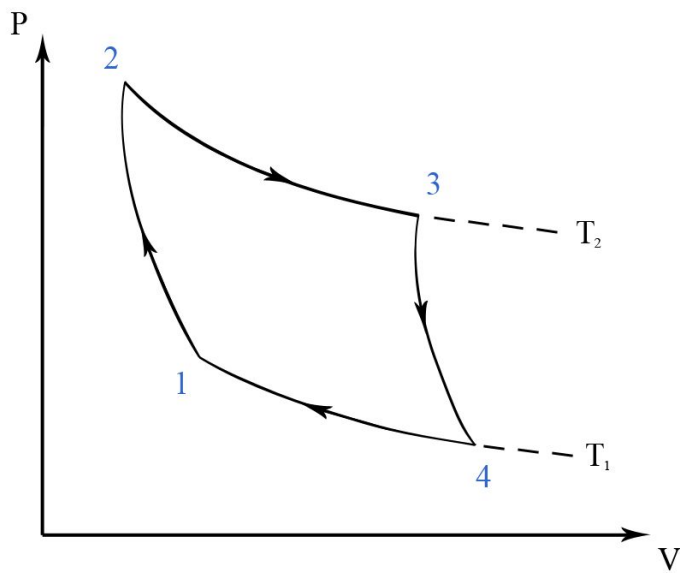
The Carnot cycle when acting as a heat engine consists of the following steps:

1. **Reversible isothermal expansion of the gas at the "hot" temperature,  $T_1$  (isothermal heat addition or absorption).** During this step (1 to 2 on Figure) the gas is allowed to expand and it does work on the surroundings. The temperature of the gas does not change during the process, and thus the expansion is isothermal. The gas expansion is propelled by absorption of heat energy  $Q_1$  and of entropy from the high temperature reservoir.

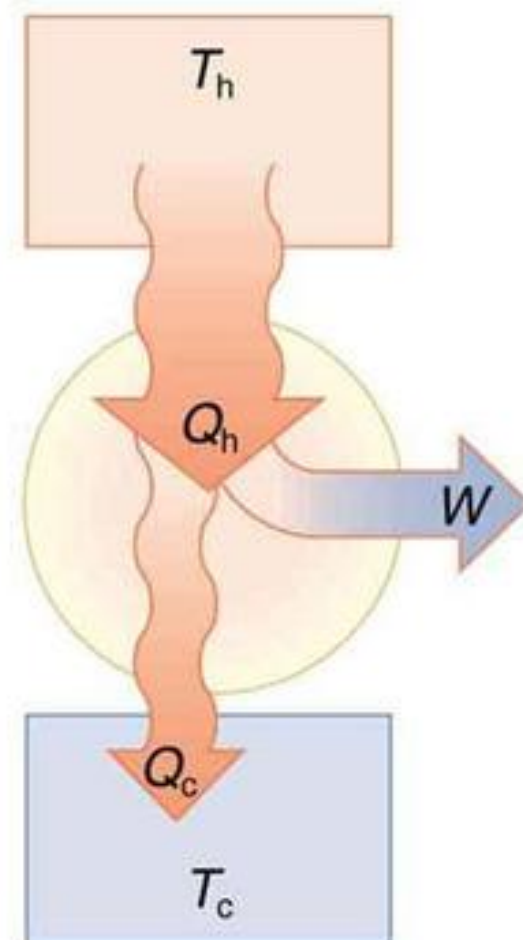
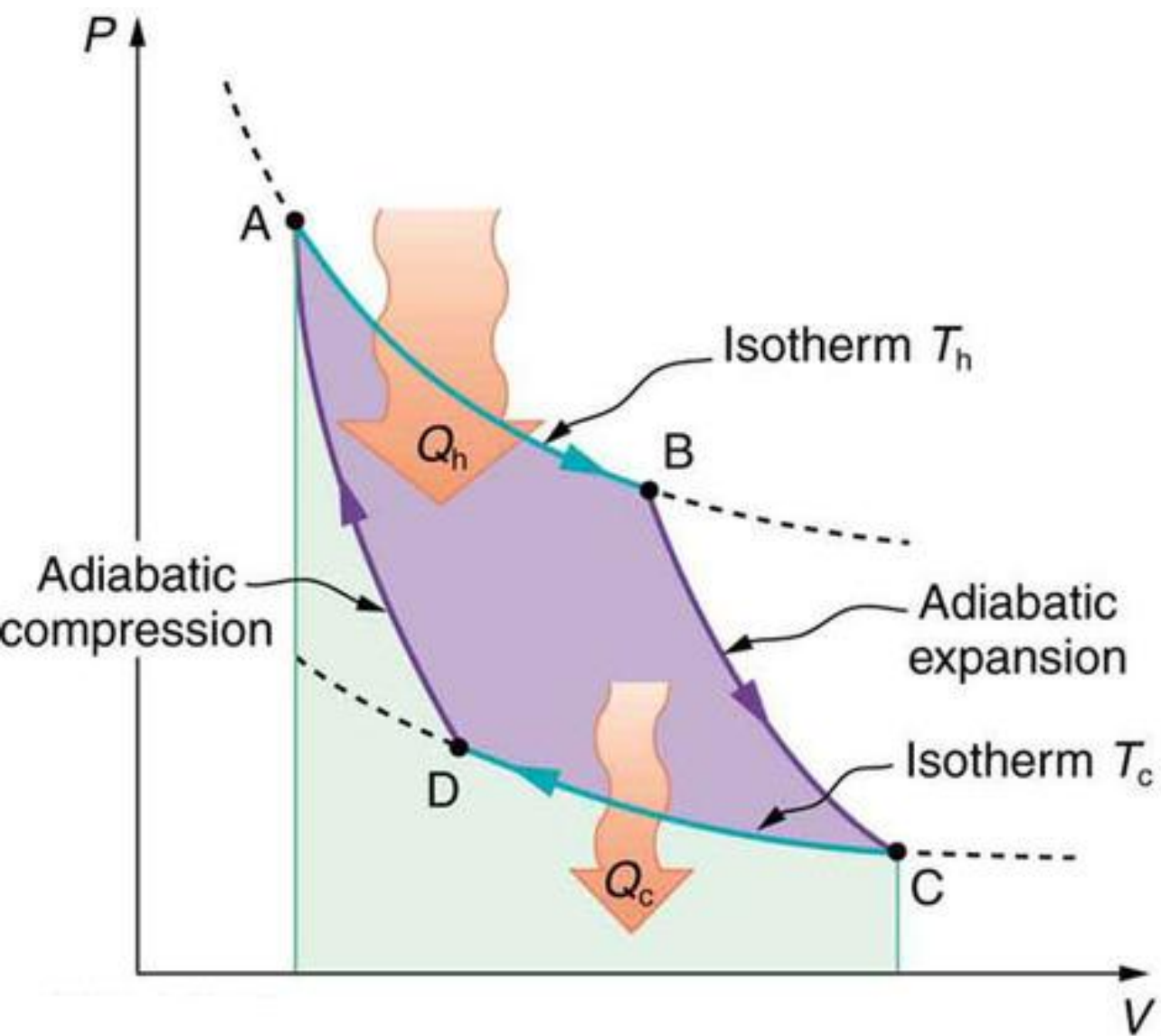
$$\Delta S = Q_1 / T_1$$

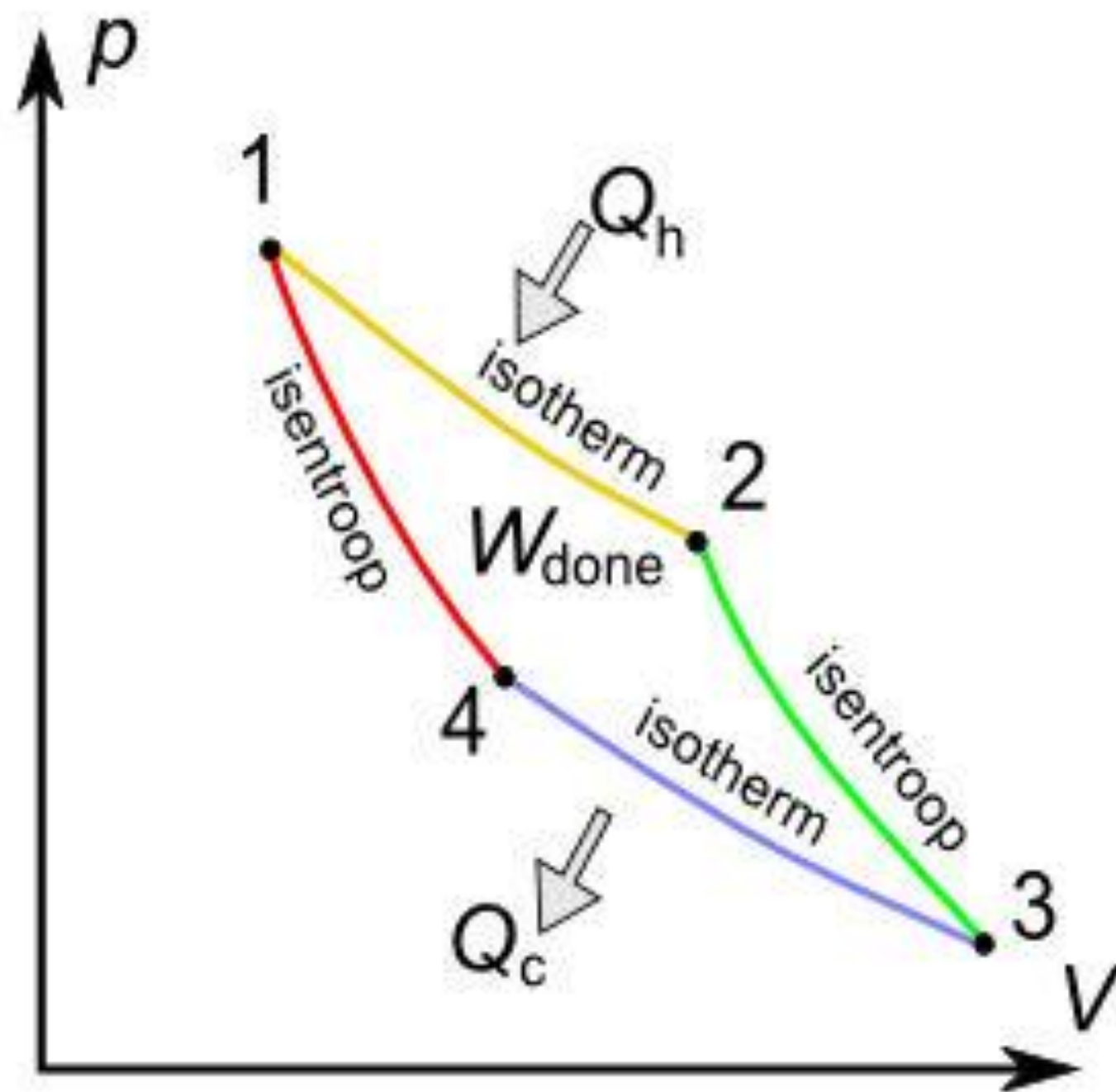
1. **Reversible adiabatic Reversible adiabatic expansion of the gas (adiabatic work output).** For this step (2 to 3 on Figure) the mechanisms of the engine are assumed to be thermally insulated, thus they neither gain nor lose heat. The gas continues to expand, doing work on the surroundings, and losing an equivalent amount of internal energy. The gas expansion causes it to cool to the "cold" temperature,  $T_2$ . The entropy remains unchanged.

- 3. Reversible isothermal compression of the gas at the "cold" temperature,  $T_2$ . (isothermal heat rejection)** (3 to 4 on Figure). Now the surroundings do work on the gas, causing an amount of heat energy  $Q_2$  and of entropy  $\Delta S = Q_2/T_2$  to flow out of the gas to the low temperature reservoir. (This is the same amount of entropy absorbed in step 1.)
- 4. Reversible adiabatic compression of the gas (adiabatic work input).** (4 to 1 on Figure 2) Once again the mechanisms of the engine are assumed to be thermally insulated. During this step, the surroundings do work on the gas, increasing its internal energy and compressing it, causing the temperature to rise to  $T_1$ . The entropy remains unchanged. At this point the gas is in the same state as at the start of step 1.



The Carnot heat-engine cycle described is a totally reversible cycle. That is, all the processes that comprise it can be reversed, in which case it becomes the Carnot refrigeration cycle. This time, the cycle remains exactly the same except that the directions of any heat and work interactions are reversed. Heat is absorbed from the low-temperature reservoir, heat is rejected to a high-temperature reservoir, and a work input is required to accomplish all this. The P-V diagram of the reversed Carnot cycle is the same as for the Carnot cycle except that the directions of the processes are reversed.





The efficiency  $\eta$  is defined to be:

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H} \quad (3)$$