

# THERMODYNAMIC ENTROPY

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Thermodynamic entropy is defined as a mathematical function. It does not have a physical explanation in the classical terms from which it was derived. In this theory thermodynamic entropy will be given clear meaning. However, it is first necessary to have read the essay titled: **FINE STRUCTURE CONSTANT ELECTRIC CHARGE**. This essay, on thermodynamic entropy, uses a result that is arrived at in that essay. The result is: The fundamental units of force cancel out. Force can still be assigned units of measurement for convenience; however, they are artificial. Furthermore, since fundamental force units cancel out, then the fundamental units of energy ( $E=fxd$ ) become meters. That is how energy will be used in this essay.

Thermodynamic entropy was discovered long before microstates were discovered. Boltzmann's definition of entropy in statistical mechanics, using microstate probabilities, still required Boltzmann's constant from ideal gas theory, a classically derived constant with units of joules/°Kelvin. These units are classical units of measurement of classical macroscopic properties. For entropy to be explained in any form, requires that the meaning of Boltzmann's constant be explained beyond calling it an arbitrary constant.

What can be said for certain about thermodynamic entropy? It can never decrease. It is impossible for the exchange of energy it describes to reverse its direction. Its definition is precise. It is defined under ideal conditions. It does not include any system for which any part can vary from its average temperature. We very closely approximate it by restricting the analysis to infinitesimal changes. It does not refer to a general process of achieving thermal equilibrium. There are no intervening conditions of disequilibrium. Thermodynamic entropy tells us that its process, including our approximation of it using infinitesimals, moves forward as time moves forward.

## Thermodynamic Equilibrium

My use of the term, thermodynamic properties, refers to those for which we may make macroscopic measurements. Pressure and temperature are representative of this definition. There is one further general requirement. The measurement of such properties must be done under conditions of equilibrium. Temperature is commonly defined as a property that demonstrates when two or more systems are in thermal equilibrium.

If two systems have the same temperature, they are in thermal equilibrium. If they are placed in contact, separated only by a wall that readily transfers heat, then, from the macroscopic perspective no heat will be exchanged. Heat is energy in transit, and there is no resultant energy transferred.

Equilibrium can be approximated even for systems undergoing change, so long as the changes are quasi-static. When external forces act on a system, or when the system exerts a force that acts on its surroundings, then all such forces must act quasi-statically. This means forces must vary so slightly that any thermodynamic imbalance is infinitesimally small. In other words, the system is always infinitesimally near a state of true equilibrium. If a property such as temperature changes, it must occur so very slowly that there is no more than an infinitesimal temperature variation between any two points within the system.

In the work that follows, all parts of a system are in states of equilibrium with one another. Different systems are not necessarily in equilibrium with one another. However, all changes that occur between systems or parts of systems occur sufficiently slowly that each part of all systems, and each system as a whole, from the macroscopic perspective, remain infinitesimally close to equilibrium.

## Definition of Thermodynamic Entropy

Entropy is defined as a mathematical function demonstrating an ideal relationship between the transfer of heat and constant temperature. The entropy function is:

$$\Delta S = \frac{\Delta Q}{T}$$

Where  $\Delta S$  is a change in entropy,  $\Delta Q$  is the transfer of heat either into or out of a system, and  $T$  is the temperature of the system in degrees Kelvin. This equation is based upon an ideal model of an engine called a Carnot engine. The engine operates in a Carnot cycle.

- a. There are two near infinite sources of heat. One is at temperature  $T_{high}$ , the other at temperature  $T_{low}$ . The Carnot engine operates cyclically between these two temperatures. The engine will absorb heat from source  $T_{high}$  and reject heat to source  $T_{low}$ . For this example the working substance is a simple gas. Before the cycle begins, the engine is in contact and thermal equilibrium with heat source  $T_{low}$ . This is the point from which the cycle will start:
- b. The engine is separated from source  $T_{low}$  and the first part of the cycle begins. The gas is adiabatically, i.e. no conduction of heat either into or out of the gas, compressed until its temperature rises to the level of  $T_{high}$ .

- c. The engine is placed in contact with source  $T_{high}$  and the second part of the cycle begins. The gas volume expands while remaining at temperature  $T_{high}$ .
- d. The engine is removed from contact with  $T_{high}$ . The heated gas continues to expand adiabatically, i.e. no heat flows in or out, until its temperature falls to that of source  $T_{low}$ .
- e. The engine is put in contact with source  $T_{low}$  and, the gas is compressed while remaining at temperature  $T_{low}$  until the engine has returned to its initial state of temperature and volume.

It is known for a Carnot cycle that:

$$\frac{\Delta Q_{high}}{T_{high}} = \frac{\Delta Q_{low}}{T_{low}}$$

The values of  $T_{high}$  and  $T_{low}$  may both vary, but the relationship remains true. This relationship is the basis of the definition of thermodynamic entropy. The entropy definition is:

$$\Delta S = \frac{\Delta Q}{T}$$

The entropy of the gas will increase when expanding while in contact with  $T_{high}$  and will decrease when compressing while in contact with  $T_{low}$ . Therefore, the increase in entropy is given by:

$$\Delta S_{increase} = \frac{\Delta Q_{high}}{T_{high}}$$

And the decrease in entropy is given by:

$$\Delta S_{decrease} = \frac{\Delta Q_{low}}{T_{low}}$$

For a Carnot cycle, their sum is:

$$\Delta S_{increase} + \Delta S_{decrease} = 0$$

There is no net change in entropy for the Carnot engine. For a series of Carnot engines joined side by side, they would have an increase in entropy given by:

$$\Delta S_{increase} = \frac{\Delta Q_{high1}}{T_{high1}} + \frac{\Delta Q_{high2}}{T_{high2}} + \frac{\Delta Q_{high3}}{T_{high3}} + \dots + \frac{\Delta Q_{highi}}{T_{highi}}$$

For the latter part of the cycle, the decrease in entropy would equal:

$$\Delta S_{decrease} = \frac{\Delta Q_{lowi}}{T_{lowi}} + \dots + \frac{\Delta Q_{low3}}{T_{low3}} + \frac{\Delta Q_{low2}}{T_{low2}} + \frac{\Delta Q_{low1}}{T_{low1}}$$

The convention is that heat entering the engine is positive and heat leaving is negative. For both series of variations of heat, it does not matter how their individual temperatures vary. The change in entropy, whether increasing or decreasing, is always equal to its final value minus its initial value. In other words, the sums of changes in entropy, either increasing or decreasing, will be the same regardless of how the temperature varies.

If the series of engines each have infinitesimally small transfers of heat, then the equations become differential. The equation for the increase in entropy becomes:

$$dS_{increase} = \frac{dQ_{high1}}{T_{high1}} + \frac{dQ_{high2}}{T_{high2}} + \frac{dQ_{high3}}{T_{high3}} + \dots + \frac{dQ_{highi}}{T_{highi}}$$

The corresponding decrease in entropy would have an analogous change in form. In the differential form, the equations for the series of Carnot engines accurately represent a continuous path on a generalized work diagram so long as the engine represented is quasi-static, i.e. no dissipative effects, and reversible, i.e. returns to initial conditions at the end of each cycle. The differential forms of these equations may be solved by means of calculus for the changes in entropy of this ideal type of engine.

The classical definition of entropy, expressed in terms of macroscopic properties, shows how entropy is calculated, but does not make clear what entropy is. It is a mathematical function and not an explained physics property. Heat is energy in transit. I am using the mks system of units, so the units of entropy are joules per degree Kelvin.

It is temperature that masks the identity of entropy. Temperature is an undefinable property in theoretical physics. It is accepted as a fundamentally unique property along with distance, time, mass, and electric charge. If the physical action, that is temperature, was identified then entropy would be explainable.

What is entropy? It is something whose nature should be easily seen, because, its derivation is part of the operation of the simple, fundamental Carnot engine. The answer can be found in the operation of the Carnot engine. The Carnot engine is the most efficient engine, theoretically speaking. Its efficiency is independent of the nature of the working medium, in this case a simple gas. The efficiency depends only upon the values of the high and low temperatures in degrees Kelvin. Degrees Kelvin must be used because the Kelvin temperature scale is derived based upon the Carnot cycle.

The engine's equation of efficiency and the definition of the Kelvin temperature scale are the basis for the derivation of the equation:

$$\frac{Q_{high}}{T_{high}} = \frac{Q_{low}}{T_{low}}$$

Something very important happens during this derivation that establishes a definite rate of operation of the Carnot cycle. The engine is defined as operating quasi-statically. The general requirement for this to be true is that the engine should operate so slowly that the temperature of the working medium should always measure the same at any point within the medium. This is a condition that must be met for a system to be described as operating infinitesimally close to equilibrium.

There are a number of rates of operation that will satisfy this condition; however, there is one specific rate, above which, the equilibrium will be lost. Any slower rate will work fine. The question is: What is this rate of operation that separates equilibrium from disequilibrium? It is important to know this because this is the rate that becomes fixed into the derivation of the Carnot engine. This occurs because the engine is defined such that the ratio of its heat absorbed to its heat rejected equals the ratio of the temperatures of the high and low heat sources:

$$\frac{Q_{high}}{Q_{low}} = \frac{T_{high}}{T_{low}}$$

This special rate of operation could be identified if the physical meaning of temperature was made clear. In this new theory, temperature is indicative of the rate of exchange of energy between molecules. It is not quantitatively the same as the rate, because, temperature is assigned unique units of measurement that are not time, distance, or a combination of these two. Temperature is assigned the units of degrees and its scale is arbitrarily fitted to the freezing and boiling points of water.

The temperature difference between these points on the Kelvin scale is set at *100* degrees. For this reason, the quantitative measurement of temperature is not the same as the quantitative measurement of exchange of energy between molecules. However, this discrepancy can be moderated with the introduction of a constant of proportionality:

$$\frac{dQ}{dt} = k_T T$$

Multiplying by  $dt$ :

$$dQ = k_T dt T$$

This equation indicates that the differential of entropy is:

$$dS = k_T dt$$

Both  $dS$  and  $dt$  are variables. It is necessary to determine a value for the constant  $k_T$ . This value may be contained in the ideal gas law:

$$E = n \frac{3}{2} kT$$

Where  $k$  is Boltzmann's constant. If I let  $n=1$ , then the equation gives the kinetic energy of a single molecule. In this case  $E$  becomes  $\Delta E$  an incremental value of energy. Substituting:

$$\Delta E = \frac{3}{2} kT$$

This suggests that for an ideal gas molecule:

$$\Delta S = \frac{3}{2} k$$

In other words, the entropy of a single ideal gas molecule is a constant. The condition under which this is true is when the gas molecules act like billiard balls and their pressure is very close to zero. Near zero pressure for any practical temperature requires that the gas molecules be low in number and widely dispersed.

I interpret this to mean, under these conditions, that the thermodynamic measurement of temperature and kinetic energy approach single molecule status. Normally, thermodynamic properties do not apply to small numbers of molecules. However, sometimes it is instructive to establish a link between individual molecules and thermodynamic properties, as is done in the development of the kinetic theory of gases. The case at hand is an inherent part of the kinetic theory of gases.

The ideal gas law written for a single gas molecule gives reason to consider that for a single molecule:

$$\Delta S = \frac{3}{2} k$$

Substituting for Boltzmann's constant:

$$\Delta S = \frac{3}{2} \left( 1.38 \times 10^{-23} \frac{\text{joules}}{\text{molecule} \cdot ^\circ\text{Kelvin}} \right) = 2.07 \times 10^{-23} \frac{\text{joules}}{\text{molecule} \cdot ^\circ\text{Kelvin}}$$

I have defined Entropy as:

$$\Delta S = k_T \Delta t$$

Therefore, I write:

$$k_T \Delta t = 2.07 \times 10^{-23} \frac{\text{joules}}{\text{molecule} \cdot ^\circ\text{Kelvin}}$$

If I could establish a value for  $\Delta t$ , then I could calculate  $k_T$ . Since this calculation is assumed to apply to a single gas molecule and is a constant value, I assume that in this special case,  $\Delta t$  is a fundamental increment of time. In this theory, there is one fundamental increment of time. It is:

$$\Delta t_c = 1.602 \times 10^{-19} \text{ seconds}$$

Substituting this value and solving for  $k_T$ :

$$k_T = \frac{2.07 \times 10^{-23} \frac{\text{joules}}{\text{molecule} \cdot ^\circ\text{Kelvin}}}{1.602 \times 10^{-19} \text{ second}} = 1.292 \times 10^{-4} \frac{\text{joules}}{\text{molecule} \cdot \text{second} \cdot ^\circ\text{Kelvin}}$$

Substituting the units for each quantity as determined by this new theory and dropping the single molecule indicator:

$$k_T = 1.292 \times 10^{-4}$$

The value  $k_T$  is a unit free constant of proportionality. It also follows that Boltzmann's constant is defined as:

$$k = \frac{2}{3} k_T \Delta t_c$$

For the ideal gas equation, the entropy of each molecule is a constant:

$$\Delta S = k_T \Delta t_c$$

However, thermodynamic entropy is defined as an aggregate macroscopic function. I have a value for the constant  $k_T$ , but the increment of time in the macroscopic function is not a constant. There are a great number of molecules involved and their interactions overlap and add together. It is a variable. I expand the meaning of entropy into its more general form and substitute  $k_T$  into the general thermodynamic definition of entropy:

$$\Delta S = k_T \Delta t$$

The  $\Delta t$  in this equation is not the same as the  $\Delta t_c$  in the equation for a single molecule. In the macroscopic version, it is the time required for a quantity of energy, in the form of

heat, to be transferred at the rate represented by the temperature in degrees Kelvin. Substituting this equation for entropy into the general energy equation:

$$\Delta E = \Delta S T = k_T \Delta t T$$

Recognizing that the increment of energy represents an increment of heat entering or leaving the engine, and solving for  $\Delta S$ :

$$\Delta S = \frac{\Delta E}{T} = \frac{\Delta Q}{T} = k_T \Delta t$$

Solving for  $\Delta t$ :

$$\Delta t = \frac{\Delta S}{k_T} = \frac{\Delta Q}{k_T T}$$

This function of  $\Delta t$  is what would have become defined as the function of entropy if temperature had been defined directly as the rate of transfer of energy between molecules. The arbitrary definition of temperature made it necessary for the definition of entropy to include the proportionality constant  $k_T$ . Writing an equation to show this:

$$\frac{\Delta Q}{k_T T} = \frac{\Delta Q}{\Delta Q / \Delta t}$$

In particular:

$$\frac{\Delta Q_{high}}{k_T T_{high}} = \frac{\Delta Q_{high}}{\frac{\Delta Q_{high}}{\Delta t}}$$

For a Carnot engine:

$$\frac{\Delta Q_{high}}{k_T T_{high}} = \frac{\Delta Q_{low}}{k_T T_{low}}$$

Therefore:

$$\frac{\Delta Q_{high}}{\Delta t} = \frac{\Delta Q_{low}}{\Delta t}$$

And the increments of time must be equivalent. This is why the increase in entropy is exactly the opposite of the decrease in entropy for the Carnot engine. The increments of

time are identical. The increment of heat entering the engine carries the positive sign, and the increment of energy leaving the engine carries the negative sign.

Now, I consider an engine that operates infinitesimally close to equilibrium conditions, but has heat loss that does not result in work. The heat that is successfully converted into work can be represented by a series of Carnot engines. For this series, the change in entropy per cycle is zero. The lost heat can be treated as if it just passes through the engine. The engine becomes a pathway for the lost heat to travel from the high heat source to the low heat source.

The entropy of the engine is not changed by this loss of heat. The entropies that are affected are those of the high heat source and the low heat source. The entropies are measures of time required for the lost heat to be released by the high heat source and later absorbed by the low heat source. The net change in entropy is:

$$\Delta S = \frac{Q_{lost}}{T_{low}} - \frac{Q_{lost}}{T_{high}}$$

The quantity of heat transferred is the same in both cases. The rates at which that heat will be transferred are different. The low temperature represents a slower rate of exchange of heat than for the high temperature. This means it takes longer for the low temperature source to absorb the quantity of lost heat than it does for the high temperature source to emit the heat.

This time difference is the change that occurs and it is what is represented by the measure of change of entropy. The high heat source loses entropy because it requires extra time for the lost heat to leave the source. The low heat source gains entropy because it requires extra time to absorb the heat that is simply passing through the engine without being converted into work. This time difference is what is calculated as thermodynamic entropy. *Thermodynamic entropy*, referred to as an arrow of time, really is an arrow of time.