

The Second Law of Thermodynamics

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1 Perpetuum Mobiles of the Second Kind

The first law of thermodynamics, by establishing the conservation of energy along with the equivalence of heat and work, shows that perpetual motion of the first kind is impossible: a device cannot continue to perform work indefinitely without an input of energy. However, based on the equivalence of heat and work, one might surmise that a device could be constructed that converts ambient heat into work. The Earth is, for all practical purposes, an infinite heat reservoir, so that such a device would effectively yield perpetual motion. This device is called a *perpetuum mobile of the second kind*. Its impossibility is guaranteed by the second law of thermodynamics.

2 The Carnot Cycle and the Clausius Theorem

One limited way of transforming heat into work is given by the *Carnot cycle*. Consider two heat sources, one at a temperature T_1 and the other at a temperature T_2 , with $T_1 > T_2$. Consider also a container of gas with a volume negligible in comparison to the volume of the heat sources. Then the Carnot cycle is the following sequence of reversible transformations:

1. The container of gas at temperature T_1 is attached to the heat source with temperature T_1 , and allowed to expand isothermally, absorbing a heat Q_1 .
2. The container is detached from the first heat source and expands adiabatically (without gain nor loss of heat) until it reaches the temperature T_2 .
3. The container is placed on the heat source with temperature T_2 , and is compressed isothermally, delivering a heat Q_2 to the heat source.
4. The container is detached from the second heat source and compressed adiabatically until its temperature reaches T_1 .

This series of transformations, shown on a pressure-volume diagram in Figure 1, forms a cycle.

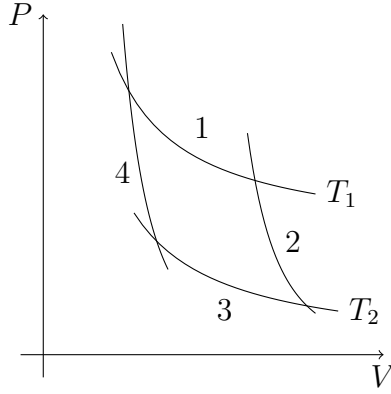


Figure 1: The Carnot cycle illustrated on a pressure-volume diagram. The numbers on the lines correspond to the steps in the cycle given above.

The Carnot cycle represents an engine that extracts work from the heat source at temperature T_1 . According to the first law of thermodynamics, the total work done by the system is equal to the net heat gained, or $Q_1 - Q_2$. We can then compute the efficiency as the ratio of this work to the heat extracted from the warmer heat source:

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Carnot's theorem, which can be proven using the second law, states that no heat engine operating between a given two temperatures can achieve greater efficiency than the Carnot cycle. The value for η given above is thus the maximum attainable value.

For a Carnot cycle, we can also write the efficiency as $\eta = 1 - \frac{T_2}{T_1}$, which serves as a definition for thermodynamic temperature. Equating the two expressions and simplifying, we have

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Or equivalently, for a Carnot cycle operating at an arbitrary number of temperatures,

$$\sum_i \frac{Q_i}{T_i} = 0$$

Generalizing to an integral around a reversible cycle, we obtain the Clausius Theorem¹

$$\oint \frac{\delta Q}{T} = 0$$

This holds true only for a reversible cycle. For an irreversible cycle, the efficiency (by Carnot's theorem) is reduced, and so the heat delivered to the system is decreased. The result is the Clausius inequality, which holds for all cycles:

¹The notation δQ is used in preference to dQ because Q is not a state function, so the differential is inexact.

$$\oint \frac{\delta Q}{T} \leq 0$$

3 Differential Formulation of Entropy

The Clausius theorem stated above takes a mathematically very significant form. Since the integral over any closed path vanishes for reversible exchanges of heat, we can define a new state function. This state function is known as *entropy*, symbolized S :

$$dS = \frac{\delta Q_{\text{rev}}}{T}$$

$$S(B) - S(A) = \int_A^B \frac{\delta Q_{\text{rev}}}{T}$$

Now, consider some general process (not necessarily reversible) starting at state A and ending at state B . We can connect these two states with an arbitrary reversible process and integrate $\frac{\delta Q}{T}$ to find the change in entropy ΔS . We can then reverse this process and combine it with the original process, and then apply the Clausius inequality:

$$-\Delta S + \int \frac{\delta Q}{T} = \oint \frac{\delta Q}{T} \leq 0$$

Solving for ΔS , we obtain:

$$\Delta S \geq \int \frac{\delta Q}{T}$$

In particular, for an adiabatic process (in which $\delta Q = 0$), $\Delta S \geq 0$. We have thus proven the most familiar expression of the second law of thermodynamics: for an isolated system, entropy must never decrease.

4 Problems

1. What is the change in entropy when 20 grams of water at 15°C is mixed with 10 grams of water at 100°C?
2. The Clausius-Clapeyron equation states that for a phase transition with latent heat λ and a change in specific volume $\Delta\nu$, the slope of the coexistence curve on a phase diagram $\frac{dP}{dT}$ is equal to $\frac{\lambda}{T\Delta\nu}$. Prove this equation.