



Entropy and sign conventions

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Abstract

It is a fundamental cornerstone of thermodynamics that entropy ($S_{U,V}$) increases in spontaneous processes in isolated systems (often called closed or thermally closed systems when the transfer of energy as work is considered to be negligible) and achieves a maximum when the system reaches equilibrium. But with a different sign convention entropy could just as well be said to decrease to a minimum in spontaneous constant U , V processes. It would then change in the same direction as the thermodynamic potentials in spontaneous processes. This article discusses but does not advocate such a change.

Introduction

It has occasionally been pointed out in the literature, e.g. Klotz (1964, p. 129), Anderson and Crerar (1993, p. 106), that although entropy is one of a number of state variables that can be used, each under its own specific conditions, to tell which way processes will proceed spontaneously, it is the only one that *increases* during the approach to equilibrium. The others are the thermodynamic potentials, for example the Gibbs energy ($G_{T,P}$), which *decrease* in that direction, which is the direction that decreases the capacity for further spontaneous change. The positive direction of entropy change in spontaneous processes in an isolated system is the result of a choice of sign convention made by Clausius (1867) a few years after he proposed the existence of entropy as a state variable.

This article concerns only classical equilibrium thermodynamics. The implications of a sign change for the direction of entropy change in statistical thermodynamics needs more careful attention than is given here.

Sign conventions

If U is the energy content of a system which may gain or lose energy only by the transfer of energy as heat (q) or work (w) into (+) and out of (−) the system, ΔU must be the algebraic sum of q and w , so we need a convention as to what direction of energy transfer $+q$, $-q$, $+w$, and $-w$ refer. With two sources of energy q and w , each having two possible transfer

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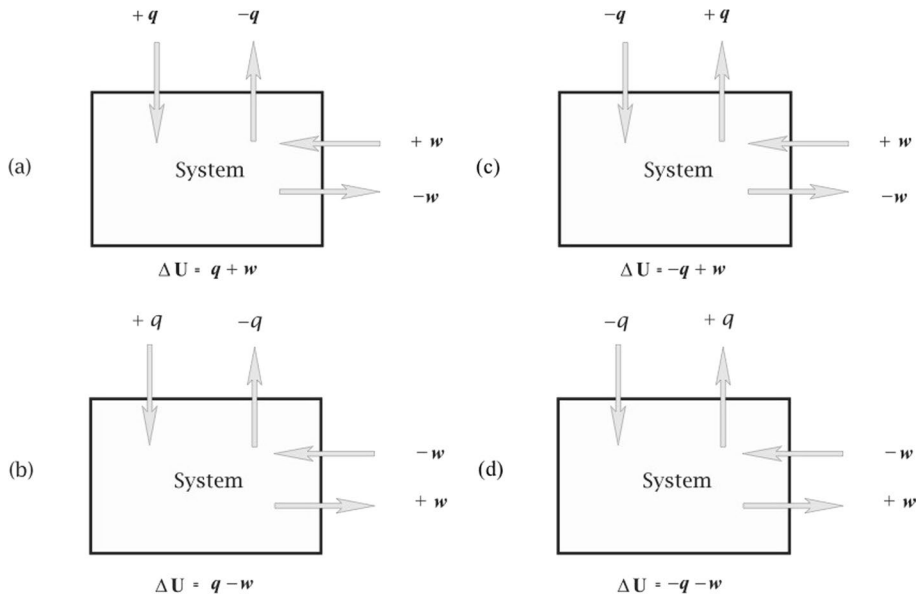


Fig. 1 (a) and (b) illustrate the two commonly used conventions for the sign of q and w in the first law of thermodynamics; (c) and (d) show the two unused conventions

directions + and $-$, there are $2 \times 2 = 4$ possible combinations of heat and work, that is, four possible conventions, but only two of these have ever been used. The one exception to this was by Clausius himself, as discussed in Section 3.1.

These two commonly used conventions are illustrated in Fig. 1a and b, and the two unused conventions are shown in Fig. 1c and d. There are no other possibilities. In the two common conventions work energy entering a system can be called positive (Fig. 1a) or negative (Fig. 1b), but heat energy entering a system is in both cases called positive. There is no fundamental reason for this difference, and with the addition of the unused conventions heat energy entering a system is allowed to be called negative as well as positive.

In this discussion the + and $-$ signs are used in two senses. First they refer to a direction of energy transfer which is used to assign a + or $-$ to q and w . Then in the equations relating ΔU to q and w the signs have their usual binary operator meaning.

The first law

Work

Because work energy that leaves the system (when the system does external work) can be called positive (Fig. 1 b, d) or negative (Fig. 1 a, c) there are two ways of expressing this work, Eqs. (2), (3)¹ and Eqs. (4), (5)².

¹ Adopted for example by Lewis and Randell (1923), Prigogine and Defay (1954), Moore (1962), ?.

² Adopted for example by Jones and Dugan (1996), Denbigh (1966), Klotz (1964), Reiss (1965).

$$\delta w_{rev}/P = dV \quad (1)$$

$$w_{rev} = \int P dV \quad (2)$$

$$w_{rev} = P \Delta V \quad \text{if pressure is constant.} \quad (3)$$

and

$$-w_{rev} = \int P dV \quad (4)$$

$$-w_{rev} = P \Delta V \quad \text{if pressure is constant.} \quad (5)$$

Equations (3) and (5) are valid whether ΔV is positive (expansion; work is done *by* the system, the system loses energy) or negative (compression; work is done *on* the system, the system gains energy). If the input arrow sign ($+w$, $-w$) is different from the sign of ΔV , the input sign takes precedence.

Heat

The choice of convention for heat transfer is more significant. In both common conventions shown in Fig. 1a and b q has a positive direction, meaning heat energy added to a system is called positive, and the entropy equations are the familiar ones,

$$\delta q_{rev}/T = dS \quad (6)$$

$$q_{rev} = \int T dS \quad (7)$$

$$q_{rev} = T \Delta S \quad \text{if temperature is constant.} \quad (8)$$

In Fig. 1a and b $-q$ refers to heat energy that leaves the system, which might be heat from an exothermic process or by simple cooling. But in Fig. 1c and d, $-q$ refers to heat energy *entering* a system, as in heat engines, resulting in minus signs for the entropy equations:

$$-q_{rev} = \int T dS \quad (9)$$

$$-q_{rev} = T \Delta S \quad \text{if temperature is constant, or} \quad (10)$$

$$-q_{rev}/T = \Delta S \quad (11)$$

So with the inclusion of the unused conventions the correspondence between work and heat equations is now complete, and Eq. (10) is simply the heat equation equivalent of the work Eq. (5). But unlike the work equations where the sign of work input ($+w$, $-w$) and ΔV may be different, ΔS has the same sign as the sign of the heat input, positive if heat input

is positive (+ q), the usual case, and negative if heat input is negative ($-q$) as discussed in Section 3.1.

Clearly, energy transfers as heat and work can be called positive or negative, but any of the conventions in Fig. 1 will give the right value for ΔU .

Reversible vs. irreversible

Entropy change ΔS in an irreversible process in a system open to energy transfer can be positive (ice \rightarrow water) or negative (water \rightarrow ice),³ but whether the amount of work or of entropy change is called positive or negative does not change the fact that the reversible work is the maximum available nor the fact that in a reversible cycle the total entropy change is zero, or $\oint \delta q_{rev}/T = 0$ (Clausius 1867, p. 129). Entropy is a state variable but work and heat are not, whether called positive or negative.

The Clausius inequality

Clausius (1867, p. 329 footnote) says that in 1865 he changed from using the convention that heat transfer *into* the system was negative ($-q$) and heat transfer *out* of the system was positive (+ q) (Fig. 1c, d) as he had previously written, to the convention that heat transfer *into* the system was positive (+ q) and heat transfer *out* of the system was negative ($-q$) (Fig. 1a, b). The effect of this, as he said, is that for cyclic processes $\oint \delta q/T \geq 0$ is changed to $\oint \delta q/T \leq 0$, the present interpretation, where the inequality refers to a cycle in which any part is irreversible and the equality refers to a completely reversible cycle.

This expression is known as the Clausius Inequality, and is the source of the fact that, using the conventions in Fig. 1a or b, entropy *increases* in any cycle in which an irreversible process occurs, i.e., any natural cycle. This expression can be understood as saying that heat input from the environment is not the only possible source of entropy in the system, that entropy can be generated *within* the system in many ways, friction, chemical reactions, even simple expansion. In such a case, $\oint \delta q/T$ is less than the total entropy generated; the $\delta q/T$ term does not account for all the contributions to dS , so

$$dS \geq \delta q/T \quad (12)$$

If we call this internally generated entropy $dS_{internal}$, then

$$dS_{internal} \geq 0 \quad \text{and} \quad (13)$$

$$dS = \delta q/T + dS_{internal} \quad (14)$$

Using the conventions in Fig. 1c, d, both $\delta q/T$ and $dS_{internal}$ become negative quantities, so by Eq. (14) dS becomes a negative quantity, and its integral between two equilibrium states A and B , instead of being $S_B - S_A$, entropy increases, becomes $S_A - S_B$, entropy decreases.

³ It is often said that entropy increases in *every* irreversible process if the environment of the system is included as part of the system, though when the environment is the rest of the universe, as it often is, this is questionable. Cosmologists are still debating the entropy of the universe (Carroll 2010).

Using his pre-1865 convention, Clausius might have said "The entropy of the universe tends to a minimum".

Entropy change, an example

Figure 2a shows an isolated system. The exterior wall of the system is impermeable to energy and rigid, so the system has a constant U and V . The piston is movable and can be locked in any position. It is impermeable but it conducts heat so that the two sides are at the same temperature. If there are equal amounts of the same gas in the two compartments, the

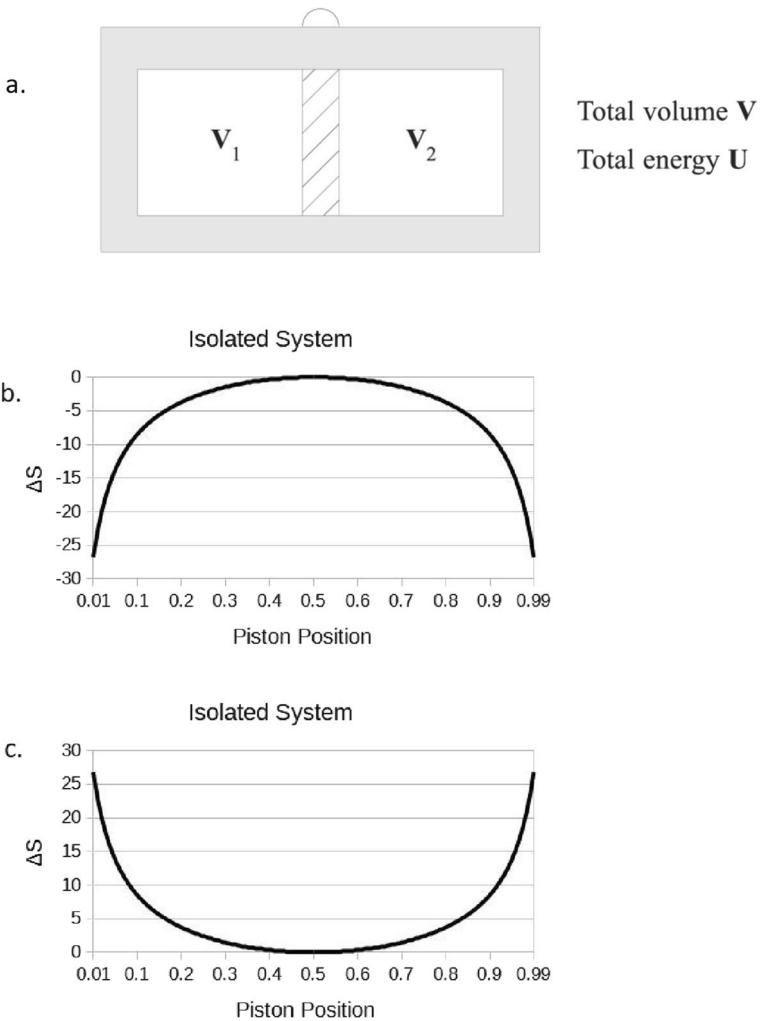


Fig. 2 An isolated system (Figure 2a) and two versions of the entropy change in $\text{J mol}^{-1} \text{K}^{-1}$ as a function of the position of the piston (Fig. 2b and c). The sign conventions in Fig. 1a and b result in Fig. 2b; the conventions in Fig. 1c and d result in Fig. 2c

equilibrium position of the piston when it is free to move is where $V_1 = V_2$. Also, according to the present convention the equilibrium position of the piston is one of maximum entropy for the system, and any other position has lower entropy.

The entropy of the system as a function of the position of the piston according to common usage is shown in Fig. 2b. It is given by the equation

$$\Delta S = 8.314 \left[\ln \frac{x}{0.5} + \ln \frac{(1-x)}{0.5} \right] \quad (15)$$

where $0 < x < 1$. It is a variation of the standard equation for the effect of volume change on entropy,

$$\Delta S = R \ln \frac{V_2}{V_1} \quad (16)$$

Figure 2c shows the effect of substituting $-\Delta S$ for ΔS in Eq. (15).

Naturally if such a sign change is made in classical thermodynamics, an equivalent change would need to be made in statistical thermodynamics. For example $S = k_B \ln W$ would be changed to $S = -k_B \ln W$.

Comment

As far as the First Law is concerned, it doesn't matter whether ΔV and ΔS are positive or negative when energy is transferred to or from a system. Whether w , q , ΔV or ΔS is positive or negative the energy terms $P \Delta V$ and $T \Delta S$ are combined with an appropriate convention so that the system energy changes in the right direction. But this does not mean that whether entropy increases or decreases is not important as shown in Fig. 2. Although it is debatable whether entropy is a thermodynamic potential because it does not minimize energy as do the other potentials, it serves the same function in showing the direction of change of spontaneous processes. We cannot decide that from now on system expansion means a decrease in volume, but we could say that from now on entropy will decrease in a spontaneous process in an isolated system, and this would have little effect on the rest of equilibrium thermodynamics. If $-q$ were to be the common or normal usage for heat input to a system, other thermodynamic equations would need some modification. For example $\Delta G = \Delta H - T \Delta S$ would become $\Delta G = \Delta H + T \Delta S$, but ΔG would be unchanged.

This would bring some consistency to changes in entropy and the thermodynamic potentials in that they would all change toward a minimum in spontaneous processes. Melting, mixing and other irreversible processes are physical reality, we have no choice, but whether we associate these effects with increasing or decreasing entropy is up to us. A sign change would mean that in statistical thermodynamics an increase in the number of indistinguishable microstates would mean a decrease in entropy rather than an increase. Had this been decided years ago by now we would be used to it. It would seem perfectly normal. A choice is involved, whether anyone consciously made that choice or not.

There are reasons for choosing sign conventions the way we do, for example Klotz (1964, p. 130) points out that in some respects increasing entropy is more appropriate in statistical thermodynamics, but it is still a choice. There is really no reason to change it simply to have consistency between entropy and the thermodynamic potentials. This change will likely never happen, and this article is not intended to advocate it. It is just

useful to know that increasing entropy is not woven into the fabric of the universe. Clausius famously said entropy tends to a maximum, and why argue with Clausius?

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