Understanding entropy

Peter G. Nelson¹

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Abstract

A new way of understanding entropy as a macroscopic property is presented. This is based on the fact that heat flows from a hot body to a cold one even when the hot one is smaller and has less energy. A quantity that determines the direction of flow is shown to be the increment of heat gained (q) divided by the absolute temperature (T). The same quantity is shown to determine the direction of other processes taking place in isolated systems provided that q is determined by the state (s) of the system. Entropy emerges as the potent energy of a system [$\Sigma(q_s/T)$], the potency being determined by $1/T$. This is shown to tie in with the statistical mechanical interpretation of entropy. The treatment is shorter than the traditional one based on heat engines.

Keywords Heat · Work · Energy · Entropy · Thermodynamics

Introduction

Many modern authors explain entropy (S) as measuring the number of microscopic states a system ranges over. This explanation is very helpful. In a spontaneous change, the number of such states increases. In classical thermodynamics, however, entropy is a macroscopic property, like pressure (p), volume (V), and temperature (T). There is no reference to the microscopic level. How then is it to be understood macroscopically?

The traditional method of introducing entropy at a macroscopic level is by analysing the operation of heat engines. This method is used in many textbooks (e.g. Denbigh 1981; Dugdale 1996; Laidler et al. 2003; Levine 2009; Atkins and de Paula 2010; Engel and Reid 2010). It has the problem of being very long, and of not making what entropy is very clear. Levine (2009: 87) tells his readers,

Don't be discouraged by the long derivation of $dS = dq_{\text{rev}}/T$ from the Kelvin-Planck statement of the second law. You are not expected to memorize this derivation. What you are expected to do is be able to apply the relation $dS = dq_{\text{rev}}/T$ to calculate ΔS for various processes.

✉ Peter G. Nelson
p.g.nelson@hull.ac.uk

¹ Department of Chemistry, University of Hull, Hull HU6 7RX, UK

Lambert (2002) tries to explain entropy by applying the idea of dispersal over energy levels to the macroscopic scale. He writes:

The entropy of a substance at any temperature T is not complex or mysterious. It is simply a measure of the total quantity of energy that had to be dispersed within the substance from 0 K to T [incrementally and reversibly and divided by T for each increment] so the substance could exist as a solid or liquid or gas at the designated temperature.

The qualification in square brackets he added later (Lambert 2005). It is needed to distinguish entropy from energy, but is where the mystery lies. Why must the dispersal be conducted “incrementally and reversibly and divided by T ”?¹

Other methods of introducing entropy macroscopically have been used, without making the concept any clearer. These include Carathéodory’s inaccessibility method (see, e.g., Chandrasekhar 1958: Chap 1) and Guggenheim’s axiomatic approach (1967). Here I present my own attempt to explain entropy at a macroscopic level.

Preliminaries

Temperature

I shall define temperature as the degree of hotness of a body and measure it by the effect it has on other properties. Later we shall require temperature, for ordinary systems, to be always positive.² We can achieve this by measuring it by the volume of a gas at constant pressure, and taking the lower fixed point to be $T=0$ at $V=0$. If we do this at low pressure, we get the same scale for all gases. For simplicity, we take $T \propto V$. The ideal gas law is then

$$pV = nRT = NkT \quad (1)$$

where n is the amount of gas, R the gas constant, N the number of molecules, and k the Boltzmann constant.

First law

I shall base the first law on the fact that the temperature of a metal block can be increased by putting the block in an oven or rubbing it with another metal block. In the first case, heat is supplied to the block; in the second, work is done on it. Supplying heat and doing work are therefore equivalent ways of imparting energy to a body.³

Thus, in general, when a quantity of heat Q is supplied to a system and an amount of work W is done on it, the increase in energy is given by:

¹ For a fuller critique, see Ben-Naim (2012).

² For a few systems, T in Eqs. 18 or 19 can be negative (Ramsey 1956). These differ from ordinary systems in having an upper limit to their energy.

³ For a summary of Joule’s experiments on heat and work, see Denbigh (1981: 15–16). Note that heat and work are not equivalent when it comes to the second law (entropy is defined by heat/ T not work/ T) (cf. Hatsopoulos and Keenan 1965: xxii–xxiii).

$$\Delta U = Q + W \quad (2)$$

U is the “internal” energy of the system (it excludes energy associated with motion of the system through space). Like p , V , and T , it is a property of the state of a system. Q and W are not state properties: for a given change in U , their values can vary, depending on how the change is carried out. If only heat is supplied, $W=0$; if only work is done, $Q=0$.

For very small changes, I shall write Eq. 2 as

$$\delta U = q + w \quad (3)$$

I take such changes to be small enough for terms of the order of δ^2 (terms in $\delta p \delta V$, $q \delta T$, etc.) to be negligible. I do not take them to be infinitesimal in order to be consistent with the statistical mechanical treatment I consider later, which takes account of fluctuations (Denbigh 1981: Sect. 11.4). I write q and w instead of δQ and δW because they do not represent changes in functions of state (cf. Planck 1927: Sect. 79).

Second law

The second law is concerned with changes in an isolated system (i.e. a system that does not take in or give out energy or matter). Simple examples of such changes are:

- When a cold block of metal is brought into contact with a hot block of metal, heat flows from the hot block to the cold one until their temperatures are the same. This occurs even if the hot block is smaller than the cold one and has less energy.
- When a tap is opened between a bulb of gas and an evacuated bulb, gas flows from the first bulb into the second until the pressure in each bulb is the same.
- When a tap is opened between a bulb containing one gas at a certain pressure and an identical bulb containing a different gas at the same pressure, diffusion takes place until each bulb contains a 1:1 mixture of both gases.
- When a racemization catalyst is introduced into a bulb containing one isomer of an optically active gas, racemization takes place until the bulb contains a 1:1 mixture of both isomers.⁴

In all these examples, a change takes place, but there is no overall change in internal energy ($\Delta U=0$). The question then is, what is causing these changes to take place?

Equalization of temperature

Let us consider the first example in more detail. What we are looking for is a quantity that characterizes spontaneous change. In the present case, we want a quantity that will increase when heat flows from the hot block to the cold one, and decrease if the flow went the other way. Such a quantity can be found as follows.

Call the cold block A and the hot one B. Let thermal contact be made between them through a fine wire for a very brief period, so that only a very small quantity of heat flows

⁴ I am supposing this. There are a few enantiomeric gases (e.g. CF_3CHFCl), but I do not know whether any have been resolved.

from B to A, and the temperatures of the blocks remain effectively the same.⁵ We are looking for a quantity σ for which

$$\sigma_t = \sigma_A + \sigma_B \quad (4)$$

$$\delta\sigma_t = \delta\sigma_A + \delta\sigma_B \geq 0 \quad (5)$$

where t refers to the total system. Such a quantity is

$$\delta\sigma_t = q_A/T_A + q_B/T_B \quad (6)$$

where q_A is the heat absorbed by A and q_B by B. Since $q_B = -q_A$, this gives

$$\delta\sigma_t = q_A/T_A + (-q_A)/T_B = q_A(T_B - T_A)/T_A T_B \quad (7)$$

As $q_A > 0$ and $T_B > T_A$, this gives $\delta\sigma_t > 0$ as required. Heat flow in the opposite direction ($q_A < 0$) would give $\delta\sigma_t < 0$. When $T_A = T_B$, there is no heat flow ($q_A = 0$), and $\delta\sigma_t = 0$. These results assume that T is positive, as we ensured earlier. Other functions of T in the denominator (e.g. T^2) would give the same result. I have chosen the simplest. This will turn out to match the scale of temperature adopted above (see discussion of Eq. 27).

Equation 6 is for a composite system. For a single block

$$\delta\sigma = q/T \quad (8)$$

This is not now an isolated system, but one that can take in or give out energy. Such a system is usually described as “closed” to distinguish it from one that can take in or give out matter (“open”). A more accurate description would be “energy-open, matter-closed” or “semi-open”.

I shall take Eq. 8 to define $\delta\sigma$ for other semi-open systems. The conditions will have to be carefully specified, as we shall see.

Equation 8 can be summed to give the value of σ relative to its value at $T=0$:

$$\sigma(T) - \sigma(0) = \sum_{T=0} q/T \quad (9)$$

Except where there are phase changes, the sum can be replaced by an integral, $\int C\delta T/T$, where C is the appropriate heat capacity ($q/\delta T$). We shall see later that $\sigma(0)=0$.

Equalization of pressure

The question now is whether σ characterizes other spontaneous changes. Let us consider the second example above, the expansion of a gas into a vacuum. If the pressure of the gas is low, this occurs without a measurable change in temperature. In this case, there is no flow of heat, so σ does not seem relevant. We know, however, that if a gas expands against a piston and does work, it cools down. Let us therefore carry out the expansion in a vertical closed cylinder with a piston, the gas being below the piston and a vacuum above (Fig. 1). The process can now be made to raise a weight. In consequence, the system cools down.

⁵ In Eq. 6, the effects of changes in temperature (δT) are of the order of $q\delta T$ and therefore negligible.

Fig. 1 Apparatus for controlled expansion of a gas

To restore it to its original temperature (T), it is necessary to supply it with energy. This can be achieved by placing the cylinder in a large bath maintained at temperature T . The gas can then take in heat.

How much heat that has to be supplied depends on the mass of the weight. It will be less for a small mass than a large one. For a very large mass, the gas will be compressed, and, instead of taking heat from the bath, will give heat to it. In general, therefore, the quantity of heat does not tell us anything about the state of the gas.

In one case, however, the quantity of heat does depend on the state of the gas. Suppose that the weight is a pile of sand, and that the amount of sand is adjusted so that the pile exerts a pressure (p_{ext}) that is exactly equal to the pressure of the gas (p). The piston will not then move. Now let a grain of sand be removed very slowly, to avoid setting the piston in oscillation (cf. Bauman 1964). The gas will then expand until its pressure drops to the value exerted by the slightly smaller pile ($p_{\text{ext}} - \delta p_{\text{ext}}$). In this case, the work done by the gas is determined by the original pressure of the gas (p), and is given by $p\delta V$, where δV is the increase in volume.⁶ To compensate for this, the gas has to absorb an equivalent amount of heat (Eq. 3 with $\delta U = 0$)⁷:

$$q_p = p\delta V \quad (10)$$

This quantity of heat is determined by the pressure of the gas, which I have indicated by the subscript.

Let us now evaluate $\delta\sigma$ as before (Eq. 8):

⁶ From the force exerted by the gas on the piston (pA , A =area) multiplied by the distance the piston moves ($\delta V/A$). The effect of the change in pressure is of the order of $\delta p_{\text{ext}}\delta V$ and therefore negligible.

⁷ In Eq. 3, w (the work done *on* the system) = $-p\delta V$.

Fig. 2 Apparatus for controlled mixing of two gases (**A**, **B**). Piston a is permeable to gas A and piston b to gas B. The piston rods are connected via cranks to weights. The apparatus is placed in a heat bath

$$\delta\sigma = q_p/T = p\delta V/T \quad (11)$$

Since $\delta V > 0$, this is again > 0 as required.

There are three points to make about this result. First, although we have obtained it for a gas that does work and is in contact with a heat bath, it still nevertheless applies to a gas that expands freely by δV .⁸ This is because the value of $\delta\sigma$ is determined by properties of state of the gas (p , V , and T). It is therefore the same whether the process is carried out without doing work or raising a weight.

Second, while Eq. 11 gives the sole change in σ when the gas expands freely, this is not the case when the gas does work in a heat bath. This is because the bath loses heat to the gas. This loss is equal to $-q_p$ and thus to $-p\delta V$. The change in σ for the bath is therefore $-p\delta V/T$ and for the total system (gas + bath) zero. This accords with the fact that, when the pressure exerted by the weight exactly balances p , the piston does not move – there is no tendency for spontaneous change.

Third, if the pressure exerted by the weight is less than the pressure of the gas, then the work done by the gas ($p_{\text{ext}}\delta V$) is less than $p\delta V$ and the heat the gas absorbs ($q_{p_{\text{ext}}} = p_{\text{ext}}\delta V$) is less than q_p (Eq. 10). We can therefore write

$$q_p - q_{p_{\text{ext}}} = (p - p_{\text{ext}})\delta V \geq 0 \quad (12)$$

Hence, from Eq. 11,

$$\delta\sigma \geq q/T \quad (13)$$

where the equality holds for $q = q_p$. This relation also holds if the gas is compressed (for expansion, $\delta V > 0$ and $p_{\text{ext}} \leq p$ in Eq. 12; for compression, $\delta V < 0$ and $p_{\text{ext}} \geq p$). The same result is obtained if $\delta U \neq 0$ (δU in Eq. 3 cancels in Eq. 12). The equality also holds for heat transfer when $\delta V \approx 0$, as in the first example above (Eq. 8). Equation 13 thus applies to any semi-open system. I use this relation below.

Other examples

We can establish that the quantity σ has a more general application by considering the other examples of change given earlier. Some ingenuity is required to get these processes to do work and absorb heat, using semi-permeable barriers. Care also has to be taken to ensure that heats are determined by properties of the system, as in the previous example.

For the third example (mixing of two gases), we can use the apparatus shown in Fig. 2 (Denbigh 1981: Chap 3, problem 1). In this, the two gases (A, B) are separated in a cylinder

⁸ As through a tap into an evacuated bulb of volume δV .

Table 1 Values of Q and $\Delta\sigma$ for the expansion of a gas at low pressure from (p_1, V_1, T) to (p_2, V_2, T) along different paths

Path	Q	$\Delta\sigma$
Const. T	$nRT \ln(V_2/V_1)$	$nR \ln(V_2/V_1)$
Const. p , then const. V	$nRT(V_2/V_1 - 1)$	$nR \ln(V_2/V_1)$
Const. V , then const. p	$nRT(1 - V_1/V_2)$	$nR \ln(V_2/V_1)$

Calculated from Eqs. 14 and 8 using Eq. 1 and $C_p - C_v = nR$ for an ideal gas. Note that the initial and final temperatures are the same

by two pistons, one permeable to one gas and the other to the other. With the cylinder in a heat bath, each gas acts as in the previous example and gives $\delta\sigma_A > 0$ and $\delta\sigma_B > 0$, hence $\delta\sigma_t = \delta\sigma_A + \delta\sigma_B > 0$.

For the fourth example (racemization of an optically active gas), we can use a similar apparatus. The net result is again an increase in σ .⁹

Entropy

We have found a property of state that increases in spontaneous changes in an isolated system. This is defined by Eq. 8, where q is the heat absorbed by a system (or subsystem when $\sigma_t = \Sigma\sigma_i$ as in Eq. 4) under certain conditions. These are usually specified as “reversible”, because the system can be restored to its original state by reversing what caused it to change. This is illustrated by the second example above (equalization of pressure) when the gas is made to do work. Replacing the grain of sand causes the gas to return to its original state, and to give back the heat it absorbed from the bath. However, the change in the first example above (equalization of temperature between metal blocks) is *not* reversible. Heat absorbed by the cold block from the hot one cannot be transferred back directly. The distinction arises from Eq. 13, where the condition for $\delta\sigma$ to be equal to q/T is either $p_{\text{ext}} = p$ (reversibility) or $\delta V = 0$. A better specification therefore is, “when q is determined by state properties of the system” (in the first example, $q_A = \delta U_A$ and $q_B = \delta U_B$; in the second, $q = p\delta V$). We can indicate this by writing q_s , where “s” signifies “state-determined”.

From Eq. 3, the general equation for q_s when only p – V work is done, is:

$$q_s = \delta U + p\delta V \quad (14)$$

This can be summed to give $Q = \Sigma q_s$ and $\Delta\sigma = \Sigma(q_s/T)$ for any change. A complication is that the former depends on the path, as shown in Table 1 (column 2).¹⁰ The latter, however, does not (column 3).

⁹ Consider a mixture in which the partial pressure of (+) isomer ($p_+ = x_+p$) is greater than that of the (–) isomer ($p_- = x_-p$). Place the mixture in an apparatus like the one pictured in Fig. 2, with an ordinary piston towards one end and a piston permeable to the (+) isomer flush with the other end. With the cylinder in a heat bath, move the ordinary piston out until $p_+ = 0.5p$ and the semi-permeable piston in until $p_- = 0.5p$. Judiciously catalyse the reaction, and move the ordinary piston in and the semi-permeable piston out until they are back in their original positions. If the pressures on the pistons are kept close to the pressures in the gas, the net heat absorbed by the system is (from Eqs. 1 and 10) $Q = n_+RT \ln(x_+/0.5) - n_-RT \ln(0.5/x_-)$. Thus, for an incremental change, for which $\delta n_- = -\delta n_+$, $q = \delta n_+RT \ln(x_+/x_-)$. Since $x_+ > x_-$, this is > 0 . Hence, $\delta\sigma$ is > 0 .

¹⁰ This does not mean that q_s is path-dependent, not state-dependent. For an incremental change ($p_2 = p_1 - \frac{1}{2}\delta p$, $V_2 = V_1 + \delta V$), the formulae for Q give, after expansion and truncation, $q = p\delta V$, $p\delta V + \frac{1}{2}\delta p\delta V$, and $p\delta V - \frac{1}{2}\delta p\delta V$ respectively, where p is the average pressure ($p_1 - \frac{1}{2}\delta p$). These values are the same, to the first order in δ .

A simple proof of this is as follows. Consider changing the state of a body from state 1 to state 2 along a path for which the heat increments are not all state-determined, and then returning it to state 1 along a path for which they are:

$$\sum_{\text{cycle}} (q/T) = \sum_1^2 (q/T) + \sum_2^1 (q_s/T) \quad (15)$$

This gives, from Eqs. 8 and 13,

$$\sum_{\text{cycle}} (q/T) = \sum_1^2 (q/T - \delta\sigma) \leq 0 \quad (16)$$

Thus, if the first stage had been carried out along a q_s path:

$$\sum_{\text{cycle}} (q_s/T) = \oint \delta\sigma = 0 \quad (17)$$

This makes σ a state function. It also explains why q has to be state-determined. Only if it is can it give a state function.

We can now call σ “entropy”¹¹ and give it the symbol S . From Eq. 9, it is the energy of a system resulting from the absorption of state-determined increments of heat (Σq_s) with the increments weighted by $1/T$. This holds whatever path is taken to obtain the sum.

The significance of the factor $1/T$ is shown in the first example above. The change in entropy when a small quantity of heat (q) is taken from or added to each metal block is given by $\pm q/T_A$ and $\pm q/T_B$. Since $T_B > T_A$, this change is greater for block A than for block B. In other words, q has a greater effect on the cold block than on the hot one. This is why, when the blocks are brought into contact, it is the cold block that gains heat and the hot one that loses it. It is as if heat is more *potent* at lower temperatures.

Entropy thus emerges as the *potent* energy of a system [$\Sigma(q_s/T)$], the potency being determined by $1/T$.

Application to heat engines and pumps

This understanding of entropy helps to explain the action of the engine Carnot devised to convert heat into work as efficiently as possible (Laidler 1993: 87–92, 370). In this engine, a gas expands in a cylinder immersed in a bath at temperature $T_>$ and does work (step 1, isothermal). It is then restored to its original state by first allowing it to expand further with an insulating jacket round the cylinder until its temperature drops to $T_<$ (step 2, adiabatic). Next, the cylinder is placed in a bath at temperature $T_<$ and the gas compressed to the point when further compression with an insulating jacket will restore the gas to its original state (step 3, isothermal). The final step is this compression (step 4, adiabatic). The steps are carried out under reversible conditions as described above.

¹¹ Greek *en*, “in”, *tropē*, “change”. The word was coined by Clausius (Laidler 1993: 104–105, 372).

In this cycle, the gas absorbs a quantity of heat $Q_>$ from the hot bath while it does work $W_> (=Q_>)$, and returns a quantity of heat $Q_<$ to the cold bath while work $W_< (=Q_<)$ is done on it (the effects of steps 2 and 4 cancel). The question then is, why is $W_>$ greater than $W_<$ so that the net result is that the gas does work ($W = W_> - W_<$)?

The formal answer is that the entropy of the gas at the end of the cycle is the same as at the beginning, so that $Q_>/T_> = Q_</T_<$ (Eq. 17). Since $T_>$ is greater than $T_<$, $Q_>$ is greater than $Q_<$, and therefore $W_>$ is greater than $W_<$.

The understanding of entropy developed in this paper illuminates this. The reason why the quantity of heat transferred to the cold bath is less than that absorbed from the hot one is that the heat transferred to the cold bath is more potent, $1/T_<$ being greater than $1/T_>$. This leaves a quantity of heat ($Q_> - Q_<$) that can be converted into work.

Similar considerations apply when a Carnot engine is operated in reverse as a heat pump. In this mode, heat is transferred from the cold bath to the hot one, but work has to be done to achieve this. This is because a greater quantity of heat has to be supplied to the hot bath than is taken from the cold one because heat at the higher temperature is less potent.

Extension

From Eqs. 8 and 14, we can write

$$\delta U = T\delta S - p\delta V \quad (18)$$

This is for a semi-open system. For an open system

$$\delta U = T\delta S - p\delta V + \sum_i (\partial U / \partial n_i)_{S,V,n_j} \delta n_i \quad (19)$$

where n_i is the amount of the i th chemical component. From this and the auxiliary functions $H (=U + pV)$, $A (=U - TS)$, and $G (=U + pV - TS)$, the standard equations of chemical thermodynamics can be derived.

Statistical mechanical interpretation

I have previously discussed the statistical mechanical interpretation of entropy, based on the first process considered above (Nelson 1994). For this, the number of microscopic states the system ranges over before thermal contact is made is given by

$$\Omega_t = \Omega_A \Omega_B \quad (20)$$

where Ω_A is the number of states block A ranges over and Ω_B the number for block B, the blocks being independent. After contact is made, Ω_t increases. If the contact is brief, the increase is given by

$$\delta \Omega_t = \Omega_B \delta \Omega_A + \Omega_A \delta \Omega_B \quad (21)$$

This can be written

$$\delta \Omega_t / \Omega_t = \delta \Omega_A / \Omega_A + \delta \Omega_B / \Omega_B \geq 0 \quad (22)$$

Comparison with Eq. 5 indicates that

$$\delta S = k' \delta \Omega / \Omega \quad (23)$$

where k' is a constant. Integration of this gives

$$S = k' \int \delta \Omega / \Omega = k' \ln \Omega \quad (24)$$

where I have set the integration constant equal to zero so that $S(0)=0$ corresponds to $\Omega=1$.

From Eqs. 23 and 24, change in entropy thus corresponds to the relative change in the number of microscopic states a system ranges over, and entropy to the logarithm of this number. Potent energy content $[\Sigma(q_s/T)]$ thus corresponds to the degree of multiplicity of microscopic states, measured on a logarithmic scale. The higher the potent energy, the greater the multiplicity. The constant k' converts the former into a number (S/k') equal to the logarithm of the latter.

This treatment can be extended to the second process considered above, expansion of a gas into a vacuum. From the quantum theory, the number of states a monatomic gas can range over when it has a particular energy is proportional to V^N , where N is the number of atoms (Denbigh 1981: Sect. 12.10). For a small expansion, therefore, the change in the number of states is given by

$$\delta \Omega / \Omega = N \delta V / V \quad (25)$$

From Eq. 23, this gives

$$\delta S = N k' \delta V / V \quad (26)$$

Now for an ideal gas, Eq. 1 holds. Substituting this into Eq. 26 gives

$$\delta S = (k'/k) p \delta V / T \quad (27)$$

This is the same as Eq. 11 if we identify k' with k .

This result depends on the definition of entropy matching the scale of temperature. We have taken $T \propto V$ for a gas at constant p and $\delta S = q/T$. Other matches include $T' \propto 1/V$ and $\delta S' = qT'$. Equations 1 and 11 are then $pV = Nk/T'$ and $\delta S' = T'p\delta V$, and substitution of the former into Eq. 26 again gives the latter. For this match, the potency factor is simply T' .

Conclusion

Thermodynamic entropy (S) determines the direction of spontaneous change in an isolated system. It represents the potent energy of a system, the increments of which (q_s/T) are determined by the state of the system and their potency by $1/T$. State-determination is a more general condition than reversibility and is needed to produce a state function (reversibility ensures state-determination because it requires a balance between external forces and internal ones). The weighting by $1/T$ arises because heat is more potent at lower temperatures as I have shown.

This understanding of entropy at a macroscopic level is fuller than the traditional one given in many textbooks. It also explains the addition Lambert (2005) had to make to his definition of entropy, which I mentioned in the introduction. My treatment has the additional merit of being shorter than the traditional one. Entropy appears as early as Eq. 8.

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