

2.6: The Entropy

Entropy and heat

The Second Law guarantees us that an engine operating between two heat baths at temperatures T_1 and T_2 must satisfy

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0, \quad (2.6.1)$$

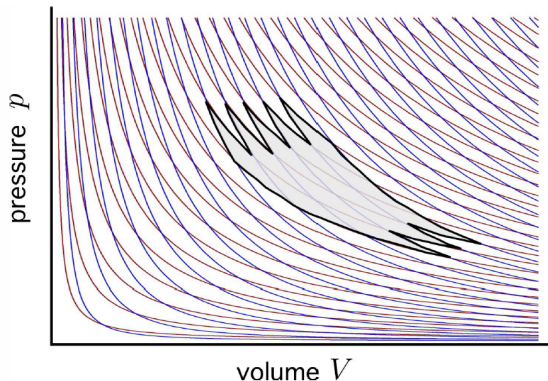
with the equality holding for reversible processes. This is a restatement of Equation ???, after writing $Q_1 = -Q_2$ for the heat transferred to the engine from reservoir #1. Consider now an arbitrary curve in the $p - V$ plane. We can describe such a curve, to arbitrary accuracy, as a combination of Carnot cycles, as shown in Fig. [mcarnot]. Each little Carnot cycle consists of two adiabats and two isotherms. We then conclude

$$\sum_i \frac{Q_i}{T_i} \rightarrow \oint_c \frac{\delta Q}{T} \leq 0, \quad (2.6.2)$$

with equality holding if all the cycles are reversible. Rudolf Clausius, in 1865, realized that one could then define a new state function, which he called the *entropy*, S , that depended only on the initial and final states of a reversible process:

$$dS = \left(\frac{\delta Q}{T} \right)_{\text{rev}} \Rightarrow S_B - S_A = \int_A^B \left(\frac{\delta Q}{T} \right)_{\text{rev}}$$

Since Q is extensive, so is S ; the units of entropy are $[S] = J/K$.



[mcarnot] An arbitrarily shaped cycle in the $p - V$ plane can be decomposed into a number of smaller Carnot cycles. Red curves indicate isotherms and blue curves adiabats, with $\gamma = \frac{5}{3}$.

The Third Law of Thermodynamics

Equation [dseqn] determines the entropy up to a constant. By choosing a standard state Υ , we can define $S_\Upsilon = 0$, and then by taking $A = \Upsilon$ in the above equation, we can define the absolute entropy S for any state. However, it turns out that this seemingly arbitrary constant S_Υ in the entropy does have consequences, for example in the theory of gaseous equilibrium. The proper definition of entropy, from the point of view of statistical mechanics, will lead us to understand how the zero temperature entropy of a system is related to its quantum mechanical ground state degeneracy. Walther Nernst, in 1906, articulated a principle which is sometimes called the Third Law of Thermodynamics,

Again, this is not quite correct, and quantum mechanics tells us that $S(T=0) = k_B \ln g$, where g is the ground state degeneracy. Nernst's law holds when $g = 1$.

We can combine the First and Second laws to write

$$dE + \delta W = T dS, \quad (2.6.3)$$

where the equality holds for reversible processes.

Entropy changes in cyclic processes

For a cyclic process, whether reversible or not, the change in entropy around a cycle is zero: $\Delta S_{\text{CYC}} = 0$. This is because the entropy S is a state function, with a unique value for every equilibrium state. A cyclic process returns to the same equilibrium state, hence S must return as well to its corresponding value from the previous cycle.

Consider now a general engine, as in Fig. [engref]. Let us compute the total entropy change in the entire Universe over one cycle. We have

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{ENGINE}} + \Delta S_{\text{HOT}} + \Delta S_{\text{COLD}},$$

written as a sum over entropy changes of the engine itself, the hot reservoir, and the cold reservoir¹⁰. Clearly $\Delta S_{\text{ENGINE}} = 0$. The changes in the reservoir entropies are

$$\Delta S_{\text{HOT}} = - \int_{T_2}^{T_1} \frac{\delta Q_{\text{HOT}}}{T} < 0, \quad \Delta S_{\text{COLD}} = \int_{T_1}^{T_2} \frac{\delta Q_{\text{COLD}}}{T} > 0,$$

because the hot reservoir loses heat $Q_2 > 0$ to the engine, and the cold reservoir gains heat $Q_1 = -Q_2 > 0$ from the engine. Therefore,

$$\Delta S_{\text{TOTAL}} = - \left(\frac{Q_2}{T_2} - \frac{Q_1}{T_1} \right) \geq 0.$$

Thus, for a reversible cycle, the net change in the total entropy of the engine plus reservoirs is zero. For an irreversible cycle, there is an increase in total entropy, due to spontaneous processes.

Gibbs-Duhem relation

Recall Equation [dwork]:

$$\delta W = - \sum_j y_j dX_j - \sum_a \mu_a dN_a. \quad (2.6.4)$$

For reversible systems, we can therefore write

$$dE = T dS + \sum_j y_j dX_j + \sum_a \mu_a dN_a. \quad (2.6.5)$$

This says that the energy E is a function of the entropy S , the generalized displacements $\{X_j\}$, and the particle numbers $\{N_a\}$:

$$E = E(S, \{X_j\}, \{N_a\}). \quad (2.6.6)$$

Furthermore, we have

$$T = \left(\frac{\partial E}{\partial S} \right)_{\{X_j, N_a\}}, \quad y_j = \left(\frac{\partial E}{\partial X_j} \right)_{S, \{X_{i \neq j}, N_a\}}, \quad \mu_a = \left(\frac{\partial E}{\partial N_a} \right)_{S, \{X_j, N_{i \neq a}\}} \quad (2.6.7)$$

Since E and all its arguments are extensive, we have

$$\lambda E = E(\lambda S, \{\lambda X_j\}, \{\lambda N_a\}). \quad (2.6.8)$$

We now differentiate the LHS and RHS above with respect to λ , setting $\lambda = 1$ afterward. The result is

$$\begin{aligned} E &= S \frac{\partial E}{\partial S} + \sum_j X_j \frac{\partial E}{\partial X_j} + \sum_a N_a \frac{\partial E}{\partial N_a} \\ &= TS + \sum_j y_j X_j + \sum_a \mu_a N_a. \end{aligned}$$

Mathematically astute readers will recognize this result as an example of Euler's theorem for homogeneous functions. Taking the differential of Equation [ETS], and then subtracting Equation [dErev], we obtain

$$S dT + \sum_j X_j dy_j + \sum_a N_a d\mu_a = 0. \quad (2.6.9)$$

This is called the *Gibbs-Duhem relation*. It says that there is one equation of state which may be written in terms of all the intensive quantities alone. For example, for a single component system, we must have $p = p(T, \mu)$, which follows from

$$S dT - V dp + N d\mu = 0. \quad (2.6.10)$$

Entropy for an ideal gas

For an ideal gas, we have $E = \frac{1}{2} f N k_B T$, and

$$\begin{aligned} dS &= \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN \\ &= \frac{1}{2} f N k_B \frac{dT}{T} + \frac{p}{T} dV + \left(\frac{1}{2} f k_B - \frac{\mu}{T} \right) dN. \end{aligned}$$

Invoking the ideal gas equation of state $pV = N k_B T$, we have

$$dS|_N = \frac{1}{2} f N k_B d \ln T + N k_B d \ln V. \quad (2.6.11)$$

Integrating, we obtain

$$S(T, V, N) = \frac{1}{2} f N k_B \ln T + N k_B \ln V + \varphi(N), \quad (2.6.12)$$

where $\varphi(N)$ is an arbitrary function. Extensivity of S places restrictions on $\varphi(N)$, so that the most general case is

$$S(T, V, N) = \frac{1}{2} f N k_B \ln T + N k_B \ln \left(\frac{V}{N} \right) + N a, \quad (2.6.13)$$

where a is a constant. Equivalently, we could write

$$S(E, V, N) = \frac{1}{2} f N k_B \ln \left(\frac{E}{N} \right) + N k_B \ln \left(\frac{V}{N} \right) + N b, \quad (2.6.14)$$

where $b = a - \frac{1}{2} f k_B \ln \left(\frac{1}{2} f k_B \right)$ is another constant. When we study statistical mechanics, we will find that for the monatomic ideal gas the entropy is

$$S(T, V, N) = N k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N \lambda_T^3} \right) \right], \quad (2.6.15)$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ is the *thermal wavelength*, which involved Planck's constant. Let's now contrast two illustrative cases.

- *Adiabatic free expansion* – Suppose the volume freely expands from V_i to $V_f = r V_i$, with $r > 1$. Such an expansion can be effected by a removal of a partition between two chambers that are otherwise thermally insulated (see Fig. [AFE]). We have already seen how this process entails

$$\Delta E = Q = W = 0. \quad (2.6.16)$$

But the entropy changes! According to Equation [SEVN], we have

$$\Delta S = S_f - S_i = N k_B \ln r. \quad (2.6.17)$$

- *Reversible adiabatic expansion* – If the gas expands quasistatically and reversibly, then $S = S(E, V, N)$ holds everywhere along the thermodynamic path. We then have, assuming $dN = 0$,

$$\begin{aligned} 0 = dS &= \frac{1}{2} f N k_B \frac{dE}{E} + N k_B \frac{dV}{V} \\ &= N k_B d \ln (V E^{f/2}). \end{aligned}$$

Integrating, we find

$$\frac{E}{E_0} = \left(\frac{V_0}{V} \right)^{2/f}. \quad (2.6.18)$$

Thus,

$$E_f = r^{-2/f} E_i \iff T_f = r^{-2/f} T_i. \quad (2.6.19)$$

Example system

Consider a model thermodynamic system for which

$$E(S, V, N) = \frac{a S^3}{N V}, \quad (2.6.20)$$

where a is a constant. We have

$$dE = T dS - p dV + \mu dN, \quad (2.6.21)$$

