I.D The Second Law

The historical development of thermodynamics follows the industrial revolution in the 19th century, and the advent of heat engines. It is interesting to see how such practical considerations as the efficiency of engines can lead to abstract ideas like entropy.

An idealized *heat engine* works by taking in a certain amount of heat Q_H, from a heat source (for example a coal fire), converting a portion of it to work W, and dumping the remaining heat Q_C into a heat sink (e.g. atmosphere). The efficiency of the engine is calculated from

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq 1. \tag{I.16}$$

An idealized *refrigerator* is like an engine running backward, i.e. using work W to extract heat Q_C from a cold system, and dumping heat Q_H at a higher temperature. We can similarly define a figure of merit for the performance of a refrigerator as

$$\omega = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}. \tag{I.17}$$

The first law rules out so called 'perpetual motion machines of the first kind', i.e. engines that produce work without consuming any energy. However, the conservation of energy is not violated by an engine that produces work by converting water to ice. Such a 'perpetual motion machine of the second kind' would certainly solve the world's energy problems, but is ruled out by the second law of thermodynamics. The observation that the natural direction for the flow of heat is from hotter to colder bodies is the content of the second law of thermodynamics. There are a number of different formulations of the second law, such as the following two statements.

• **Kelvin's Statement:** *No process is possible whose sole result is the complete conversion of heat into work.*

• **Clausius's Statement:** *No process is possible whose sole result is the transfer of heat from a colder to a hotter body.*

A perfect engine is ruled out by the first statement, a perfect refrigerator by the second. In fact the two statements are equivalent as shown below.

Proof of the equivalence of the Kelvin and Clausius statements proceeds by showing that if one is violated so is the other.

(a) Let us assume that there is a machine that violates Clausius's statement by taking heat Q from a cooler temperature T_C to a higher temperature T_H. Now consider an engine operating between these two temperature, taking heat Q_H from T_H and

dumping Q_C at T_C. The combined system takes $Q_H - Q$ from T_H, produces work equal to $Q_H - Q_C$ and dumps $Q_C - Q$ at T_C. If we adjust the engine output such that $Q_C = Q$, the net result is a 100% efficient engine, in violation of Kelvin's statement. (b) Alternatively, assume a machine that violates Kelvin's law by taking heat Q and converting it completely to work. The work output of this machine can be used to run a refrigerator, with the net outcome of transferring heat from a colder to a hotter body, in violation of Clausius's statement.

Although these statements may appear as rather trivial and qualitative descriptions, they have important quantitative implications as demonstrated in the next sections.

I.E Carnot Engines & Thermodynamic Temperature

• *A Carnot Engine is any engine that is reversible, runs in a cycle, with all of its heat exchanges taking place at a source temperature T_H, and a sink temperature T_C.*

   A *reversible* process is one that can be run backward in time by simply reversing its inputs and outputs. It is the thermodynamic equivalent of frictionless motion in mechanics. Since time reversibility implies equilibrium, a reversible transformation must be quasi-static, but the reverse is not necessarily true (e.g., if there is energy dissipation due to friction). An engine that runs in a *cycle* returns to its original internal state at the end of the process. The distinguishing characteristic of the Carnot engine is that heat exchanges with the surroundings are carried out only at two temperatures. The zeroth law allows us to select two isotherms at temperatures T_H and T_C for these heat exchanges. To complete the Carnot cycle we have to connect these isotherms by reversible *adiabatic* paths in the coordinate space. Since heat is not a function of state, we don't know how to construct such paths in general. Fortunately, we have sufficient information at this point to construct a Carnot engine using an ideal gas as its internal working substance. For the purpose of demonstration, let us compute the adiabatic curves for a monatomic ideal gas with an internal energy

$$E = \frac{3}{2} N k_B T = \frac{3}{2} PV.$$

Along a quasi-static path

$$\dbar Q = dE - \dbar W = d(\frac{3}{2} PV) + P dV = \frac{5}{2} P dV + \frac{3}{2} V dP. \tag{I.18}$$

The adiabatic condition $\dbar Q = 0$, then implies a path

$$\frac{dP}{P} + \frac{5}{3} \frac{dV}{V} = 0, \implies PV^\gamma = \text{constant}, \tag{I.19}$$

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with $\gamma = 5/3$. The adiabatic curves are clearly distinct from the isotherms, and we can select two such curves to intersect our isotherms, thereby completing a Carnot cycle. The assumption of $E \propto T$ is not necessary, and in the test 1 review problems you will construct adiabatics for any $E(T)$. In fact, a similar construction is possible for any two parameter system with $E(J, x)$.

- **Carnot's Theorem:** *No engine operating between two reservoirs (at temperatures T_H and T_C) is more efficient than a Carnot engine operating between them.*

Proof: Since a Carnot engine is reversible, it can be run backward as a refrigerator. Use the non-Carnot engine to run the Carnot engine backward. Let us denote the heat exchanges of the non-Carnot and Carnot engines by Q_H, Q_C, and Q'_H, Q'_C, respectively. The net effect of the two engines is to transfer heat equal to $Q_H - Q'_H = Q_C - Q'_C$ from T_H to T_C. According to Clausius's statement, the quantity of transferred heat cannot be negative, i.e. $Q_H \geq Q'_H$. Since the same quantity of work W, is involved in this process, we conclude that

$$\frac{W}{Q_H} \leq \frac{W}{Q'_H}, \quad \Longrightarrow \quad \eta_{\text{Carnot}} \geq \eta_{\text{non-Carnot}}. \tag{I.20}$$

Corollary: All reversible (Carnot) engines have the same *universal* efficiency $\eta(T_H, T_C)$, since each can be used to run the other one backward.

The Thermodynamic Temperature Scale: As shown earlier, it is at least theoretically possible to construct a Carnot engine using an ideal gas (or any other two parameter system) as working substance. We now find that independent of the material used, and design and construction, all such cyclic and reversible engines have the same maximum theoretical efficiency. Since this maximum efficiency is only dependent on the two temperatures, it can be used to construct a temperature scale. Such a temperature scale has the attractive property of being independent of the properties of any material (e.g. the ideal gas). To construct such a scale we first find out how $\eta(T_H, T_C)$ depends on the two temperatures. Consider two Carnot engines running in series, one between temperatures T_1 and T_2, and the other between T_2 and T_3 $(T_1 > T_2 > T_3)$. Denote the heat exchanges, and work outputs, of the two engines by Q_1, Q_2, W_{12}, and Q_2, Q_3, W_{23} respectively. Note that the heat dumped by the first engine is taken in by the second, so that the combined effect is another Carnot engine (since each component is reversible) with heat exchanges Q_1, Q_3, and work output $W_{13} = W_{12} + W_{23}$. The three heats are related by

$$Q_2 = Q_1 - W_{12} = Q_1[1 - \eta(T_1, T_2)],$$

$$Q_3 = Q_2 - W_{23} = Q_2[1 - \eta(T_2, T_3)] = Q_1[1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)],$$

$$Q_3 = Q_1 - W_{13} = Q_2[1 - \eta(T_1, T_3)].$$

Comparison of the final two expressions yields

$$[1 - \eta(T_1, T_3)] = [1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)]. \tag{I.21}$$

This property implies that $1 - \eta(T_1, T_2)$ can be written as a ratio of the form $f(T_2)/f(T_1)$, which by convention is set to T_2/T_1, i.e.

$$1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1} \equiv \frac{T_2}{T_1},$$
$$\implies \eta(T_H, T_C) = \frac{T_H - T_C}{T_H}. \tag{I.22}$$

Eq.(I.22) defines temperature up to a constant of proportionality, which is again set by choosing the triple point of water, ice, and steam to $273.16^0 K$. Throughout this chapter, I have used the symbols Θ and T interchangeably. In fact, by running a Carnot cycle for a perfect gas, it can be proved (see test 1 review problems) that the ideal gas and thermodynamic temperature scales are equivalent. Clearly the thermodynamic scale is not useful from a practical stand-point; its advantage is conceptual, in that it is independent of the properties of any substance. All thermodynamic temperatures are positive, since according to eq.(I.22) the heat extracted from a temperature T is proportional to it. If a negative temperature existed, an engine operating between it and a positive temperature would extract heat from both reservoirs and convert the sum total to work, in violation of Kelvin's statement of the second law.

I.F   Entropy

The following theorem allows us to construct another function of state using the second law.

• **Clausius's Theorem:** *For any cyclic transformation (reversible or not), $\oint đQ/T \leq 0$, where $đQ$ refers to the heat increment supplied to the system at temperature T.*

Proof: We can subdivide the cycle into a series of infinitesimal transformations in which the system receives energy in the form of heat $đQ$ and work $đW$. The system need not be in equilibrium at each interval. Direct all the heat exchanges of the system to one port of a Carnot engine, which has another reservoir at a fixed temperature T_0. Since the sign

of dQ is not specified, the Carnot engine must operate a series of infinitesimal cycles in either direction. To deliver heat dQ to the system at some stage, the engine has to extract heat dQ_R from the fixed reservoir. If the heat is delivered to a part of the system which is locally at a temperature T, then according to eq.(I.22),

$$dQ_R = T_0 \frac{dQ}{T}. \tag{I.23}$$

After the cycle in completed, the system and the Carnot Engine return to their original states. The net effect of the combined process is extracting heat $Q_R = \oint dQ_R$ from the reservoir and converting it to external work W. The work $W = Q_R$ is the sum total of the work elements done by the Carnot engine, *and* the work performed by the system in the complete cycle. By Kelvin's statement of the second law, $Q_R = W \leq 0$, i.e.

$$T_0 \oint \frac{dQ}{T} \leq 0, \quad \Longrightarrow \quad \oint \frac{dQ}{T} \leq 0, \tag{I.24}$$

since $T_0 > 0$. Note that T in eq.(I.24) refers to the temperature of the whole system only for quasi-static processes in which it can be uniquely defined throughout the cycle. Otherwise, it is just a local temperature (say at a boundary of the system) at which the Carnot engine deposits the element of heat.

Consequences of Clausius's theorem:

(1) For a *reversible cycle* $\oint dQ_{\mathrm{rev}}/T = 0$, since by running the cycle in the opposite direction $dQ_{\mathrm{rev}} \to -dQ_{\mathrm{rev}}$, and by the above theorem dQ_{rev}/T is both non-negative and non-positive, hence zero. This result implies that the integral of dQ_{rev}/T between any two points A and B is independent of path, since for two paths (1) and (2)

$$\int_A^B \frac{dQ_{\mathrm{rev}}^{(1)}}{T_1} + \int_B^A \frac{dQ_{\mathrm{rev}}^{(2)}}{T_2} = 0, \quad \Longrightarrow \quad \int_A^B \frac{dQ_{\mathrm{rev}}^{(1)}}{T_1} = \int_A^B \frac{dQ_{\mathrm{rev}}^{(2)}}{T_2}. \tag{I.25}$$

(2) Using eq.(I.25) we can construct yet another function of state, the *entropy S*. Since the integral is independent of path, and only depends on the two end points, we can set

$$S(B) - S(A) \equiv \int_A^B \frac{dQ_{\mathrm{rev}}}{T}. \tag{I.26}$$

For reversible processes, we can now compute the heat from $dQ_{\mathrm{rev}} = TdS$. This allows us to construct adiabatic curves for a general (multi-variable) system from the condition of constant S. Note that eq.(I.26) only defines the entropy up to an overall constant.

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(3) Consider an irreversible change from A to B. Make a complete cycle by returning from B to A along a reversible path. Then

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{\text{rev}}}{T} \leq 0, \quad \Longrightarrow \quad \int_A^B \frac{dQ}{T} \leq S(B) - S(A). \tag{I.27}$$

In differential form, this implies that $dS \geq dQ/T$ for any transformation. In particular, consider adiabatically isolating a number of subsystems, each initially separately in equilibrium. As they come to a state of joint equilibrium, since the net $dQ = 0$, we must have $\delta S \geq 0$. Thus an adiabatic system attains a maximum value of entropy in equilibrium since spontaneous internal changes can only increase S. The direction of increasing entropy thus points out the arrow of time, and the path to equilibrium.

(4) For a reversible (hence quasi-static) transformation, $dQ = TdS$ and $dW = \sum_i J_i dx_i$, and the first law implies

$$dE = dQ + dW = TdS + \sum_i J_i dx_i. \tag{I.28}$$

Although eq.(I.28) was obtained from a reversible transformation, as a relation between functions of state it is a generally valid identity of thermodynamics. Also note that in this equation S and T appear as conjugate variables, with S playing the role of a displacement, and T as the corresponding force.

(5) The number of *independent variables* necessary to describe a thermodynamic system also follows from eq.(I.28). If there are n methods of doing work on a system, represented by n conjugate pairs (J_i, x_i), then $n+1$ independent coordinates are necessary to describe the system. (We shall ignore possible constraints between the mechanical coordinates.) For example, choosing $(E, \{x_i\})$ as coordinates, it follows from eq.(I.28) that

$$\left.\frac{\partial S}{\partial E}\right|_{\mathbf{x}} = \frac{1}{T}, \quad \text{and} \quad \left.\frac{\partial S}{\partial x_i}\right|_{E, x_{j \neq i}} = -\frac{J_i}{T}. \tag{I.29}$$

($\mathbf{x}$ and $\mathbf{J}$ will be used as short–hand notations for the parameter sets $\{x_i\}$ and $\{J_i\}$.)

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