Thermodynamics
À la Manière de TASAKI

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Chapter 0

Introduction

This note provides a gentle introduction to thermodynamics, the classical macro-scopic theory governing the interconversion of heat and work. Following the treatment in [Tas01], we will develop the subject through an axiomatic approach:

- Definition 1.1.5

  A thermodynamic system in thermal equilibrium is characterized by a single intensive parameter "temperature" together with a finite set of extensive parameters.

- Definition 1.2.2 – Joule's Experiment

  There exists at least one adiabatic process in which the extensive parameters of a state remain constant while the "temperature" increases. During this "temperature" increasing process, positive work must be done on the system.

- Definition 1.2.3 – The First Law of Thermodynamics

  The work done by a thermodynamic system during an adiabatic process depends solely on the initial and final states.

- Definition 1.2.6 – Planck's Statement

  The temperature-increasing adiabatic process described in Joule's experiment is irreversible.

- Definition 1.3.2

  Thermal interactions between systems behave "well."

- Definition 1.4.2 – Adiabatic Expansion

  For any given state, there exists a lower "temperature" state that is accessible via an adiabatic process.

We assume familiarity with both mathematics and physics, particularly Newtonian mechanics.

Chapter 1

Thermodynamics

Thermodynamics is a branch of classical, macroscopic physics. A typical system
– say, a tablespoon of water – contains approximately Avogadro's number $\sim 10^{23}$
of molecules, making it impossible to track their motions by solving such an
enormous number of equations of motion. Instead, macroscopic observations
and experiments rely on statistical averages; remarkably, only a small number
of parameters survive, and these determine the macroscopic state of a substance.

> We (temporarily) restrict our attention to simple systems, defined
> as systems that are macroscopically homogeneous, isotropic, and
> unchanged, that are large enough so that surface effects can be ne-
> glected, and that are not acted on by electric, magnetic, or gravita-
> tional fields [Cal60].

1.1   Equilibrium States

We consider physical systems under special conditions – equilibrium states.

1.1.1   Extensive Parameters

In brief, a thermodynamic system is a black box equipped with mechanically
accessible channels: through these mechanical handles, we can measure work,
energy, and other mechanical quantities that reveal both mechanical and non-
mechanical properties of the system.

Consider a single kind, i.e., a single-component substance, as a simple ther-
modynamic system. Such a system, say X, may have different states, but our
interest here is restricted to equilibrium states, in which all macroscopic prop-
erties remain unchanged in time. A finite set of parameters fully characterizes
any thermally equilibrium state of the system.

Definition 1.1.1 (Extensive Parameters)**.** Let X be a thermodynamic system.
We assume that its equilibrium state is fully determined by specifying a finite

set of non-negative parameters,

$$\begin{pmatrix} X^1 \\ \vdots \\ X^n \end{pmatrix} \in \mathbb{R}_{\geq 0}{}^n, \tag{1.1}$$

such that for any scalar $\lambda > 0$:

$$\lambda \begin{pmatrix} X^1 \\ \vdots \\ X^n \end{pmatrix} = \begin{pmatrix} \lambda X^1 \\ \vdots \\ \lambda X^n \end{pmatrix}. \tag{1.2}$$

Parameters satisfying this homogeneity property – that is, quantities that scale linearly with the size of the system – are called extensive parameters.

Example 1.1.1 (Fluids)**.** Consider a fixed volume, say a container full of fluid with volume V, and let m be its mass. The following parameters represent its macroscopic state, $\begin{pmatrix} V \\ m \end{pmatrix}$. Consider the case $\lambda = 2$. The left-hand side, $2 \begin{pmatrix} V \\ m \end{pmatrix}$ represents the operation of taking two identical containers of the same fluid and regarding them as a single system. The right-hand side, $\begin{pmatrix} 2V \\ 2m \end{pmatrix}$ is a system with twice the value and twice the mass. The homogeneity assumption states that these two systems are identified – they represent the same macroscopic state, $2 \begin{pmatrix} V \\ m \end{pmatrix} = \begin{pmatrix} 2V \\ 2m \end{pmatrix}$.

Remark 1 (Amount of Substance)*.* For a single-component system of substance, say X, we define the amount $n(X)$ of substance by

$$n(X) := \frac{m}{M(X)}, \tag{1.3}$$

where $M(X)$ is an arbitrary constant associated with the substance. As one easily verifies, $n(X)$ is also an extensive parameter. Since $M(X)$ is arbitrary, several choices are possible:

- $M(X) = 1$

  In this case, the amount of substance coincides with its mass.

- $M(X)$ is the "atomic weight" of X

  Relative to ^{12}C, the relative atomic mass of X is given by:

  $$A_r(X) := \frac{m(X)}{m\left(^{12}C\right)/12}. \tag{1.4}$$

  See Atomic Weights and Isotopic Compositions - Column Descriptions.[1]

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[1] https://www.nist.gov/pml/atomic-weights-and-isotopic-compositions-column-descriptions

By consulting a table of Standard Atomic Weights[2] or via some classical gravimetric analysis, one may choose an appropriate value for $M(X)$.

For a multicomponent system, $X = \{X_i \mid i \in I\}$ of some index I, assuming the chemical composition does not change, we may define

$$n(X_i) := \frac{m_i}{M(X_i)}, i \in I, \tag{1.5}$$

and the total amount of substance $n(X)$ is given by their sum, $n(X) = \sum_{i \in I} n(X_i)$.

Thus, given a table of atomic masses, we can determine the empirical formula for a multicomponent system X. For example, the following substances both have the empirical formula CH:

- acetylene (C_2H_2)

- benzene (C_6H_6)

If the Boyle-Charles law provides a good approximation, i.e., when the "temperature" is sufficiently high and the density is sufficiently low, then for any gas we may determine the following ratio:

$$R := \frac{pV}{mT}, \tag{1.6}$$

where p is the pressure, V the volume, m the mass, and T absolute "temperature" to be introduced later in Definition 1.4.3. Experimentally, one finds

$$R_{\text{acetylene}} \approx 3 R_{\text{benzene}}. \tag{1.7}$$

Thus, if we choose $M_{\text{acetylene}}$ and M_{benzene} such that $\frac{M_{\text{acetylene}}}{M_{\text{benzene}}} \approx 3$, then we obtain the following approximate relation

$$\frac{pV}{nT} = \text{constant}, \tag{1.8}$$

for both acetylene and benzene. Hence, if we select the empirical formula acetylene $= C_k H_l$, for some integers k and l, then benzene $= C_{3k} H_{3l}$. Such a relation is an example of an equation of state; see Example 1.3.1.

Exercise 1.1.1. Find the definition, numerical value, and unit of the molar gas constant R from CODATA.[3]

We now use the amount of substance, N, as an extensive parameter of a system, so its macroscopic state is represented as $\begin{pmatrix} V \\ N \end{pmatrix}$.

Definition 1.1.2 (Juxtaposition)**.** By juxtaposition, we mean placing two systems side by side without any physical, chemical, or thermal interaction. The

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[2]https://www.nist.gov/pml/periodic-table-elements
[3]https://physics.nist.gov/cuu/Constants/

resulting object is itself another thermodynamic system. Let X and Y be two systems, and define their juxtaposition by

$$X \oplus Y = \begin{pmatrix} X^1 \\ \vdots \\ X^n \end{pmatrix} \oplus \begin{pmatrix} Y^1 \\ \vdots \\ Y^m \end{pmatrix} \tag{1.9}$$

Note that these two systems may, in general, have different numbers of extensive parameters; that is, n and m need not coincide. Since $X \oplus Y$ is another thermodynamic system, it must satisfy the homogeneity property:

$$\lambda \left(X \oplus Y \right) = \left(\lambda X \right) \oplus \left(\lambda Y \right), \lambda > 0, \tag{1.10}$$

1.1.2 Walls

Some extensive parameters of a system have mechanical accesses. A typical example is the volume of a gas contained in a cylinder with a movable piston.

Definition 1.1.3 (Walls – Insertion and Removal)**.** Let $0 < \lambda < 1$. Consider the following operation:

$$X \mapsto \lambda X \oplus (1 - \lambda) X. \tag{1.11}$$

Experimentally, this operation can be realized by inserting a thin, impermeable wall that prevents the passage of substances. For an equilibrium state of a system, we assume that both the insertion and the removal of such a wall can be performed with no mechanical work.

Example 1.1.2. Let X be a system in Example 1.1.1, specified by $\begin{pmatrix} V \\ N \end{pmatrix}$.
Suppose we insert a thin wall in order to slice the system into two subsystems. During this wall insertion process, only the edge of the wall is exposed to the pressure due to the fluid. This edge has a length of order L, and the wall must be pushed a distance of the same order L. Hence, the mechanical work W required scales as $W \in \Theta(L^2)$. Given any permissible error $\epsilon > 0$, we may choose a sufficiently large $L > 0$ such that $\left| \frac{W}{V} \right| < \epsilon$. Indeed, the ratio $\left| \frac{W}{V} \right|$ scales as $\frac{1}{L}$, so $\frac{W}{V} \dashrightarrow 0$ as $L \dashrightarrow +\infty$. Hence, in the thermodynamic limit $L \dashrightarrow +\infty$, we may idealize that the thin wall insertion requires no work for an equilibrium state of the system.

Remark 2. If a wall separates two different systems, for instance, the juxtaposition of X and Y, $X \oplus Y$, the sudden removal of the wall can cause a sudden expansion, compression, or turbulence. To remove a wall with no mechanical work, the two states must be mechanically balanced, meaning that the relevant parameters, such as pressures, agree on both sides.

Definition 1.1.4 (Adiabatic Walls and Isolated Systems)**.** A wall is called adiabatic iff it prevents any energy transfer other than mechanical work between the system and the ambient environment. Since the concept of "heat" is not

yet introduced, we regard an adiabatic wall as a physical constraint that blocks all non-mechanical interactions across the boundary.

A system is called isolated iff it does not interact with its environment in any way. Experimentally, an isolated system is realized by enclosing it entirely within an ideal double wall with a vacuum, such as a thermos.

Definition 1.1.5 (Postulate: Equilibrium States of Adiabatic Systems). Let X be a thermodynamic system. By enclosing X within adiabatic walls, we isolate it from its environment. Fix its extensive parameters $X^1, \ldots, X^n$. We postulate that the isolated system will eventually become an equilibrium state of the following form:

$$\left(T; \begin{pmatrix} X^1 \\ \vdots \\ X^n \end{pmatrix} \right), \tag{1.12}$$

where T represents the equilibrium "temperature," a parameter determined solely by the initial state of X. Such a relaxation of a system under thermal isolation is sometimes referred to as the "minus first law" of thermodynamics.

We further assume that the equilibrium "temperature" is an intensive parameter. Namely, for any scale factor $\lambda > 0$, the scaled system λX becomes its equilibrium state

$$\left(T; \begin{pmatrix} \lambda X^1 \\ \vdots \\ \lambda X^n \end{pmatrix} \right). \tag{1.13}$$

Thus, under the scaling $X \mapsto \lambda X$, the equilibrium "temperature" remains unchanged.

Remark 3 (Positive "Temperature"). When using degrees Celsius, add 273.15; or when using degree Fahrenheit, add 459.67, so that $T > 0$. See SI Units – Temperature.[4]

1.2 Adiabatic Processes

We now consider processes in which a system is isolated from its environment.

1.2.1 Adiabatic and Quasistatic Processes

Definition 1.2.1 (Adiabatic and Quasistatic Adiabatic Processes). Let $X_1 \mapsto X_2$ be a process between two states of a system. If the system is enclosed within adiabatic walls, it is "thermally" isolated from the environment. Under this adiabatic condition, the transition of thermodynamic states is denoted by

$$(T_1; X_1) \xrightarrow{\text{a}} (T_2; X_2), \tag{1.14}$$

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[4]`https://www.nist.gov/pml/owm/si-units-temperature`

where both the initial and the final states are equilibrium states. For a given initial "temperature" T_1 and the initial equilibrium state $(T_1; X_1)$, the final equilibrium state X_2, the final state X_2 uniquely determines the final "temperature" along the adiabatic process.

> Note that an adiabatic process, physically, does not have to be gentle, or "static" or anything of the kind. It can be arbitrarily violent![5]

If the process is so slow that not only initial and final states, but also all intermediate states, remain in equilibrium, then such a virtual process is called quasistatic. We denote a quasistatic adiabatic process by

$$(T_1; X_1) \xrightarrow{\text{qa}} (T_2; X_2). \tag{1.15}$$

> Quasi-static processes are done slowly enough that the system remains at thermodynamic equilibrium at each instant, despite the fact that the system changes over time. The thermodynamic equilibrium of the system is necessary for the system to have well-defined values of macroscopic properties such as the temperature and the pressure of the system at each instant of the process. Therefore, quasi-static processes can be shown as well-defined paths in state space of the system.[6]

As basic postulates of thermodynamics, we assume the following for quasistatic adiabatic processes:

- Continuity of temperature

  The final "temperature" of a quasistatic adiabatic process $(T_1; X_1) \xrightarrow{\text{qa}} (T_2; X_2)$ depends continuously on the final state X_2:

  $$X_2 \dashrightarrow X_1 \Rightarrow T_2 \dashrightarrow T_1. \tag{1.16}$$

  In other words, the "temperature" function t satisfies $\lim_{X_2 \to X_1} t(X_2) = t(X_1)$, where $t(X_1) = T_1$ and $t(X_2) = T_2$.

- Existence of inverse processes

  Every quasistatic adiabatic process $(T_1; X_1) \xrightarrow{\text{qa}} (T_2; X_2)$ has an inverse, $(T_1; X_1) \xleftarrow{\text{qa}} (T_2; X_2)$. Both the forward and the inverse processes are quasistatic. Hence, we denote

  $$(T_1; X_1) \xleftrightarrow{\text{qa}} (T_2; X_2). \tag{1.17}$$

Remark 4. We will give another characterization of adiabatic processes in Definition 1.2.3 in terms of energy.

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[5]Elliott H. Lieb and Jakob Yngvason "A Guide to Entropy and the Second Law of Thermodynamics"

[6]University Physics Volume 2 §3.4 Thermodynamic Processes

Definition 1.2.2 (Postulate: Existence of "Temperature" Increasing Adiabatic Process). Let $(T_1; X)$ be an equilibrium state. For any $T_2 > T_1$, we postulate that there exists an adiabatic process that keeps the extensive parameters fixed:

$$(T_1; X) \xrightarrow{\text{a}} (T_2; X). \tag{1.18}$$

During this process, positive work must be done on the system; equivalently, the work done by the system is negative.

Remark 5. This principle is consistent with classical experiments on the interconversion of mechanical work and "heat," such as Joule's experiment, see, for example, December 1840: Joule's abstract on converting mechanical power into heat[7], College Physics 2e §14.1 Heat, and University Physics Volume 2 §1.4 Heat Transfer, Specific Heat, and Calorimetry.

Lemma 1.2.1. *Let X_1, X_2 be physically accessible states, i.e., there exist operations connecting them: $X_1 \mapsto X_2$ and $X_2 \mapsto X_1$. Then, for any $T_1, T_2 > 0$, either*

$$(T_1; X_1) \xrightarrow{a} (T_2; X_2) \tag{1.19}$$

or

$$(T_1; X_1) \xleftarrow{a} (T_2; X_2) \tag{1.20}$$

exists.

Proof. By assumption, there exists a quasistatic adiabatic process

$$(T_1; X_1) \xrightarrow{\text{qa}} (T'; X_2), \tag{1.21}$$

where T' is, a prior unknown, final "temperature" of this process.

- $T' < T_2$ case

  If $T' < T_2$, by Definition 1.2.2, there is an adiabatic process

  $$(T'; X_2) \xrightarrow{\text{a}} (T_2; X_2). \tag{1.22}$$

  Combining these two processes yields the desired adiabatic process:

  $$(T_1; X_1) \xrightarrow{\text{qa}} (T'; X_2) \xrightarrow{\text{a}} (T_2; X_2). \tag{1.23}$$

- $T' \geqq T_2$ case

  If $T' = T_2$, we obtain the desired adiabatic process, $(T_1; X_1) \xrightarrow{\text{qa}} (T' = T_2; X_2)$. So we may suppose $T' > T_2$. By Definition 1.2.1, the quasistatic adiabatic process is invertible. Hence, there is

  $$(T_1; X_1) \xleftarrow{\text{qa}} (T'; X_2). \tag{1.24}$$

  Since $T_2 < T'$, we can construct

  $$(T_2; X_2) \xrightarrow{\text{a}} (T'; X_2) \xrightarrow{\text{qa}} (T_1; X_1). \tag{1.25}$$

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[7]https://www.aps.org/publications/apsnews/200912/physicshistory.cfm

Thus, in call cases, either $(T_1; X_1) \overset{a}{\rightarrow} (T_2; X_2)$ or $(T_1; X_1) \overset{a}{\leftarrow} (T_2; X_2)$ exists. ■

Definition 1.2.3 (Postulate: First Law of Thermodynamics)**.** We postulate that, for an adiabatic process, the work done by the system depends only on the initial and final states, regardless of the "path" connecting them.

In other words, since works behave like "flows," there is a corresponding state quantity "stock" for each state. We call such "stocks" the internal energies. Let $U(T_1; X_1)$ denote the internal energy of the initial state and $U(T_2; X_2)$ the internal energy of the final state:

$$U(T_1; X_1) \underset{\Downarrow W_{\mathrm{ad}}}{\cdots\cdots\!\!\!>} U(T_2; X_2) \quad W_{\mathrm{ad}} = U(T_1; X_1) - U(T_2; X_2). \qquad (1.26)$$

For a system, we fix a reference equilibrium state $(T_*; X_*)$, where X_* is physically accessible from the states we consider. For a scaled system $\lambda X, \lambda > 0$, the corresponding reference is $(T_*, \lambda X_*)$. By Lemma 1.2.1, either the forward process $(T_*, \lambda X_*) \overset{a}{\rightarrow} (T; \lambda X)$ exists or the backward process $(T_*, \lambda X_*) \overset{a}{\leftarrow} (T; \lambda X)$ exists. We then define

$$U(T; \lambda X) := \begin{cases} -W_{\mathrm{ad}}\left((T_*, \lambda X_*) \overset{a}{\rightarrow} (T; \lambda X)\right) & \text{if } (T_*, \lambda X_*) \overset{a}{\rightarrow} (T; \lambda X) \text{ exists} \\ W_{\mathrm{ad}}\left((T_*, \lambda X_*) \overset{a}{\leftarrow} (T; \lambda X)\right) & \text{otherwise.} \end{cases}$$
$$\qquad (1.27)$$

We also assume that U has suitable analytical properties, for instance, U is continuous:

$$(T_1; X_1) \dashrightarrow (T_2; X_2) \Rightarrow U(T_1; X_1) \dashrightarrow U(T_2, ; X_2). \qquad (1.28)$$

See College Physics §15.1 The First Law of Thermodynamics, University Physics Volume 2 §3.3 First Law of Thermodynamics, and Definition 1.3.3.

Lemma 1.2.2. *For a fixed system X, let U denote an internal energy. Then U is an increasing function of the "temperature." Namely,*

$$T_1 < T_2 \Rightarrow U(T_1; X) < U(T_2; X). \qquad (1.29)$$

Proof. By Definition 1.2.2, for any equilibrium state $(T_1; X)$, and any $T_2 > T_1$, there exists an adiabatic process

$$(T_1; X) \overset{a}{\rightarrow} (T_2; X), T_1 < T_2. \qquad (1.30)$$

Along this adiabatic process, some positive work must be done on the system. Hence, the world done by the system is negative:

$$U(T_1; X) \underset{\Downarrow W < 0}{\cdots\cdots\!\!\!>} U(T_2; X) \qquad (1.31)$$

Thus, $W = U(T_1; X) - U(T_2; X) < 0$. ■

Definition 1.2.4 (Heat Capacity at Constant Volume). For a thermodynamic system in an equilibrium state $(T; X)$, the heat capacity at constant volume is defined by

$$C_V(T; X) := \frac{\partial U(T; X)}{\partial T}.$$

(1.32)

This partial derivative is taken all extensive parameters, particularly the volume V in X, fixed. See College Physics §14.2 Temperature Change and Heat Capacity and University Physics Volume 2 §3.5 Heat Capacities of an Ideal Gas.

1.2.2 Reversible Process

Definition 1.2.5 (Reversible Process). An adiabatic process $(T_1; X_1) \xrightarrow{a} (T_2; X_2)$ is called reversible iff there exists an adiabatic process

$$(T_1; X_1) \xleftarrow{a} (T_2; X_2).$$

(1.33)

If such an inverse process does not exist, or if it is not an adiabatic process, then the original process is called irreversible.

By Definition 1.2.1, a quasistatic adiabatic process is reversible. That is, $(T_1; X_1) \xleftrightarrow{qa} (T_2; X_2)$.

Definition 1.2.6 (Postulate: Planck's Statement). If an adiabatic process $(T_1; X) \xrightarrow{a} (T_2; X)$ exists, then it must satisfy $T_1 \leqq T_2$. The "temperature-increasing" adiabatic process in Definition 1.2.2

$$(T_1; X) \xrightarrow{a} (T_2; X),$$

(1.34)

with $T_1 < T_2$, is irreversible.

1.3 Isothermal Processes

We consider processes that occur under a constant "temperature" condition, from $(T; X_1)$ to $(T; X_2)$, for instance. Experimentally, such a process is achieved by maintaining thermal contact with a "temperature" reservoir – also known as a "heat" bath or a thermostat – such as the atmosphere and the ocean of the Earth. The essential feature of a "heat' bath is its large size.

> An isothermal process is a change in the state of the system at a constant temperature. This process is accomplished by keeping the system in thermal equilibrium with a large heat bath during the process. Recall that a heat bath is an idealized "infinitely" large system whose temperature does not change. In practice, the temperature of a finite bath is controlled by either adding or removing a finite amount of energy as the case may be.[8]

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[8]University Physics Volume 2 §3.4 Thermodynamic Processes

1.3.0   Heat Baths – Construction

Let X_1, X_2 be states of a system, let Y be a state another system, and $\lambda > 0$ be a scaling parameter. Consider $X_1 \oplus \lambda Y$ and a fixed process of the subsystem $X_1 \mapsto X_2$. If the system $X_1 \oplus \lambda Y$ is kept isolated from the external environment, then overall adiabatic process can be written in the following form:

$$(T; X_1 \oplus \lambda Y) \xrightarrow{\text{a}} (T_\lambda; X_2 \oplus \lambda Y), \tag{1.35}$$

where T_λ is a resulting final "temperature." Both the final "temperature" and the work W_λ done by the whole system during this adiabatic process

$$U(T; X_1 \oplus \lambda Y) \underset{\Downarrow W_\lambda}{\dashrightarrow} U(T_\lambda; X_2 \oplus \lambda Y) \tag{1.36}$$

depend on the scaling parameter $\lambda > 0$.

Definition 1.3.1 (Heat Transfer). Let us define the heat transfer Q_λ from λY to X_1 by

$$Q_\lambda := U(T; \lambda Y) - U(T_\lambda; \lambda Y) = \lambda \left(U(T; Y) - U(T_\lambda; Y) \right). \tag{1.37}$$

That is, the heat transfer is characterized by the following energy transfer:

$$\begin{cases} U(T; \lambda Y) \dashrightarrow U(T_\lambda; \lambda Y) \\ \qquad\qquad \Big\Vert Q_\lambda \\ U(T; X_1) \underset{\Downarrow W_X}{\dashrightarrow} U(T_\lambda; X_2) \end{cases} \tag{1.38}$$

where the work W_X done by the subsystem during the process is defined by

$$U(T; X_1) \underset{\Downarrow W_X}{\dashrightarrow} U(T_\lambda; X_2). \tag{1.39}$$

Lemma 1.3.1. *If we write*

$$W_\lambda := W_X + Q_\lambda = U(T; X_1) - U(T_\lambda; X_2) + Q_\lambda \tag{1.40}$$

then Q_λ can be regarded as the total heat transfer from the finite-sized "heat bath" λY to X_1.

Remark 6. In our formulation, the mechanical equivalence of heat and energy is manifest, see College Physics §14.1 Heat, University Physics Volume 2 §1.4 Heat Transfer, Specific Heat, and Calorimetry, University Physics Volume 2 §3.2 Work, Heat, and Internal Energy, Remark 5 and Definition 1.3.3.

Proof. Introduce the notation $((T; X) \mid (T'; \lambda Y))$ to denote X and λY are separated by an adiabatic wall $\mid$. If the whole system is enclosed by adiabatic walls, slowly replacing the adiabatic wall $\mid$ by a diathermal wall, we obtain the corresponding adiabatic process

$$((T; X) \mid (T'; \lambda Y)) \xrightarrow{\text{a}} \left(\widetilde{T}; X \oplus \lambda Y \right). \tag{1.41}$$

Since no work is done during this process, see Definition 1.1.3, we may apply the energy conservation statement in Definition 1.2.3:

$$U(T; X) + U(T'; \lambda Y) = U\left(\widetilde{T}; X \oplus \lambda Y\right) = U\left(\widetilde{T}; X\right) + U\left(\widetilde{T}; \lambda Y\right). \quad (1.42)$$

Rearranging, we obtain the transferred energy from λY to X, namely the gain of X and the loss of λY:

$$U\left(\widetilde{T}; X\right) - U(T; X) = U(T'; \lambda Y) - U\left(\widetilde{T}; \lambda Y\right). \quad (1.43)$$

Therefore, for the process in (1.38), Q_λ is indeed the transferred heat from λY to X_1. ∎

To construct a heat bath as a constant T-reservoir, we require the the thermal interaction between systems to behave regularly in the thermodynamic limit.

Definition 1.3.2 (Postulate: Finite Heat Transfer in Thermodynamic Limit)**.** We assume $\lim_{\lambda\to\infty} Q_\lambda$ exists and is finite. That is, even when we take $\lambda \dashrightarrow \infty$ limit, the heat transfer Q_λ does not diverge:

$$\lim_{\lambda\to\infty} Q_\lambda < +\infty. \quad (1.44)$$

In other words, the thermal interaction between X and λY remains well-behaved in the termodynamic limit.

Lemma 1.3.2. *In the thermodynamic limit $\lambda \dashrightarrow \infty$, the final "temperature" of the system remains constant, $\lim_{\lambda\to\infty} T_\lambda = T$.*

Proof. Let $\epsilon > 0$. By the standard definition of convergence via ϵ-δ, $t_\lambda \dashrightarrow t$ as $\lambda \dashrightarrow +\infty$ means that there exists $\lambda_\epsilon > 0$ such that

$$\lambda \geqq \lambda_\epsilon \Rightarrow |t_\lambda - t| < \epsilon. \quad (1.45)$$

Suppose, for contradiction that $T \neq \lim_{\lambda\to\infty} T_\lambda$. Then, for any $\lambda > 0$, there exists $\delta > 0$ such that $|T_\lambda - T| \geqq \delta$. From Lemma 1.2.2, the mapping $T \mapsto U(T; Y)$ is an increasing function. Hence, if $T_\lambda \neq T$, we have $U(T; Y) - U(T_\lambda; Y) \neq 0$, so there exists some $\delta' > 0$ with $|U(T; Y) - U(T_\lambda; Y)| \geqq \delta'$. Therefore, as $\lambda \dashrightarrow +\infty$, the heat transfer would satisfy

$$|Q_\lambda| = \lambda |U(T; Y) - U(T_\lambda; Y)| \geqq \lambda\delta' \dashrightarrow +\infty, \quad (1.46)$$

which contradicts the assumption in Definition 1.3.2. ∎

In this limit $\lambda \dashrightarrow +\infty$, the scaled system λY acts as environmental heat bath, maintaining the "temperature" of the system X constant. Processes occurring under constant "temperature" are called isothermal:

1.3.1   Isothermal Processes and Heats

Definition 1.3.3 (Heat Bath and Isothermal Process). For $X_1 \oplus \lambda Y, \lambda > 0$, if we identify X_1 as a system and λY as the environment, λY under $\lambda \dashrightarrow +\infty$ is called a heat bath or T-reservoir. In this limit, the work done (1.40) through $X_1 \mapsto X_2$ converges:

$$W := \lim_{\lambda \to \infty} W_\lambda = \lim_{\lambda \to \infty} U(T; X_1) - U(T_\lambda; X_2) + Q_\lambda = U(T; X_1) - U(T; X_2) + Q. \tag{1.47}$$

This relation expresses the energy conservation for an isothermal process $X_1 \mapsto X_2$ under a constant T:

$$U(T; X_1) \xrightarrow[\Downarrow W]{\Downarrow Q} U(T; X_2). \tag{1.48}$$

This relation is also called the first law of thermodynamics – energy conservation – see Definition 1.2.3.

Remark 7 (Impossibility of Perpetual Motion Machine of First Kind). As a direct consequence of energy conservation, no "engine" can produce positive work without an external energy source. That is, a perpetual motion machine of the first kind is impossible.

It is worth noting that the difference $Q - W = U(T; X_2) - U(T; X_1)$ depends only on the initial and the final states, not on the specific path from X_1 to X_2 under the constant T, see Figure 3.7 in University Physics Volume 2 §3.3 First Law of Thermodynamics.

Definition 1.3.4 (Isothermal Processes). As established in Definition 1.3.3, an operation $X_1 \mapsto X_2$ under constant "temperature" T an isothermal process:

$$(T; X_1) \xrightarrow{\mathrm{i}} (T; X_2). \tag{1.49}$$

An isothermal process is called a quasistatic isothermal process iff it is so slow that any intermediate state can be seen as an equilibrium state:

$$(T; X_1) \xrightarrow{\mathrm{qi}} (T; X_2). \tag{1.50}$$

Any quasistatic isothermal process has the inverse

$$(T; X_1) \xleftrightarrow{\mathrm{qi}} (T; X_2), \tag{1.51}$$

see Definition 1.2.1.

Definition 1.3.5 (Cycles). A process is called a cycle iff both initial and final states coincide.

Theorem 1.3.1 (Kelvin's Statement). *For any isothermal cycle, the work W_{cyc} done by the system is non-positive:*

$$W_{cyc} \leqq 0. \tag{1.52}$$

Proof. Let X and Y be systems and $\lambda > 0$. Consider a cyclic operation $X \mapsto X$ and the corresponding adiabatic process for $X \oplus \lambda Y$:

$$(T; X \oplus \lambda Y) \xrightarrow{\mathrm{a}} (T_\lambda; X \oplus \lambda Y). \tag{1.53}$$

By Definition 1.2.6, we obtain $T \leqq T_\lambda$. Hence, from Lemma 1.2.2,

$$\begin{aligned} U(T; X) &\leqq U(T_\lambda; X) \\ U(T; Y) &\leqq U(T_\lambda; Y) \end{aligned} \tag{1.54}$$

The transferred heat Q_λ in Definition 1.3.1 satisfies

$$Q_\lambda = \lambda \left(U(T; Y) - U(T_\lambda; Y) \right) \leqq 0, \tag{1.55}$$

Therefore, the work done by the system is

$$W_\lambda := U(T; X) - U(T_\lambda; X') + Q_\lambda \leqq 0. \tag{1.56}$$

If we take $\lambda \dashrightarrow +\infty$ limit, we obtain the desired result, $W := \lim_{\lambda \to \infty} W_\lambda \leqq 0$, since $T_\lambda \dashrightarrow T$ if $\lambda \dashrightarrow \infty$ and, hence, the transition $X \mapsto X$ becomes an isothermal cyclic process. ∎

Remark 8 (Impossibility of Perpetual Motion Machine of Second Kind). As a consequence, no perpetual motion machine of the second kind – no cyclic process under constant "temperature" can produce positive work without external input.

Lemma 1.3.3. *The work done during any quasistatic isothermal cycle is zero.*

Proof. Let $(T; X) \xrightarrow{\mathrm{qi}} (T; X)$ be a quasistatic isothermal cycle and let W denote the work done along this cycle. By Theorem 1.3.1, the work along any isothermal cycle is non-positive, $W \leqq 0$. By Definition 1.3.4, there exists a backward process, $(T; X) \xleftarrow{\mathrm{qi}} (T; X)$. Since this backward process is cyclic, the work done by this inverse cycle is non-positive, $-W \leqq 0$. ∎

1.3.2 Maximum Work and Helmholtz' Free Energy

A central goal of thermodynamics is to determine the conditions under which a system can deliver the maximum available work, often referred to as the "exergy" or the work potential.

Maximum Work

Definition 1.3.6 (Maximum Work). Let X_1, X_2 be two states of a system. The maximum work obtainable in a transition $X_1 \mapsto X_2$ at constant T is defined by

$$W_{\max}(T; X_1 \mapsto X_2) := \max \left\{ W \;\middle|\; U(T; X_1) \xrightarrow[\Downarrow W]{\Downarrow Q} U(T; X_2) \right\}, \tag{1.57}$$

where max is taken over all isothermal processes connecting X_1 and X_2.

Theorem 1.3.2 (Principle of Maximum Work)**.** *The maximum work is achieved during a quasistatic isothermal process,* $(T; X_1) \xrightarrow{qi} (T; X_2)$.

Proof. Let W denote the work done by the system during a quasistatic isothermal process, and let W' denote the work during an arbitrary isothermal process connecting the same states. We will show $W' \leqq W$. By Definition 1.3.4, the quasistatic process has a reversible inverse $(T; X_1) \xleftarrow{qi} (T; X_2)$. Since

$$(T; X_1) \underset{qi}{\overset{i}{\rightleftarrows}} (T; X_2) \tag{1.58}$$

forms an isothermal cycle on $(T; X_1)$, we may apply Theorem 1.3.1. the net work done by this cycle is non-positive, $W' - W \leqq 0$. ∎

Corollary 1.3.2.1 (Path Independence of Maximum Work)**.** *The maximum work* $W_{\max} (T; X_1 \mapsto X_2)$ *is path-independent.*

Proof. By Theorem 1.3.2, the maximum work $W_{\max} (T; X_1 \mapsto X_2)$ is achieved by a quasistatic isothermal process. Therefore, it suffices to show the work done by any quasistatic process is the same.

Consider two quasistatic isothermal processes:

$$(T; X_1) \underset{qi}{\overset{qi}{\rightrightarrows}} (T; X_2) \tag{1.59}$$

Combine the first process and the second process backward, we obtain a quasistatic isothermal cycle:

$$(T; X_1) \underset{qi}{\overset{qi}{\rightleftarrows}} (T; X_2) \tag{1.60}$$

By Lemma 1.3.3, the net work done by such a cycle is zero. Hence, the work done along two quasistatic processes must be equal. ∎

Exercise 1.3.1 (Properties of Maximum Work). Show the following properties of maximum work:

1. Scaling

   For $\lambda > 0$,

   $$W_{\max} (T; \lambda X_2 \mapsto \lambda X_1) = \lambda W_{\max} (T; X_1 \mapsto X_2). \tag{1.61}$$

2. Reversibility

   For the reverse process of $X_1 \mapsto X_2$,

   $$W_{\max} (T; X_2 \mapsto X_1) = -W_{\max} (T; X_1 \mapsto X_2). \tag{1.62}$$

3. Additive for consecutive processes

   For a sequence of processes $X_1 \mapsto X_2$ and $X_2 \mapsto X_3$,

   $$W_{\max}\left(T; X_1 \mapsto X_3\right) = W_{\max}\left(T; X_1 \mapsto X_2\right) + W_{\max}\left(T; X_2 \mapsto X_3\right).$$
   (1.63)

4. Additivity for independent systems

   If we juxtapose two quasistatic processes:

   $$\begin{aligned}(T; X_1) &\xrightarrow{\text{qi}} (T; X_2) \\ (T; Y_1) &\xrightarrow{\text{qi}} (T; Y_2)\end{aligned}$$
   (1.64)

   namely, $(T; X_1 \oplus Y_1) \xrightarrow{\text{qi}} (T; X_2 \oplus Y_2)$, the maximum work is additive:

   $$W_{\max}\left(T; X_1 \oplus Y_1 \mapsto X_2 \oplus Y_2\right) = W_{\max}\left(T; X_1 \mapsto X_2\right) + W_{\max}\left(T; Y_1 \mapsto Y_2\right)$$
   (1.65)

Helmholtz' Free Energy

By Corollary 1.3.2.1, the maximum work $W_{\max}\left(T; X_1 \mapsto X_2\right)$ is path-independent for any isothermal transition $(T; X_1)$ to $(T; X_2)$. This allow us to introduce a corresponding stock associated with the flow of maximum work.

Definition 1.3.7 (Helmholtz's Free Energy). Since $W_{\max}\left(T; X_1 \mapsto X_2\right)$ depends only on the initial and final states, we may define a state function F – the Helmholtz free energy – via the stock-flow diagram

$$F\left[T; X_1\right] \underset{\Downarrow W_{\max}}{\dashrightarrow} F\left[T; X_2\right].$$
(1.66)

That is, the Helmholtz's free energy is defined so that the maximum available work in an isothermal process equals the loss of F, $W_{\max}\left(T; X_1 \mapsto X_2\right) = F\left[T; X_1\right] - F\left[T; X_2\right]$. Hence, Helmholtz free energy represents the maximum useful work obtainable from a system at constant temperature. This is sometimes referred to as the principle of maximum work – no isothermal process can extract more work from a system than the loss of the Helmholtz free energy.

As with internal energy in Definition 1.2.3, we choose a reference state $(T_*; X_*)$ accessible to all state under consideration. For a scaled system $(T; \lambda X), \lambda > 0$, we use the corresponding scaled state $(T_*; \lambda X_*)$ and define

$$F[T; \lambda X] \coloneqq W_{\max}\left(T; \lambda X \mapsto \lambda X_*\right).$$
(1.67)

Finally, we assume several mild analytical conditions such as continuity in "temperature:"

$$T_1 \dashrightarrow T_2 \Rightarrow F[T_1; X] \dashrightarrow F[T_2; X].$$
(1.68)

1.3.3 Equation of State and Pressure

Let us consider a state $\begin{pmatrix} V \\ N \end{pmatrix}$ introduced in Example 1.1.1.

Example 1.3.1 (Fluids – Pressure)**.** Let $V = Al$ be the volume of a cylindrical cross-section A and height l, equipped with a movable piston. Consider the following quasistatic isothermal process:

$$\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) \to \left(T; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix} \right), \tag{1.69}$$

where $V + \Delta V = A (l + \Delta l)$.

Let W be the mechanical work W done by the system during this small displacement Δl, and let f be the force the system exerts on the piston. If Δl is sufficiently small, neglecting terms of order $(\Delta l)^2$, we have

$$W = f\Delta l = \frac{f}{A} A\Delta l = p\Delta V, \tag{1.70}$$

where $p = \frac{f}{A}$ is the pressure. Because the process is quasistatic isothermal, $W = W_{\max}$. Thus, the pressure may be extracted from

$$
\begin{aligned}
p\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) &:= \lim_{\Delta V \to +0} \frac{W_{\max}\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \mapsto \begin{pmatrix} V + \Delta V \\ N \end{pmatrix} \right)}{\Delta V} \\
&= -\lim_{\Delta V \to +0} \frac{F\left[T; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix} \right] - F\left[T; \begin{pmatrix} V \\ N \end{pmatrix} \right]}{\Delta V} \\
&= -\frac{\partial F\left[T; \begin{pmatrix} V \\ N \end{pmatrix} \right]}{\partial V}.
\end{aligned}
\tag{1.71}
$$

The pressure of the system is given by the following state function:

$$\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) \mapsto p\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) \tag{1.72}$$

which is called the equation of state.

Exercise 1.3.2 (Intensive Property). Show that pressure is an intensive parameter. Namely, for any $\lambda > 0$,

$$p\left(T; \lambda \begin{pmatrix} V \\ N \end{pmatrix} \right) = p\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right). \tag{1.73}$$

Example 1.3.2 (Ideal Gas)**.** As discussed in Remark 1, the pressure of a fluid under "temperature" T satisfies

$$p\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) \approx \frac{NRT}{V}. \tag{1.74}$$

A simple toy model of gas is the ideal gas, which is characterized by the following assumptions:

1. Equation of state

   The above approximation is indeed exact:

   $$p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) = \frac{NRT}{V}. \qquad (1.75)$$

2. Heat capacity

   The heat capacity C_V, defined in Definition 1.2.4, is proportional only to the amount of substance, independent of T:

   $$C_V\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) = cNR. \qquad (1.76)$$

   This is well-known Regnault's law.

See College Physics §13.3 The Ideal Gas Law and University Physics Volume 2 §3.5 Heat Capacities of an Ideal Gas.

Recalling (1.71), we compute Helmholtz's free energy of the ideal gas:

$$F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right] - F\left[T; \begin{pmatrix} V_* \\ N \end{pmatrix}\right] = -\int_{V_*}^{V} \frac{NRT}{V'} \mathrm{d}V' = -NRT \ln \frac{V}{V_*}, \qquad (1.77)$$

where we select V_* such that

$$F\left[T; \begin{pmatrix} V_* \\ N \end{pmatrix}\right] = 0, \qquad (1.78)$$

see Definition 1.3.7.

Note that ln stands for log, see Algebra and Trigonometry 2e §6.3 Logarithmic Functions and Algebra and Trigonometry 2e §6.5 Logarithmic Properties.

For convenience, we may further select a reference volume proportional to the amount of substance, $V_* = v(T)N$, where $v(T)$ is a positive value. With this choice, we have

$$F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right] = -NRT \ln \frac{V}{v(T)N}. \qquad (1.79)$$

Exercise 1.3.3. Plot $x \mapsto -\ln(x)$ on $(0, +\infty)$.

Apply this to the ideal gas (1.79), one can show that $V \mapsto F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right]$ is a decreasing function. That is, for the same amount of ideal gas, the smaller the volume V, the more work the system can perform.

By Definition 1.2.4,

$$U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) - U\left(T_*; \begin{pmatrix} V \\ N \end{pmatrix}\right) = \int_{T_*}^{T} cNR\mathrm{d}T' = cNR(T - T_*) \qquad (1.80)$$

where we set, as a reference,

$$U\left(T_*; \begin{pmatrix} V \\ N \end{pmatrix}\right) = 0, \tag{1.81}$$

see Definition 1.2.3. Thus, we may write

$$U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) = cNRT + Nu, \tag{1.82}$$

where $u = -cRT_*$ is a constant. In particular, the internal energy of an ideal gas remains constant under isothermal processes.

Now, consider a quasistatic adiabatic process:

$$\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) \xrightarrow{\mathrm{qa}} \left(T'; \begin{pmatrix} V' \\ N \end{pmatrix}\right) \tag{1.83}$$

Let $\Delta V := V' - V$ and $\Delta T := T' - T$. Let p denote the mechanical pressure of the ideal gas. The work ΔW done by the ideal gas is, up to terms of order $(\Delta V)^2$,

$$\Delta W = p\Delta V = \frac{NRT}{V}\Delta V, \tag{1.84}$$

where we used the equation of state. By energy conservation, in this infinitesimal adiabatic process,

$$U(T; V, N) \xdashrightarrow[\Downarrow \Delta W]{} U(T'; V', N) \tag{1.85}$$

so that we have

$$\Delta W = U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) - U\left(T'; \begin{pmatrix} V' \\ N \end{pmatrix}\right) = -cNR\Delta T. \tag{1.86}$$

Hence, we obtain the following differential equation:

$$\frac{NRT}{V}\mathrm{d}V = -cNR\mathrm{d}T. \tag{1.87}$$

Separating variables:

$$c\int \frac{\mathrm{d}T}{T} = -\int \frac{\mathrm{d}V}{V}, \tag{1.88}$$

we find the Poisson relation for an ideal gas:

$$T^c V = \text{constant under an adiabatic process.} \tag{1.89}$$

Example 1.3.3 (The heat capacity of an ideal gas at constant pressure)**.** Consider an ideal gas $\begin{pmatrix} V \\ N \end{pmatrix}$ contained in cylindrical chamber of cross-sectional area A and and height h, so that $V = Ah$. Suppose the top panel is a movable piston supporting a mass m under gravity $|g|$. Then the gas is under constant external pressure $p = \frac{m|g|}{A}$. Now

$$pV = pAh = m\,|g|\,h \tag{1.90}$$

Consider the composite system, consists of the ideal gas and the mechanical system of a movable piston under constant pressure p. The total internal energy of this composite system is $U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) + pV$. Suppose the external pressure and the thermodynamical pressure of the gas coincide. Then, the corresponding heat capacity at constant pressure is

$$\frac{\partial}{\partial T}\left(U(T; X) + pV\right) = cNR + \frac{\partial}{\partial T} NRT = (c+1)NR. \qquad (1.91)$$

Thus, the heat capacity at constant pressure of an ideal gas is $C_p = (c+1)NR$.

1.4   Heat and Carnot's Theorem

Definition 1.4.1 (Maximum Heat Transfer From Heat Bath)**.** For an isothermal process, $(T; X_1) \xrightarrow{i} (T; X_2)$, define the maximum heat transfer $Q_{\max}(T; X_1 \mapsto X_2)$ from the T-reservoir to the system by

$$Q_{\max}(T; X_1 \mapsto X_2) := \max\left\{ Q \;\middle|\; U(T; X_1) \xrightarrow[\Downarrow W]{\Downarrow Q} U(T; X_2) \right\}, \qquad (1.92)$$

where the max is taken over all isothermal processes connecting X_1 and X_2. It follows immediately from Definition 1.3.6 and Definition 1.3.7 that

$$\begin{aligned} Q_{\max}(T; X_1 \mapsto X_2) &= W_{\max}(T; X_1 \mapsto X_2) + U(T; X_2) - U(T; X_1) \\ &= F[T; X_1] - F[T; X_2] + U(T; X_2) - U(T; X_1) \end{aligned} \qquad (1.93)$$

By Theorem 1.3.2, $Q_{\max}(T; X_1 \mapsto X_2)$ is achieved by a quasistatic isothermal process $(T; X_1) \xrightarrow{\text{qi}} (T; X_2)$.

1.4.1   Generalized Isothermal Processes

Let us construct a generalized isothermal process with a T'-reservoir, namely, a process from (T, X_1) to (T', X_2) carried out under a constant "temperature" T'.

Theorem 1.4.1 (Generalized Isothermal Processes)**.** *Consider the following processes:*

$$((T; X_1) \mid (T'; \lambda Y)) \xrightarrow{a} \left(\widetilde{T}; X_1 \oplus \lambda Y\right) \xrightarrow{a} (T'_\lambda; X_2 \oplus \lambda Y), \qquad (1.94)$$

where the first adiabatic process corresponds to the adiabatic wall removal in Lemma 1.3.1. Then, under the thermodynamic limit $\lambda \dashrightarrow +\infty$, we obtain a generalized isothermal process under T'-reservoir:

$$(T; X_1) \xrightarrow{i'} (T'; X_2). \qquad (1.95)$$

Proof. The associated state transitions are as follows, see (1.38):

$$\begin{cases} U(T'; \lambda Y) \xdashrightarrow{\hspace{2cm}} U(T'_\lambda; \lambda Y) \\ \qquad\qquad\qquad \Big\Vert_{Q'_\lambda} \\ U(T; X_1) \underset{\Downarrow W'_X}{\xdashrightarrow{\hspace{2cm}}} U(T'_\lambda; X_2) \end{cases} \tag{1.96}$$

By Definition 1.3.2 and Lemma 1.3.2, both the heat transfer Q'_λ and the work done by the whole system $W'_\lambda := U(T; X_1) - U(T; T_2) + Q'_\lambda$ have well-defined limits as $\lambda \dashrightarrow +\infty$. Thus, we obtain

$$U(T; X_1) \underset{\Downarrow W'}{\overset{\Downarrow Q'}{\xdashrightarrow{\hspace{1.5cm}}}} U(T'; X_2) \tag{1.97}$$

where $Q' := \lim_{\lambda \to \infty} Q'_\lambda$, $W' := \lim_{\lambda \to \infty} W'_\lambda$, and $T = \lim_{\lambda \to \infty} T'_\lambda$. $\blacksquare$

Remark 9 (Wall-Removal i'-Process). If we take $X_2 = X_1$, the corresponding process becomes

$$(T; X_1) \xrightarrow{\text{i'}} (T'; X_1). \tag{1.98}$$

Since the state remains X_1, the i'-process produces zero work. As noted in Definition 1.1.3, such a wall-removal i'-process requires no work. Thus, in this special case $X_2 = X_1$, both the work done by the system and the work required to remove the wall vanish.

Corollary 1.4.1.1. *If a quasistatic adiabatic process $(T; X_1) \overset{qa}{\longleftrightarrow} (T'; X_3)$ exists, then the maximum work done by the system from $(T; X_1)$ to $(T'; X_2)$ under a T'-reservoir is given by the following sequence of quasistatic processes:*

$$(T; X_1) \xrightarrow{qa} (T'; X_3) \xrightarrow{qi} (T'; X_2). \tag{1.99}$$

The maximum heat transfer from the environment is obtained by the same quasistatic process.

Proof. Let W' be the work done by an arbitrary generalized isothermal process $(T; X) \xrightarrow{\text{i'}} (T'; X')$ under the T'-reservoir. Compare this process with the following sequence of quasistatic processes:

$$(T; X_1) \underset{qa}{\overset{\text{i'}}{\xrightarrow{\hspace{3cm}}}} (T'; X_3) \xrightarrow{qi} (T'; X_2) \tag{1.100}$$

The work W'_{qa} done by the first quasistatic adiabatic process satisfies the following energy conservation:
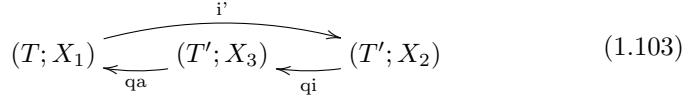
$$U(T; X_1) \underset{\Downarrow W'_{\text{qa}}}{\xdashrightarrow{\hspace{1.5cm}}} U(T'; X_3) \tag{1.101}$$

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The second quasistatic isothermal process satisfies

$$U(T; X_3) \xrightarrow[\Downarrow W'_{qi}]{\Downarrow Q'_{qi}} U(T'; X_2) \tag{1.102}$$

Thus, the total work W_q done by these quasistatic processes is $W_q = W'_{qa} + W'_{qi}$.

Reverse these quasistatic processes, and consider the following cycle:

$$(T; X_1) \underset{qa}{\overset{i'}{\longleftrightarrow}} (T'; X_3) \underset{qi}{\longleftarrow} (T'; X_2) \tag{1.103}$$

Let W_{cyc} be the work done by the above cycle:

$$W_{cyc} = W' - W_q. \tag{1.104}$$

Since the entire cycle is under the T'-reservoir, we may apply Theorem 1.3.1, $W_{cyc} \leqq 0$. Hence, $W' \leqq W_q$.

Let Q' be the heat transfer from the T'-reservoir through $(T; X_1) \xrightarrow{i'} (T'; X_2)$, see (1.97). Computing the total work in terms of heat and changes in free energy:

$$\begin{aligned}
0 \geqq W_{cyc} &= (Q' - U(T'; X_2) + U(T; X_1)) \\
&\quad - (U(T; X_1) - U(T'; X_3) + F[T'; X_3] - F[T'; X_2]) \\
&= Q' + F[T'; X_2] - F[T'; X_3] + U(T'; X_3) - U(T'; X_2) \\
&= Q' + Q_{max}(T' : X_2 \mapsto X_3).
\end{aligned} \tag{1.105}$$

Hence, we conclude:

$$Q' \leqq -Q_{max}(T' : X_2 \mapsto X_3) = Q'_{qi}, \tag{1.106}$$

showing that the quasistatic process yields the maximum heat transfer from the reservoir. ∎

Definition 1.4.2 (Postulate: Adiabatic Accessible Lower "Temperature" State)**.**
Let $T > 0$, and X_0 be a state. We postulate that there exists a state $(T'; X_1)$ with $0 < T' < T$ such that a quasistatic adiabatic

$$(T; X_0) \xrightarrow{qa} (T'; X_1) \tag{1.107}$$

is physically realizable.

Experimentally, through adiabatic expansion of gas, the system performs positive work on the surroundings, and its "temperature" decreases. See College Physics 2e §15.2 The First Law of Thermodynamics and Some Simple Processes and University Physics Volume 2 §3.6 Adiabatic Processes for an Ideal Gas, and consult in particular discussions on the "adiabatic expansion process."

Lemma 1.4.1 (Positive Heat Transfer)**.** *For any* $(T; X_0)$*, there exists* X_1 *with*

$$Q_{max}(T; X_0 \mapsto X_1) > 0. \tag{1.108}$$

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Proof. Given $(T; X_0)$, let $(T'; X_1)$ be an adiabatic accessible lower "temperature state as postulated in Definition 1.4.2. Consider the following isothermal cycle:

$$(T; X_1) \xrightarrow{\text{qi}} (T; X_0) \xrightarrow{\text{qa}} (T'; X_1) \qquad (1.109)$$
$$\underset{\text{i}}{\longleftarrow}$$

where the process $(T'; X_1) \xrightarrow{\text{i}} (T; X_1)$ is the generalized isothermal process under T-reservoir – not T'! – as in Theorem 1.4.1. By Definition 1.4.2, we have $0 < T' < T$.

Let W_{cyc} be the work done by the above isothermal cycle under the T-reservoir. By 1.3.1, we have $W_{\text{cyc}} \leqq 0$. Expanding the contributions from each process in the cycle:

$$
\begin{aligned}
0 \geqq W_{\text{cyc}} =& W_{\text{qi}} + W_{\text{qa}} + W_{\text{i}}, \\
=& F[T; X_1] - F[T; X_0] + U(T; X_0) - U(T'; X_1) + 0 \\
>& F[T; X_1] - F[T; X_0] + U(T; X_0) - U\left(T(> T'); X_1\right) \\
=& -Q_{\max}(T; X_0 \mapsto X_1),
\end{aligned}
\qquad (1.110)
$$

where we use Lemma 1.2.2 and Definition 1.4.1. ■

1.4.2 Carnot's Theorem and Absolute Temperature

Let us start with a key lemma:

Lemma 1.4.2 (Tanaka Lemma). *Let $(T; X) \xrightarrow{qi} (T; X')$ be a quasistatic isothermal process. If $Q_{\max}(T; X \mapsto X') = 0$, then there exists the corresponding quasistatic adiabatic process: $(T; X) \xrightarrow{qa} (T; X')$. In other words, an isothermal process with zero heat transfer is effectively adiabatic, where the heat bath plays no active role.*

Proof. By Lemma 1.2.1, for $T' = T$ case, either $(T; X) \xrightarrow{\text{a}} (T; X')$ or $(T; X) \xleftarrow{\text{a}} (T; X')$ exists. Suppose $(T; X) \xrightarrow{\text{a}} (T; X')$ exists; for the other case, one can interchange X and X', see Remark 10 for this complementary part. Consider the corresponding operation $X \mapsto X'$ as a quasistatic adiabatic process:

$$(T; X) \xrightarrow{\text{qa}} (T'; X'), \qquad (1.111)$$

where the final "temperature" T' is a priori unknown. We claim that T' is indeed T.

Suppose, for contradiction, that $T' > T$. Then, the adiabatic process

$$(T; X) \xleftarrow{\text{qa}} (T'; X') \longrightarrow (T; X') \qquad (1.112)$$
$$\underset{\text{a}}{\longrightarrow}$$

would decrease "temperature" under an adiabatic process, which is impossible by Definition 1.2.6. Hence, $T' \leqq T$.

To show $T' = T$, suppose $T' < T$ for contradiction. By Lemma 1.2.2, we have $U(T'; X') < U(T; X')$. Now consider the following cycle:

$$(T; X) \underset{\text{qi}}{\overset{\text{qa}}{\rightleftarrows}} (T'; X') \xrightarrow{\text{i}} (T; X') \tag{1.113}$$

where $(T'; X') \xrightarrow{\text{i}} (T; X')$ is a generalized isothermal process under the T-reservoir. The whole cycle is isothermal under the T-reservoir. So, by Theorem 1.3.1, the net work done satisfies, by hypothesis $Q_{\max}(T; X \mapsto X') = 0$,

$$0 \geqq W_{\text{cyc}} = U(T; X') - U(T; X) + Q_{\max}(T; X \mapsto X') + U(T; X) - U(T'; X'). \tag{1.114}$$

We obtain $U(T; X') - U(T'; X') \leqq 0$, which is absurd. ∎

Remark 10. If $(T; X) \xleftarrow{\text{a}} (T; X')$ exists, then we may consider the corresponding quasistatic process:

$$\left(\widetilde{T}; X \right) \xleftarrow{\text{qa}} (T; X') \tag{1.115}$$

Suppose $\widetilde{T} > T$. Then, we have the following "temperature" decreasing adiabatic process:

$$(T; X) \xleftarrow{\text{a}} (T; X') \xleftarrow{\text{qa}} \left(\widetilde{T}; X' \right) \tag{1.116}$$

which contradicts with Definition 1.2.6. Hence, $\widetilde{T} \leqq T$. Next, suppose $\widetilde{T} < T$, for contradiction. Form the following isothermal cycle:

$$(T; X) \underset{\text{i'}}{\overset{\text{qi}}{\rightleftarrows}} (T; X') \xrightarrow{\text{qa}} \left(\widetilde{T}; X \right) \tag{1.117}$$

where i'-process is under the T-reservoir. By Lemma 1.2.2, $U(T; X) > U\left(\widetilde{T} < T; X \right)$ as $T > \widetilde{T}$. The total work done by this cycle is

$$\begin{aligned} W &= U(T; X) - U(T; X') \\ &\quad + Q_{\max}(T; X \mapsto X') + U(T; X') - U\left(\widetilde{T}; X \right) + 0 \\ &= U(T; X) - U\left(\widetilde{T}; X \right). \end{aligned} \tag{1.118}$$

By Theorem 1.3.1, $W \leqq 0$ i.e., $U(T; X) \leqq U\left(\widetilde{T}; X \right)$, which is a contradiction.

Theorem 1.4.2 (The Universality of $Q_{\max}$ (Carnot)). *Let $(T_L; X_0)$ and X_1 satisfy $Q_{\max}(T_L; X_0 \mapsto X_1) > 0$, see Lemma 1.4.1. For T_H, consider $Q_{\max}(T_H; X_0' \mapsto$*

X'_1), where $(T_H; X'_0)$ and $(T_H; X'_1)$ are states such that the following quasistatic adiabatic processes exist:

$$
\begin{array}{cc}
(T_H; X'_0) & (T_H; X'_1) \\
\Big\uparrow qa & \Big\downarrow qa \\
(T_L; X_0) & (T_L; X_1)
\end{array}
\tag{1.119}
$$

We claim that the ratio of the maximum heat transfers, $Q_{\max}(T_L; X_0 \mapsto X_1)$ and $Q_{\max}(T_H; X'_0 \mapsto X'_1)$ depends neither on the specific systems nor on the states, but only on the "temperatures" T_L and T_H:

$$
f_C(T_H, T_L) := \frac{Q_{\max}(T_H; X'_0 \mapsto X'_1)}{Q_{\max}(T_L; X_0 \mapsto X_1)}
\tag{1.120}
$$

We call f_C the Carnot function.

Definition 1.4.3 (Absolute Temperature). Before proving Theorem 1.4.2, let us define absolute temperatures that we have already used in Remark 1 and Example 1.3.2. Observe that, for an arbitrary intermediate temperature $_M$ and corresponding transitions,

$$
f_C(T_H, T_L) = \frac{Q_{\max}(T_H; \sim)}{Q_{\max}(T_M; \sim)} \frac{Q_{\max}(T_M; \sim)}{Q_{\max}(T_L; \sim)} = \frac{f_C(T_H, T_M)}{f_C(T_L, T_M)},
\tag{1.121}
$$

where $\sim$ stands for the corresponding transitions under the given temperatures. Since the Carnot function $f_C(T_H, T_L)$ depends only on T_H and T_L, this motivates the introduction of an absolute temperature scale such as Kelvin or Rankine, so that the Carnot function coincides with the ratio of temperatures:

$$
f_C(T_H, T_L) = \frac{T_H}{T_L}.
\tag{1.122}
$$

We use an absolute temperature, instead of empirical "temperature" for equilibrium states.

Exercise 1.4.1 (Temperature Conversions). Find conversions among Celsius, Kelvin, Fahrenheit, and Rankine scales, see College Physics §13.1 Temperature and University Physics Volume 2 §1.2 Thermometers and Temperature Scales.

Let us define one of the most important concepts in Thermodynamics, the Carnot cycle.

Definition 1.4.4 (Carnot Cycle and Heat Engine). The following cycle – a heat "engine" – is called Carnot cycle:

$$
\begin{array}{ccc}
(T_H; X'_0) & \xrightarrow{qi} & (T_H; X'_1) \\
\Big\uparrow qa & & \Big\downarrow qa \\
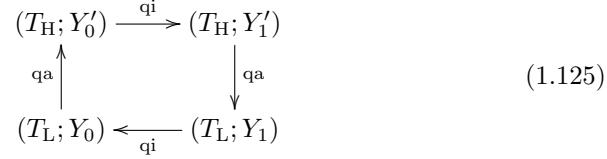(T_L; X_0) & \xleftarrow{qi} & (T_L; X_1)
\end{array}
\tag{1.123}
$$

The work W_{cyc} done by the cycle is

$$
\begin{aligned}
W_{\mathrm{cyc}} &= W_{\max}\left(T_{\mathrm{H}}; X_0' \mapsto X_1'\right) + U(T_{\mathrm{H}}; X_1') - U(T_{\mathrm{L}}; X_1) \\
&\quad + W_{\max}\left(T_{\mathrm{L}}; X_1 \mapsto X_0\right) + U(T_{\mathrm{L}}; X_0) - U(T_{\mathrm{H}}; X_0') \\
&= W_{\max}\left(T_{\mathrm{H}}; X_0' \mapsto X_1'\right) + U(T_{\mathrm{H}}; X_1') - U(T_{\mathrm{H}}; X_0') \\
&\quad - \left(W_{\max}\left(T_{\mathrm{L}}; X_0 \mapsto X_1\right) + U(T_{\mathrm{H}}; X_0') - U(T_{\mathrm{L}}; X_0)\right) \\
&= Q_{\max}\left(T_{\mathrm{H}}; X_0' \mapsto X_1'\right) - Q_{\max}\left(T_{\mathrm{L}}; X_0 \mapsto X_1\right),
\end{aligned}
\tag{1.124}
$$

where we used Definition 1.4.1.

By Definition 1.4.1, $Q_{\max}\left(T_{\mathrm{H}}; X_0' \mapsto X_1'\right)$ is the heat transfer from T_{H}-reservoir to the system. Similarly, along the process $T_1 \mapsto T_0$, the heat transfer from the T_{L}-reservoir to the system is $Q_{\max}\left(T_{\mathrm{H}}; X_1 \mapsto X_0\right) = -Q_{\max}\left(T_{\mathrm{H}}; X_0 \mapsto X_1\right) <$ 0. That is, $Q_{\max}\left(T_{\mathrm{H}}; X_0 \mapsto X_1\right) > 0$ represents the heat transfer from the system to T_{L}-reservoir. This type of energy transformation – converting heat from T_{H}-reservoir into work while wasting heat $Q_{\max}\left(T_{\mathrm{H}}; X_0 \mapsto X_1\right) > 0$ to T_{L}-reservoir – is called a heat engine, see Definition 1.4.5 and University Physics Volume 2 §4.2 Heat Engines.
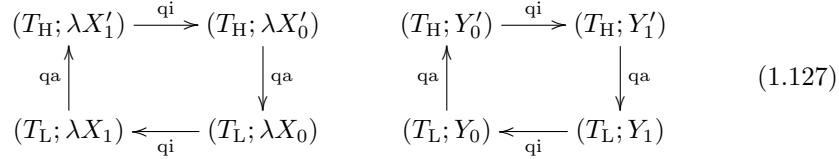
Proof of Theorem 1.4.2. Let Y_0 be an arbitrary state. By Lemma 1.4.1, there exists Y_1 such that $Q_{\max}\left(T_{\mathrm{L}}; Y_0 \mapsto Y_1\right) > 0$. Consider the Carnot cycle:

$$
\begin{array}{ccc}
(T_{\mathrm{H}}; Y_0') & \xrightarrow{\ \mathrm{qi}\ } & (T_{\mathrm{H}}; Y_1') \\
{\scriptstyle \mathrm{qa}} \big\uparrow & & \big\downarrow {\scriptstyle \mathrm{qa}} \\
(T_{\mathrm{L}}; Y_0) & \xleftarrow[\ \mathrm{qi}\ ]{} & (T_{\mathrm{L}}; Y_1)
\end{array}
\tag{1.125}
$$
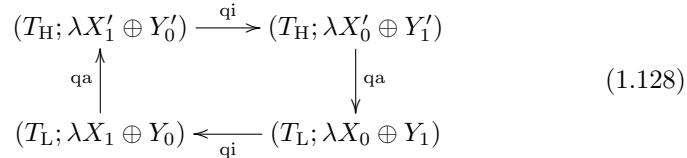
Define a positive scaling parameter:

$$
\lambda := \frac{Q_{\max}\left(T_{\mathrm{L}}; Y_0 \mapsto Y_1\right)}{Q_{\max}\left(T_{\mathrm{L}}; X_0 \mapsto X_1\right)} > 0.
\tag{1.126}
$$

Now, consider the following scaled but opposite Carnot cycle of λX together with (1.125):

$$
\begin{array}{ccccccc}
(T_{\mathrm{H}}; \lambda X_1') & \xrightarrow{\ \mathrm{qi}\ } & (T_{\mathrm{H}}; \lambda X_0') & \qquad & (T_{\mathrm{H}}; Y_0') & \xrightarrow{\ \mathrm{qi}\ } & (T_{\mathrm{H}}; Y_1') \\
{\scriptstyle \mathrm{qa}} \big\uparrow & & \big\downarrow {\scriptstyle \mathrm{qa}} & & {\scriptstyle \mathrm{qa}} \big\uparrow & & \big\downarrow {\scriptstyle \mathrm{qa}} \\
(T_{\mathrm{L}}; \lambda X_1) & \xleftarrow[\ \mathrm{qi}\ ]{} & (T_{\mathrm{L}}; \lambda X_0) & & (T_{\mathrm{L}}; Y_0) & \xleftarrow[\ \mathrm{qi}\ ]{} & (T_{\mathrm{L}}; Y_1)
\end{array}
\tag{1.127}
$$
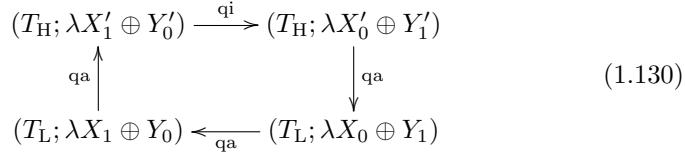
They can be processed simultaneously since they share the same temperature profiles:

$$
\begin{array}{ccc}
(T_{\mathrm{H}}; \lambda X_1' \oplus Y_0') & \xrightarrow{\ \mathrm{qi}\ } & (T_{\mathrm{H}}; \lambda X_0' \oplus Y_1') \\
{\scriptstyle \mathrm{qa}} \big\uparrow & & \big\downarrow {\scriptstyle \mathrm{qa}} \\
(T_{\mathrm{L}}; \lambda X_1 \oplus Y_0) & \xleftarrow[\ \mathrm{qi}\ ]{} & (T_{\mathrm{L}}; \lambda X_0 \oplus Y_1)
\end{array}
\tag{1.128}
$$

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The bottom quasistatic isothermal process satisfies:

$$Q_{\max} \left(T_{\mathrm{L}}; \lambda X_0 \oplus Y_1 \mapsto \lambda X_1 \oplus Y_0 \right)$$
$$= \lambda Q_{\max} \left(T_{\mathrm{L}}; X_0 \mapsto X_1 \right) - Q_{\max} \left(T_{\mathrm{L}}; Y_0 \mapsto Y_1 \right) \qquad (1.129)$$
$$= 0,$$

by the definition of the scale parameter $\lambda > 0$. Applying Lemma 1.4.2, a corresponding quasistatic adiabatic process exists. The resulting cycle is an isothermal cycle under T_{H}-reservoir:

$$
\begin{array}{ccc}
(T_{\mathrm{H}}; \lambda X_1' \oplus Y_0') & \xrightarrow{\text{qi}} & (T_{\mathrm{H}}; \lambda X_0' \oplus Y_1') \\
{\scriptstyle\text{qa}}\uparrow & & \downarrow{\scriptstyle\text{qa}} \\
(T_{\mathrm{L}}; \lambda X_1 \oplus Y_0) & \xleftarrow{\text{qa}} & (T_{\mathrm{L}}; \lambda X_0 \oplus Y_1)
\end{array}
\qquad (1.130)
$$

Hence, we may apply Theorem 1.3.1: the total work done is zero. Using Definition 1.4.4, we obtain

$$
\begin{aligned}
0 &= -\lambda \left(Q_{\max} \left(T_{\mathrm{H}}; X_0' \mapsto X_1' \right) - Q_{\max} \left(T_{\mathrm{L}}; X_0 \mapsto X_1 \right) \right) \\
&\quad + Q_{\max} \left(T_{\mathrm{H}}; Y_0' \mapsto Y_1' \right) - Q_{\max} \left(T_{\mathrm{L}}; Y_0 \mapsto Y_1 \right) \\
&= -\frac{Q_{\max} \left(T_{\mathrm{L}}; Y_0 \mapsto Y_1 \right)}{Q_{\max} \left(T_{\mathrm{L}}; X_0 \mapsto X_1 \right)} \left(Q_{\max} \left(T_{\mathrm{H}}; X_0' \mapsto X_1' \right) - Q_{\max} \left(T_{\mathrm{L}}; X_0 \mapsto X_1 \right) \right) \\
&\quad + Q_{\max} \left(T_{\mathrm{H}}; Y_0' \mapsto Y_1' \right) - Q_{\max} \left(T_{\mathrm{L}}; Y_0 \mapsto Y_1 \right) \\
&= -Q_{\max} \left(T_{\mathrm{L}}; Y_0 \mapsto Y_1 \right) \frac{Q_{\max} \left(T_{\mathrm{H}}; X_0' \mapsto X_1' \right)}{Q_{\max} \left(T_{\mathrm{L}}; X_0 \mapsto X_1 \right)} + Q_{\max} \left(T_{\mathrm{H}}; Y_0' \mapsto Y_1' \right).
\end{aligned}
$$
$$(1.131)$$

Since $Q_{\max} \left(T_{\mathrm{L}}; Y_0 \mapsto Y_1 \right) > 0$, we obtain

$$f_{\mathrm{C}} := \frac{Q_{\max} \left(T_{\mathrm{H}}; X_0' \mapsto X_1' \right)}{Q_{\max} \left(T_{\mathrm{L}}; X_0 \mapsto X_1 \right)} = \frac{Q_{\max} \left(T_{\mathrm{H}}; Y_0' \mapsto Y_1' \right)}{Q_{\max} \left(T_{\mathrm{L}}; Y_0 \mapsto Y_1 \right)} \qquad (1.132)$$

which establishes the universality of the Carnot function f_{C}, independence of the physical system. ∎

Remark 11. See College Physics 2e §15.4 Carnot's Perfect Heat Engine: The Second Law of Thermodynamics Restated, University Physics Volume 2 §4.5 The Carnot Cycle, and June 12, 1824: Sadi Carnot publishes treatise on heat engines[9].

1.4.3 Efficiency of Heat Engines

Definition 1.4.5 (Efficiency of Heat Engines)**.** Let $0 < T_{\mathrm{L}} < T_{\mathrm{H}}$ be two absolute temperatures. If a heat engine absorbs $Q_{\mathrm{H}} > 0$ of heat from the T_{H}-reservoir

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[9]https://www.aps.org/publications/apsnews/200906/physicshistory.cfm

and wastes $Q_L > 0$ to the T_L-reservoir, the work W done by the engine is defined via:

$$E \xrightarrow[\Downarrow W \quad \Downarrow Q_L]{\Downarrow Q_H} E \qquad W = Q_H - Q_L. \tag{1.133}$$

The efficiency ε of this heat engine is

$$\varepsilon := \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H}. \tag{1.134}$$

See College Physics §15.2 The First Law of Thermodynamics and Some Simple Processes and University Physics Volume 2 §4.2 Heat Engines.

Lemma 1.4.3 (The Efficiency of Carnot Cycle). *The efficiency of the Carnot cycle in Definition 1.4.4, if it is viewed as a heat engine, is*

$$\varepsilon_C = 1 - \frac{T_L}{T_H}, \tag{1.135}$$

where $T_L < T_H$ are the absolute temperatures of the cold and hot reservoirs.

Proof. By Definition 1.4.3, the Carnot function satisfies

$$f_C(T_H, T_L) = \frac{T_H}{T_L} = \frac{Q_{\max}(T_H; X_0' \mapsto X_1')}{Q_{\max}(T_L; X_0 \mapsto X_1)} \tag{1.136}$$

and the work done in the Carnot cycle is

$$W_{\text{cyc}} = Q_{\max}\left(T_H; X_0' \mapsto X_1'\right) - Q_{\max}\left(T_L; X_0 \mapsto X_1\right). \tag{1.137}$$

Hence, the efficiency is

$$1 - \frac{Q_{\max}(T_L; X_0 \mapsto X_1)}{Q_{\max}(T_H; X_0' \mapsto X_1')} = 1 - \frac{T_L}{T_H}, \tag{1.138}$$

as claimed. ∎

Remark 12 (Maximum Efficiency). Carnot's cycle is sometimes called a perfect heat engine: College Physics §15.4 Carnot's Perfect Heat Engine: The Second Law of Thermodynamics Restated and University Physics Volume 24.5 The Carnot Cycle. This means that for any heat engine operating between two heat baths with $T_L < T_H$, its efficiency is always less than or equal to that of Carnot's cycle.

Exercise 1.4.2. Carnot showed that no heat engine can exceed the efficiency of a Carnot's cycle. Let us illustrate his claim.

Consider an arbitrary heat engine:

$$e \xrightarrow[\Downarrow w \quad \Downarrow q_L]{\Downarrow q_H} e \tag{1.139}$$

1. Define the efficiency ε' of this process.

2. Let $\lambda := \frac{q_{\mathrm{H}}}{Q_{\mathrm{H}}}$ and consider the inverse of the λ-scaled Carnot cycle as in Lemma 1.4.3.

3. Combine these two processes – the engine (1.139) and the scaled inverse Carnot process in Lemma 1.4.3 – to form a new heat engine:

$$E' \xdashrightarrow[\;\Downarrow W' \quad \Downarrow Q'_{\mathrm{L}}\;]{\Downarrow Q'_{\mathrm{H}}} E' \tag{1.140}$$

Determine W', Q'_{H}, and Q'_{L}.

4. Show that the combined system thermally interacts with only one heat bath.

5. If we identify such a cycle as an isothermal process. Then, by Theorem 1.3.1, conclude $\varepsilon' \leqq \varepsilon_{\mathrm{C}}$.

Carnot's theorem can be proved under milder assumptions with full mathematical rigor, see Theorem 1.5.4.

1.5 Entropy

Heat cannot be completely converted to mechanical work; there is always some inevitable loss. The thermodynamic quantity that provides an analytical expression of loss of availability is called entropy.

1.5.1 Entropy

Definition 1.5.1 (Entropy). For an equilibrium state $(T; X)$, we define the entropy as

$$S(T; X) := \frac{U(T; X) - F[T; X]}{T}. \tag{1.141}$$

For a quasistatic isothermal process, $(T; X_1) \xrightarrow{\mathrm{qi}} (T; X_2)$, recalling Definition 1.4.1, the heat transfer $Q_{\max}(T; X_1 \mapsto X_2)$ from T-reservoir is

$$Q_{\max}(T; X_1 \mapsto X_2) = U(T; X_2) - F[T; X_2] - (U(T; X_1) - F[T; X_1]) \tag{1.142}$$

Hence, entropy S satisfies, along the quasistatic isothermal process $(T; X_1) \xrightarrow{\mathrm{qi}} (T; X_2)$, entropy satisfies

$$S(T; X_1) \xdashrightarrow{\Downarrow Q_{\max}/T} S(T; X_2) \quad S(T; X_2) - S(T; X_1) = \frac{Q_{\max}(T; X_1 \mapsto X_2)}{T} \tag{1.143}$$

See also College Physics §15.6 Entropy and the Second Law of Thermodynamics and University Physics Volume 2 §4.6 Entropy. That is, the entropy $S(T; X)$ acts as a stock, and the corresponding flow is the maximum heat transfer per temperature.

Remark 13 (Availability and Unavailability). Recalling the natures of Helmholtz' free energy F and internal energy U, the very definition of entropy $S := \frac{U-F}{T}$ implies the following:

> When entropy increases, a certain amount of energy becomes permanently unavailable to do work. The energy is not lost, but its character is changed, so that some of it can never be converted to doing work—that is, to an organized force acting through a distance.[10]

Exercise 1.5.1. Determine the corresponding SI unit for the entropy S. See NIST Guide to the SI, Chapter 4: The Two Classes of SI Units and the SI Prefixes[11].

Lemma 1.5.1. *Under the quasistatic adiabatic processes in Theorem 1.4.2:*

$$\begin{array}{ccc} (T_H; X_0') & & (T_H; X_1') \\ {\scriptstyle qa}\Big\updownarrow & & \Big\updownarrow{\scriptstyle qa} \\ (T_L; X_0) & & (T_L; X_1) \end{array} \tag{1.144}$$

the change in entropy is invariant:

$$S(T_H; X_0') - S(T_L; X_0) = S(T_H; X_1') - S(T_L; X_1). \tag{1.145}$$

Proof. By Theorem 1.4.2 and Definition 1.4.3, for the given quasistatic adiabatic processes, the Carnot function satisfies

$$\frac{T_H}{T_L} = \frac{Q_{\max}(T_H; X_0' \mapsto X_1')}{Q_{\max}(T_L; X_0 \mapsto X_1)}. \tag{1.146}$$

Hence, using Definition 1.5.1, we have

$$\begin{aligned} S(T_H; X_1') - S(T_H; X_0') &= \frac{Q_{\max}(T_H; X_0' \mapsto X_1')}{T_H} \\ &= \frac{Q_{\max}(T_L; X_0 \mapsto X_1)}{T_L} \\ &= S(T_L; X_1) - S(T_L; X_0). \end{aligned} \tag{1.147}$$

This proves the invariance of entropy change under quasistatic adiabatic processes. ∎

Remark 14 (Entropy and Quasistatic Adiabatic Process). As we did for internal energy in Definition 1.2.3 and Helmholtz's free energy in Definition 1.3.7, we may choose a reference point so that the entropy itself is invariant under quasistatic

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[10]College Physics 2e §15.6 Entropy and the Second Law of Thermodynamics: Disorder and the Unavailability of Energy

[11]Chapter 4 of `https://www.nist.gov/pml/special-publication-811`

adiabatic processes. Let $(T_*; \lambda X_*)$ be such a reference point for $\lambda > 0$. We assign the corresponding entropy value λS_* for a scaled system:

$$S(T_*; \lambda X_*) := \lambda S_*. \tag{1.148}$$

Then, for any state $(T; \lambda X)$ and a quasistatic adiabatic process $(T; \lambda X) \overset{\text{qa}}{\longleftrightarrow} (T_*; \lambda X_*)$,

$$S(T; \lambda X) := \lambda S_*. \tag{1.149}$$

In particular, if we choose $(T_\mathrm{L}; X_0)$ as the reference point $(T_*; X_*)$, we obtain $0 = S(T_\mathrm{H}; X_1') - S(T_\mathrm{L}; X_1)$. That is, along a quasistatic adiabatic process, say $(T_L; X_1) \overset{\text{qa}}{\longrightarrow} (T_H; X_1')$, entropy remains constant:

$$S(T_\mathrm{L}; X_1) = S(T_\mathrm{H}; X_1'). \tag{1.150}$$

Theorem 1.5.1. *Entropy S is an increasing function of temperature. Moreover, for a state $(T; X)$, if both entropy S and internal energy are differentiable at $(T; X)$:*

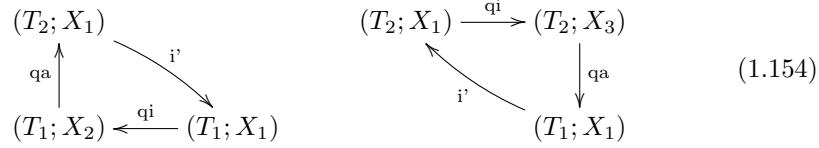$$\frac{\partial U(T; X)}{\partial T} = T \frac{\partial S(T; X)}{\partial T}. \tag{1.151}$$

Remark 15 (The Heat Capacity). Recalling Definition 1.2.4, we have

$$C_V(T; X) = T \frac{\partial S(T; X)}{\partial T}. \tag{1.152}$$

Proof. Let $0 < T_1 < T_2$. For an arbitrary state X_1 state, select states X_2, X_3 satisfying

$$(T_2; X_1) \overset{\text{qa}}{\longleftrightarrow} (T_1; X_2)$$
$$(T_1; X_1) \overset{\text{qa}}{\longleftrightarrow} (T_2; X_3). \tag{1.153}$$

Consider the following two cycles:

$$
\begin{array}{cc}
\begin{array}{ccc}
(T_2; X_1) & & \\
\Big\uparrow {\scriptstyle \text{qa}} & \searrow {\scriptstyle \text{i'}} & \\
(T_1; X_2) & \xleftarrow{\ \text{qi}\ } & (T_1; X_1)
\end{array}
&
\begin{array}{ccc}
(T_2; X_1) & \xrightarrow{\ \text{qi}\ } & (T_2; X_3) \\
\nwarrow & & \Big\downarrow {\scriptstyle \text{qa}} \\
{\scriptstyle \text{i'}} & & (T_1; X_1)
\end{array}
\end{array}
\tag{1.154}
$$

- Left cycle

  The process $(T_2; X_1) \overset{\text{i'}}{\longrightarrow} (T_1; X_1)$ is a T_1-isothermal process with no work, see Remark 9. Since the entire cycle is under the T_1-reservoir, by Theorem 1.3.1, the total work satisfies

$$
\begin{aligned}
0 \geq & W_{\max}(T_1; X_1 \mapsto X_2) + W_{\text{ad}}((T_1; X_2) \to (T_2; X_2)) + 0 \\
= & F[T_1; X_1] - F[T_1; X_2] + U(T_1; X_2) - U(T_2; X_1) \\
= & F[T_1; X_1] - F[T_1; X_2] + U(T_1; X_2) - U(T_2; X_1) - U(T_1; X_1) + U(T_1; X_1) \\
= & T_1 (S(T_1; X_2) - S(T_1; X_1)) - U(T_2; X_1) + U(T_1; X_1)
\end{aligned}
\tag{1.155}
$$

By Remark 14, the entropy is invariant under quasistatic adiabatic processes, $S(T_1; X_2) = S(T_2; X_1)$. Hence,

$$T_1 \left(S(T_2; X_1) - S(T_1; X_1) \right) - U(T_2; X_1) + U(T_1; X_1) \leqq 0. \qquad (1.156)$$

Arranging, we obtain

$$S(T_2; X_1) - S(T_1; X_1) \leqq \frac{U(T_2; X_1) - U(T_1; X_1)}{T_1}. \qquad (1.157)$$

- Right cycle

  Along the right cycle, since it is an isothermal cycle under the T_2-reservoir, the total the total work satisfies:

$$
\begin{aligned}
0 \geqq & W_{\max}(T_2; X_1 \mapsto X_3) + W_{\mathrm{ad}}((T_2; X_3) \to (T_1; X_1)) + 0 \\
= & F[T_2; X_1] - F[T_2; X_3] + U(T_2; X_3) - U(T_1; X_1) - U(T_2; X_1) + U(T_2; X_1) \\
= & T_2 \left(S(T_2; X_3) - S(T_2; X_1) \right) - U(T_1; X_1) + U(T_2; X_1) \\
= & T_2 \left(S(T_1; X_1) - S(T_2; X_1) \right) - U(T_1; X_1) + U(T_2; X_1)
\end{aligned}
$$

$$(1.158)$$

  Hence, we obtain

$$\frac{U(T_2; X_1) - U(T_1; X_1)}{T_2} \leqq S(T_2; X_1) - S(T_1; X_1). \qquad (1.159)$$

  By Lemma 1.2.2, U is an increasing function of temperature. Thus, the left-hand side is positive since $T_1 < T_2$, and we conclude that the entropy is also an increasing function of temperature:

$$S(T_1; X_1) < S(T_2; X_1). \qquad (1.160)$$

Combining the outcomes, we obtain

$$\frac{1}{T_2} \frac{U(T_2; X_1) - U(T_1; X_1)}{T_2 - T_1} \leqq \frac{S(T_2; X_1) - S(T_1; X_1)}{T_2 - T_1} \leqq \frac{1}{T_1} \frac{U(T_2; X_1) - U(T_1; X_1)}{T_2 - T_1}$$

$$(1.161)$$

Taking the limit $T_2 \dashrightarrow T_1$, we obtain the desired result. ∎

Corollary 1.5.1.1. *As chosen above, if two states are accessible with a quasistatic adiabatic process, say $(T_1; X_1) \overset{qa}{\longleftrightarrow} (T_2; X_2)$, then $S(T_1; X_1) = S(T_2; X_2)$ holds. Conversely, if $S(T_1; X_1) = S(T_2; X_2)$, then there exists a quasistatic adiabatic process connecting these two states.*

Proof. Suppose $S(T_1; X_1) = S(T_2; X_2)$. Starting from the state $(T_1; X_1)$, consider the following quasistatic adiabatic process:

$$(T_1; X_1) \overset{\mathrm{qa}}{\longrightarrow} (T_3; X_2), \qquad (1.162)$$

where T_3 is the final temperature by this adiabatic process. We will show T_3 coincides T_2, i.e., this is the desired quasistatic adiabatic process.

Because the process is quasistatic adiabatic process, the entropy remains constant, $S(T_1; X_1) = S(T_3; X_2)$. Hence, $S(T_2; X_2) = S(T_3; X_2)$. As shown in Theorem 1.5.1, the entropy for fixed X_2, $S(\_; X_2)$, is increasing function of temperature. Hence, the equality $S(T_2; X_2) = S(T_3; X_2)$ implies $T_2 = T_3$. ∎

Example 1.5.1 (Entropy and Helmholtz's Free Energy of Ideal Gas)**.** Fix the constant $v(T)$ appeared in (1.79) of Example 1.3.2. Consider a state $\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)$ with a reference point

$$\left(T; \lambda \begin{pmatrix} V \\ N \end{pmatrix}\right) \overset{\text{qa}}{\longleftrightarrow} \left(T; \lambda \begin{pmatrix} V_* \\ N \end{pmatrix}\right).$$

$$S\left(T_*; \lambda \begin{pmatrix} V_* \\ N \end{pmatrix}\right) := \lambda c N R, \lambda > 0. \tag{1.163}$$

By Example 1.3.2, we have F and S for the ideal gas. Hence,

$$S\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) := \frac{U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) - F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right]}{T} = \frac{cNRT + Nu + NRT \ln \frac{V}{v(T)N}}{T} \tag{1.164}$$

The entropy remains constant under a quasistatic adiabatic process, as shown in Remark 14. Thus, we have

$$\lambda \left(\frac{Nu}{T} + NR \ln \frac{V}{v(T)N}\right) = 0. \tag{1.165}$$

Taking exponential, we obtain

$$v(T) = \frac{V}{N} \exp\left(\frac{u}{RT}\right). \tag{1.166}$$

Recalling Example 1.3.2, the Poisson relation for an ideal gas is $T^c V = T_*{}^c V_*$:

$$V = \left(\frac{T_*}{T}\right)^c V_*, \tag{1.167}$$

we establish:

$$v(T) = \left(\frac{T_*}{T}\right)^c \frac{V_*}{N} \exp\left(\frac{u}{RT}\right) = \left(\frac{T_*}{T}\right)^c v_* \exp\left(\frac{u}{RT}\right). \tag{1.168}$$

Substituting back, we obtain the entropy for an ideal gas:

$$S\left(T; \lambda \begin{pmatrix} V \\ N \end{pmatrix}\right) = \lambda \left(cNR + NR \ln\left(\left(\frac{T}{T^*}\right)^c \frac{V}{V_*}\right)\right)$$

$$= \lambda \left(cNR + NR \ln\left(\left(\frac{T}{T^*}\right)^c \frac{V}{v_* N}\right)\right). \tag{1.169}$$

We also have

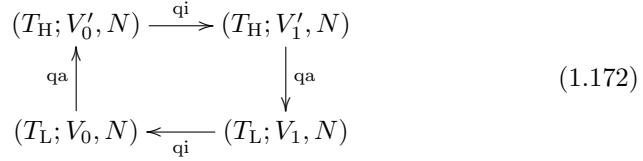$$F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right] = -NRT \ln \frac{V}{v(T)N} = -NRT \ln \left(\left(\frac{T}{T_*}\right)^c \frac{V}{V_*}\right) + Nu. \quad (1.170)$$

Example 1.5.2 (Ideal Gas Thermometer). Recalling Example 1.5.1, let us examine an ideal gas used as thermometer. The Helmholtz free energy of an ideal gas is

$$F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right] = -NRT \ln \left(\left(\frac{T}{T_*}\right)^c \frac{V}{V_*}\right) + Nu, \quad (1.171)$$

where the temperature is an absolute temperature in Definition 1.4.3. We will see that the temperature in (1.75) of Example 1.3.2 is indeed the absolute temperature. Consider the following Carnot cycle:

$$
\begin{array}{ccc}
(T_{\mathrm{H}}; V_0', N) & \xrightarrow{\mathrm{qi}} & (T_{\mathrm{H}}; V_1', N) \\
{\scriptstyle \mathrm{qa}} \uparrow & & \downarrow {\scriptstyle \mathrm{qa}} \\
(T_{\mathrm{L}}; V_0, N) & \xleftarrow{\quad \mathrm{qi} \quad} & (T_{\mathrm{L}}; V_1, N)
\end{array}
\quad (1.172)
$$

As shown in Example 1.3.2, under quasistatic isothermal processes, the internal energy does not change. Hence, we have

$$
\begin{aligned}
f_{\mathrm{C}}(T_{\mathrm{H}}, T_{\mathrm{L}}) &:= \frac{Q_{\max}\left(T_{\mathrm{H}}; V_0' \mapsto V_1'\right)}{Q_{\max}\left(T_{\mathrm{L}}; V_0 \mapsto V_1\right)} \\
&= \frac{F\left[T_{\mathrm{H}}; \begin{pmatrix} V_0' \\ N \end{pmatrix}\right] - F\left[T_{\mathrm{H}}; \begin{pmatrix} V_1' \\ N \end{pmatrix}\right] + U\left(T_{\mathrm{H}}; \begin{pmatrix} V_1' \\ N \end{pmatrix}\right) - U\left(T_{\mathrm{H}}; \begin{pmatrix} V_0' \\ N \end{pmatrix}\right)}{F\left[T_{\mathrm{L}}; \begin{pmatrix} V_0 \\ N \end{pmatrix}\right] - F\left[T_{\mathrm{L}}; \begin{pmatrix} V_1 \\ N \end{pmatrix}\right] + F\left[T_{\mathrm{L}}; \begin{pmatrix} V_1 \\ N \end{pmatrix}\right] - F\left[T_{\mathrm{L}}; \begin{pmatrix} V_0 \\ N \end{pmatrix}\right]} \\
&= \frac{F\left[T_{\mathrm{H}}; \begin{pmatrix} V_0' \\ N \end{pmatrix}\right] - F\left[T_{\mathrm{H}}; \begin{pmatrix} V_1' \\ N \end{pmatrix}\right]}{F\left[T_{\mathrm{L}}; \begin{pmatrix} V_0 \\ N \end{pmatrix}\right] - F\left[T_{\mathrm{L}}; \begin{pmatrix} V_1 \\ N \end{pmatrix}\right]} \\
&= \frac{NRT_{\mathrm{H}} \ln\left(\frac{V_1'}{V_0'}\right)}{NRT_{\mathrm{L}} \ln\left(\frac{V_1}{V_0}\right)}
\end{aligned}
$$

$$(1.173)$$

Poisson equation in Example 1.3.2 implies:

$$
\begin{aligned}
(T_{\mathrm{H}})^c V_1' &= (T_{\mathrm{L}})^c V_1 \\
(T_{\mathrm{H}})^c V_0' &= (T_{\mathrm{L}})^c V_0.
\end{aligned}
\quad (1.174)
$$

Taking the ratio, we have

$$\frac{V_1'}{V_0'} = \frac{V_1}{V_0} \quad (1.175)$$

Substituting this back, we obtain

$$f_{\mathrm{C}}(T_{\mathrm{H}}, T_{\mathrm{L}}) = \frac{T_{\mathrm{H}}}{T_{\mathrm{L}}}. \tag{1.176}$$

Thus, the temperature in the ideal gas state equation $pV = NRT$ coincides with the absolute temperature.

Example 1.5.3 (Entropy and Heat Transfer). Along a quasistatic isothermal process $(T; X) \xrightarrow{\mathrm{qi}} (T; X')$ define

$$\begin{aligned} \Delta Q &:= Q_{\max}(T; X \mapsto X') \\ \Delta S &:= S(T; X') - S(T; X). \end{aligned} \tag{1.177}$$

Then, by Definition 1.5.1, (1.143) gives

$$\Delta S = \frac{\Delta Q}{T}. \tag{1.178}$$

If the transition $X \mapsto X'$ is quasistatic and adiabatic, then no heat transfer, $\Delta Q = 0$ and no entropy change $\Delta S = 0$, see Remark 14. Thus, both sides are zero.

From (T, X) to (T', X'), consider the following sequence of quasistatic isothermal and quasistatic adiabatic processes:

$$(T, X) \xrightarrow{\mathrm{qi}} (T; X_1) \xrightarrow{\mathrm{qa}} (T_1, X_1) \xrightarrow{\mathrm{qi}} (T_1; X_2) \xrightarrow{\mathrm{qa}} (T_2, X_2) \xrightarrow{\mathrm{qi}} \cdots (T', X') \tag{1.179}$$

Such a path from $(T; X)$ to $(T'; X')$ is not unique, but along any specific path, we can collect the entropy change:

$$S(T'; X') - S(T; X) = \sum_{k=1}^{n} \Delta S_k = \sum_{k=1}^{n} \frac{\Delta Q_k}{T_k}, \tag{1.180}$$

where $(T_n; X_n) = (T'; X')$, $(T_0; X_0) = (T; X)$, and

$$\Delta Q_k = \Delta Q_k + 0 = Q_{\max}(T_{k-1}; X_{k-1} \mapsto X_k) + 0 \tag{1.181}$$

is the net heat transfer to the system along $(T_{k-1}, X_{k-1}) \xrightarrow{\mathrm{qi}} (T_{k-1}; X_k) \xrightarrow{\mathrm{qa}} (T_k, X_k)$ for $k \in \{1, \cdots, n\}$. If we formally take the limit $n \dashrightarrow \infty$, we obtain the Riemann integral representation of the entropy difference:

$$S(T'; X') - S(T; X) = \int_{(T;X)}^{(T';X')} \frac{\mathrm{d}Q}{T}. \tag{1.182}$$

See University Physics Volume 2 §4.6 Entropy.

1.5.2 Entropy Principle

Theorem 1.5.2 (Entropy Principle). *Let X_1, X_2 be physically accessible states. For $T_1, T_2 > 0$, an adiabatic process exists $(T_1; X_1) \xrightarrow{a} (T_2; X_2)$ iff $S(T_1; X_1) \leqq S(T_2; X_2)$.*

Remark 16. As a consequence, an adiabatic process from $(T_1; X_1)$ to $(T_2; X_2)$ is reversible iff $S(T_1; X_1) = S(T_2; X_2)$. Since any quasistatic process is reversible by Definition 1.2.1 and Corollary 1.5.1.1, the entropy remains constant under quasistatic processes.

Proof. ($\Rightarrow$) Assume $S(T_1, X_1) \leqq S(T_2; X_2)$. Along $X_1 \mapsto X_2$, consider the following quasistatic adiabatic process:

$$(T_1; X_1) \xrightarrow{\mathrm{qa}} (T_3; X_2), \tag{1.183}$$

where T_3 is the resulting temperature. Since a quasistatic adiabatic process preserves entropy,

$$S(T_3; X_2) = S(T_1; X_1) \leqq S(T_2; X_2). \tag{1.184}$$

By Theorem 1.5.1, we conclude $T_3 \leqq T_2$. By Definition 1.2.2, there exists an adiabatic process

$$(T_3; X_2) \xrightarrow{a} (T_2; X_2). \tag{1.185}$$

Thus, we obtain the desired adiabatic process:

$$(T_1; X_1) \xrightarrow{\mathrm{qa}} (T_3; X_2) \xrightarrow{a} (T_2; X_2). \tag{1.186}$$

($\Leftarrow$) Conversely, suppose an adiabatic process

$$(T_1; X_1) \xrightarrow{\mathrm{qa}} (T_2; X_2) \tag{1.187}$$

exists. Along the reverse change $X_2 \mapsto X_1$, consider quasistatic adiabatic process

$$(T_2; X_2) \xrightarrow{\mathrm{qa}} (T_4; X_1). \tag{1.188}$$

Combining the two processes, we have

$$(T_1; X_1) \xrightarrow{\mathrm{qa}} (T_2; X_2) \xrightarrow{\mathrm{qa}} (T_4; X_1). \tag{1.189}$$

By Definition 1.2.6, $T_1 \leqq T_4$ holds. Since quasistatic adiabatic processes preserve entropy, $S(T_1; X_1) = (T_2; X_2)$. Entropy is increasing in temperature at fixed X by Theorem 1.5.1. Hence $S(T_1; X_1) = (T_2; X_2) \leqq S(T_4; X_1)$. ∎

Theorem 1.5.3 (Entropy is Essentially Unique). *Let $\lambda > 0$. If S' satisfies the entropy principle in Theorem 1.5.2,*

$$\begin{aligned} S'(T; \lambda X) &= \lambda S'(T; X) \\ S'(T; X \oplus Y) &= S'(T; X) + S'(T; Y), \end{aligned} \tag{1.190}$$

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then there exist constants $A > 0$ and B such that

$$S'(T; \lambda X) = AS(T; \lambda X) + \lambda B. \tag{1.191}$$

In other words, the entropy is unique up to an affine transformation with a positive scale.

Proof. Let $T > 0$, and X_1, X_2 be two physically accessible states of some system. Suppose $S(T; X_1) < S(T; X_2)$ and define:

$$A := \frac{S'(T; \lambda X_2) - S'(T; \lambda X_1)}{S(T; \lambda X_2) - S(T; \lambda X_1)} = \frac{S'(T; X_2) - S'(T; X_1)}{S(T; X_2) - S(T; X_1)}. \tag{1.192}$$

Since $S(T; X_1) < S(T; X_2)$ implies the adiabatic process $S(T; X_1) \xrightarrow{\text{a}} S(T; X_2)$ is irreversible, the same must hold for S', $S'(T; X_1) < S'(T; X_2)$. Thus $A > 0$.

Define B via:

$$\begin{aligned}
\lambda B &:= S'(T; \lambda X_2) - AS(T; \lambda X_2) \\
&= S'(T; \lambda X_1) - AS(T; \lambda X_1) \\
&= \lambda \left(S'(T; X_1) - AS(T; X_1) \right).
\end{aligned} \tag{1.193}$$

Next, we will show for X of an arbitrary accessible state from X_1, $S'(T; \lambda X) = AS(T; \lambda X) + \lambda B$. If $S(T; X) \leqq S(T; X_1)$ then define $\lambda_A \geqq 0$:

$$\lambda_A := \frac{S(T; X_1) - S(T; X)}{S(T; X_2) - S(T; X_1)}. \tag{1.194}$$

Equivalently, $\lambda_A S(T; X_2) - \lambda_A S(T; X_1) = S(T; X_1) - S(T; X)$ holds. Then

$$\begin{aligned}
S\left(T; (\lambda_A + 1) X_1\right) &= (\lambda_A + 1) S(T; X_1) \\
&= \lambda_A S(T; X_2) + S(T; X) \\
&= S\left(T; X \oplus \lambda_A X_2\right).
\end{aligned} \tag{1.195}$$

Similarly, we obtain $S\left(T; (\lambda_A + 1) \lambda X_1\right) = S\left(T; \lambda X \oplus \lambda_A \lambda X_2\right)$. By Corollary 1.5.1.1, there exists a quasistatic adiabatic process

$$\left(T; (\lambda_A + 1) \lambda X_1\right) \xrightarrow{\text{qa}} \left(T; \lambda X \oplus \lambda_A \lambda X_2\right). \tag{1.196}$$

Hence

$$S'\left(T; (\lambda_A + 1) \lambda X_1\right) = S'\left(T; \lambda X \oplus \lambda_A \lambda X_2\right). \tag{1.197}$$

Moreover,

$$\frac{S(T; \lambda X_1) - S(T; \lambda X)}{S(T; \lambda X_2) - S(T; \lambda X_1)} = \lambda_A = \frac{S'(T; \lambda X_1) - S'(T; \lambda X)}{S'(T; \lambda X_2) - S'(T; \lambda X_1)}. \tag{1.198}$$

Solving for $S'(T; \lambda X)$, we obtain the desired result for the state $(T; \lambda X)$,

$$\begin{aligned}
S'(T; \lambda X) - S'(T; \lambda X_1) &= \lambda_A \left(S'(T; \lambda X_2) - S'(T; \lambda X_1) \right) \\
&= A \left(S(T; \lambda X) - S(T; \lambda X_1) \right) \\
S'(T; \lambda X) &= AS(T; \lambda X) + S'(T; \lambda X_1) - AS(T; \lambda X_1) \\
&= AS(T; \lambda X) + \lambda B.
\end{aligned} \tag{1.199}$$

If $S(T; X) > S(T; X_1)$, we define $\lambda'_A > 0$, define

$$\lambda'_A := \frac{S(T; X) - S(T; X_1)}{S(T; X_2) - S(T; X_1)} > 0. \tag{1.200}$$

Then

$$S\left(T; X_1 \oplus \lambda'_A X_2\right) = S\left(T; \lambda'_A X_1 \oplus X\right). \tag{1.201}$$

Scaling gives the corresponding identity for λX. With the same discussion, we conclude

$$\frac{S(T; \lambda X) - S(T; \lambda X_1)}{S(T; \lambda X_2) - S(T; \lambda X_1)} = \lambda'_A = \frac{S(T; \lambda X) - S(T; \lambda X_1)}{S(T; \lambda X_2) - S(T; \lambda X_1)}. \tag{1.202}$$

■

1.5.3 Entropy for Composite System

Definition 1.5.2. For a composite system

$$\{(T_1; X_1) \,|\, \cdots \,|\, (T_n; X_n)\} \tag{1.203}$$

where $|$ denotes an adiabatic wall as in Lemma 1.3.1, we define its entropy by

$$S\left(\{(T_1; X_1) \,|\, \cdots \,|\, (T_n; X_n)\}\right) := \sum_{j=1}^{n} S\left(T_j; X_j\right). \tag{1.204}$$

Lemma 1.5.2 (Entropy Principle for Composite System). *Suppose $(X_1, \cdots, X_n)$ and $(X'_1, \cdots, X'_m)$ are physically accessible. Then an adiabatic process*

$$\left(\{(T_1; X_1) \,|\, \cdots \,|\, (T_n; X_n)\}\right) \xrightarrow{a} \left(\{(T'_1; X'_1) \,|\, \cdots \,|\, (T'_m; X'_m)\}\right) \tag{1.205}$$

exists iff

$$S\left(\{(T_1; X_1) \,|\, \cdots \,|\, (T_n; X_n)\}\right) \leqq S\left(\{(T'_1; X'_1) \,|\, \cdots \,|\, (T'_m; X'_m)\}\right). \tag{1.206}$$

Proof. It suffices to consider the binary case, $\{(T_1; X_1) \,|\, (T_2; X_2)\}$. Its entropy is

$$S\left(T_1; X_1\right) + S\left(T_2; X_2\right). \tag{1.207}$$

Fix the value $S\left(T_2; X_2\right)$. We may adjust the temperature of the second component to T_1 by choosing an accessible state $\widetilde{X_2}$ such that

$$S\left(T_2; X_2\right) = S\left(T_1; \widetilde{X_2}\right). \tag{1.208}$$

By Theorem 1.5.2, there exists a quasistatic adiabatic process:

$$(T_2; X_2) \xleftrightarrow{\text{qa}} \left(T_1; \widetilde{X_2}\right). \tag{1.209}$$

Thus, we have

$$\{(T_1; X_1)|(T_2; X_2)\} \overset{\text{qa}}{\longleftrightarrow} \left\{(T_1; X_1)\Big|\left(T_1; \widetilde{X_2}\right)\right\} \overset{\text{qa}}{\longleftrightarrow} \left(T_1; X_1 \oplus \widetilde{X_2}\right) \qquad (1.210)$$

where the final step is the adiabatic wall removal. Since the total system is already at T_1, the wall removal can be done quasistatically and adiabatically.

Repeating this process for all components, we obtain

$$S\left(\{(T_1; X_1)\,|\cdots|\,(T_n; X_n)\}\right) = S\left(T_1; X_1 \oplus \widetilde{X_2} \oplus \cdots \oplus \widetilde{X_n}\right) \qquad (1.211)$$

and similarly,

$$S\left(\{(T_1'; X_1')\,|\cdots|\,(T_m'; X_m')\}\right) = S\left(T_1'; X_1' \oplus \widetilde{X_2'} \oplus \cdots \oplus \widetilde{X_m'}\right) \qquad (1.212)$$

That is, an adiabatic process

$$\left(T_1; X_1 \oplus \widetilde{X_2} \oplus \cdots \oplus \widetilde{X_n}\right) \overset{\text{a}}{\to} \left(T_1'; X_1' \oplus \widetilde{X_2'} \oplus \cdots \oplus \widetilde{X_m'}\right) \qquad (1.213)$$

exists iff the following inequality is the case:

$$S\left(T_1; X_1 \oplus \widetilde{X_2} \oplus \cdots \oplus \widetilde{X_n}\right) \leqq S\left(T_1'; X_1' \oplus \widetilde{X_2'} \oplus \cdots \oplus \widetilde{X_m'}\right). \qquad (1.214)$$

Since quasistatic adiabatic processes are reversible, we obtain the desired result, namely,

$$S\left(\{(T_1; X_1)\,|\cdots|\,(T_n; X_n)\}\right) \leqq S\left(\{(T_1'; X_1')\,|\cdots|\,(T_m'; X_m')\}\right) \qquad (1.215)$$

iff the following adiabatic process exists:

$$
\begin{array}{ccc}
\left(\{(T_1; X_1)\,|\cdots|\,(T_n; X_n)\}\right) & & \left(\{(T_1'; X_1')\,|\cdots|\,(T_m'; X_m')\}\right) \\
\Big\downarrow \text{qa} & & \Big\uparrow \text{qa} \\
\left(T_1; X_1 \oplus \widetilde{X_2} \oplus \cdots \oplus \widetilde{X_n}\right) & \xrightarrow{\;\;a\;\;} & \left(T_1'; X_1' \oplus \widetilde{X_2'} \oplus \cdots \oplus \widetilde{X_m'}\right)
\end{array}
\qquad (1.216)
$$

∎

As discussed in Remark 12 and Exercise 1.4.2, Carnot's cycles achieve the maximum possible efficiency among all heat engines. We now preset a more rigorous formulation of this result, following [LY99].

Theorem 1.5.4 (Maximum Efficiency (Carnot)). *Under the hypothesis of Theorem 1.5.1, no heat engine can operate with greater efficiency than a Carnot's cycle.*

After [LY99]. Consider a heat engine, a cyclic process around $(T; X)$. Its efficiency is $1 - \frac{Q_\mathrm{L}}{Q_\mathrm{H}}$, corresponding to the following diagram:

$$U(T; X) \xrightarrow[\Downarrow W \quad \Downarrow Q_\mathrm{L}]{\Downarrow Q_\mathrm{H}} U(T; X) \quad W = Q_\mathrm{H} - Q_\mathrm{L}. \tag{1.217}$$

Let $(T_\mathrm{L}; L)$ and $(T_\mathrm{H}; H)$ be two finite heat baths, with initial temperatures $0 < T_\mathrm{L} < T_\mathrm{H}$. During one cycle, the transition of the composite system is represented as

$$((T_\mathrm{H}; H) \mid (T; X) \mid (T_\mathrm{L}; L)) \xrightarrow{\mathrm{a}} ((T_\mathrm{H}'; H) \mid (T; X) \mid (T_\mathrm{L}'; L)). \tag{1.218}$$

The cold T_L-reservoir absorbs

$$Q_L := U\left(T_\mathrm{L}'; L\right) - U\left(T_\mathrm{L}; L\right) \tag{1.219}$$

of heat from the cycle, while the hot T_H-reservoir supplies

$$Q_H := U\left(T_\mathrm{H}; H\right) - U\left(T_\mathrm{H}'; H\right). \tag{1.220}$$

Diagrammatically:

$$
\begin{array}{ccc}
U(T_\mathrm{H}; H) & \cdots\cdots\!\!\!\longrightarrow & U(T_\mathrm{H}'; H) \\[4pt]
& \Big\Downarrow Q_\mathrm{H} & \\[4pt]
U(T; X) \underset{\Downarrow W}{\cdots\cdots} & \longrightarrow & U(T; X) \qquad W = Q_\mathrm{H} - Q_\mathrm{L}. \\[4pt]
& \Big\Downarrow Q_\mathrm{L} & \\[4pt]
U(T_\mathrm{L}; L) & \cdots\cdots\!\!\!\longrightarrow & U(T_\mathrm{L}'; L)
\end{array}
\tag{1.221}
$$

Assume $Q_\mathrm{H} > 0$ and $Q_\mathrm{L} > 0$. Then, by 1.2.2,

$$T_\mathrm{L} < T_\mathrm{L}', T_\mathrm{H}' < T_\mathrm{H}. \tag{1.222}$$

By Lemma 1.5.2,

$$S\left((T_\mathrm{H}; H) \mid (T; X) \mid (T_\mathrm{L}; L)\right) \leqq S\left((T_\mathrm{H}'; H) \mid (T; X) \mid (T_\mathrm{L}'; L)\right). \tag{1.223}$$

Using Definition 1.5.2, this becomes

$$S\left(T_\mathrm{H}; H\right) + S\left(T_\mathrm{L}; L\right) \leqq S\left(T_\mathrm{H}'; H\right) + S\left(T_\mathrm{L}'; L\right. \tag{1.224}$$

Rearranging, we have

$$S\left(T_\mathrm{H}; H\right) - S\left(T_\mathrm{H}'; H\right) \leqq S\left(T_\mathrm{L}'; L\right) - S\left(T_\mathrm{L}; L\right) \tag{1.225}$$

If $T \mapsto S(T; H)$ is differentiable in some neighborhood of $T_\mathrm{H}{}' \leqq T \leqq T_\mathrm{H}$, the left-hand side becomes

$$
\begin{aligned}
S(T_\mathrm{H}; H) - S(T_\mathrm{H}{}'; H) &= \int_{T_\mathrm{H}'}^{T_\mathrm{H}} \frac{\partial S(T; H)}{\partial T} \mathrm{d}T \\
&= \int_{T_\mathrm{H}'}^{T_\mathrm{H}} \frac{1}{T} \frac{\partial U(T; H)}{\partial T} \mathrm{d}T \\
&\geqq \frac{1}{T_\mathrm{H}} \int_{T_\mathrm{H}'}^{T_\mathrm{H}} \frac{\partial U(T; H)}{\partial T} \mathrm{d}T \\
&= \frac{1}{T_\mathrm{H}} \left(U(T_\mathrm{H}; H) - U(T_\mathrm{H}{}'; H) \right) \\
&= \frac{Q_\mathrm{H}}{T_\mathrm{H}}.
\end{aligned}
\tag{1.226}
$$

Similarly, if $T \mapsto S(T; L)$ is differentiable in some neighborhood of $T_\mathrm{L}{}' \leqq T \leqq T_\mathrm{L}$, left-hand side becomes

$$
\begin{aligned}
S(T_\mathrm{L}; L) - S(T_\mathrm{L}{}'; L) &= \int_{T_\mathrm{L}}^{T_\mathrm{L}'} \frac{\partial S(T; L)}{\partial T} \mathrm{d}T \\
&= \int_{T_\mathrm{L}}^{T_\mathrm{L}'} \frac{1}{T} \frac{\partial U(T; L)}{\partial T} \mathrm{d}T \\
&\leqq \frac{1}{T_\mathrm{L}} \int_{T_\mathrm{L}}^{T_\mathrm{L}'} \frac{\partial U(T; L)}{\partial T} \mathrm{d}T \\
&= \frac{1}{T_\mathrm{L}} \left(U(T_\mathrm{L}{}'; L) - U(T_\mathrm{L}; L) \right) \\
&= \frac{Q_\mathrm{L}}{T_\mathrm{L}}.
\end{aligned}
\tag{1.227}
$$

Thus, we obtain $\frac{Q_\mathrm{H}}{T_\mathrm{H}} \leqq \frac{Q_\mathrm{L}}{T_\mathrm{L}}$, or equivalently,

$$
1 - \frac{Q_\mathrm{L}}{Q_\mathrm{H}} \leqq 1 - \frac{T_\mathrm{L}}{T_\mathrm{H}}.
\tag{1.228}
$$

The right-hand side $1 - \frac{T_\mathrm{L}}{T_\mathrm{H}}$ is the efficiency of the Carnot's cycle with two heat baths $T_\mathrm{L} < T_\mathrm{H}$. ∎

Definition 1.5.3 (Thermal Contact and Thermal Equilibrium)**.** Consider the wall removal process in Lemma 1.3.1 with $\lambda = 1$:

$$
((T; X) \mid (T'; Y)) \xrightarrow{\mathrm{a}} \left(\widetilde{T}; X \oplus Y \right)
\tag{1.229}
$$

Let Q denote the heat transfer from Y to X:

$$
Q = U\left(\widetilde{T}; X \right) - U(T; X) = U(T'; Y) - U\left(\widetilde{T}; Y \right).
\tag{1.230}
$$

If $Q = 0$, these two systems are said to be in thermal equilibrium, written

$$(T; X) \sim (T'; Y) \tag{1.231}$$

meaning that, under the process (1.229), no heat transfer occurs between X and Y.

Theorem 1.5.5 (Thermal Contact and Thermal Equilibrium). *For the adiabatic wall removal process in* (1.229), *the following statements hold:*

- *If the heat transfer between X and Y is zero, then $T = \widetilde{T} = T'$.*

- *If $T \neq T'$, then entropy of the composite system increases.*

- *If $(T; X) \sim (T'; Y)$ and $(T'; Y) \sim (T''; Z)$, then $(T; X) \sim (T''; Z)$.*

Proof. Assume first that the heat transfer in (1.229) is zero. By Definition 1.5.3,

$$U\left(\widetilde{T}; X\right) - U(T; X) = 0 = U(T'; Y) - U\left(\widetilde{T}; Y\right). \tag{1.232}$$

By Lemma 1.2.2, both differences vanish only when $T = \widetilde{T} = T'$.

Now assume $T \neq T'$. Then heat transfer must occur. Let

$$Q = U\left(\widetilde{T}; X\right) - U(T; X) = U(T'; Y) - U\left(\widetilde{T}; Y\right) \tag{1.233}$$

be the heat transfer from Y to X. Without loss of generality, we may suppose $Q > 0$, otherwise, interchange $X \leftrightarrow Y$. Lemma 1.2.2 implies

$$T < \widetilde{T} < T'. \tag{1.234}$$

The entropy change is

$$\begin{aligned}
\Delta S &:= S\left(\widetilde{T}; X \oplus Y\right) - S(T; X) - S(T'; Y) \\
&= S\left(\widetilde{T}; X\right) - S(T; X) - S(T'; Y) + S\left(\widetilde{T}; Y\right) \\
&= \int_T^{\widetilde{T}} \frac{\partial S(t; X)}{\partial t} dt - \int_{\widetilde{T}}^{T'} \frac{\partial S(t; Y)}{\partial t} dt
\end{aligned} \tag{1.235}$$

By Theorem 1.5.1, we obtain:

$$\begin{aligned}
\Delta S &= \int_T^{\widetilde{T}} \frac{1}{t} \frac{\partial U(t; X)}{\partial t} dt - \int_{\widetilde{T}}^{T'} \frac{1}{t} \frac{\partial U(t; Y)}{\partial t} dt \\
&> \frac{1}{\widetilde{T}} \int_T^{\widetilde{T}} \frac{\partial U(t; X)}{\partial t} dt - \frac{1}{\widetilde{T}} \int_{\widetilde{T}}^{T'} \frac{\partial U(t; Y)}{\partial t} dt \\
&= \frac{1}{\widetilde{T}} \left(U\left(\widetilde{T}; X\right) - U(T; X) - U(T'; Y) + U\left(\widetilde{T}; Y\right)\right)
\end{aligned} \tag{1.236}$$

Since the process is adiabatic and no net work is done, the last expression is zero, $U(T; X) + U(T'; Y) = U\left(\widetilde{T}; X \oplus Y\right)$. Therefore,

$$\Delta S > 0. \tag{1.237}$$

Remark 17 (Second Law of Thermodynamics). This is the Clausius form of the second law of thermodynamics: spontaneous heat transfer occurs only from higher to lower temperature.

> The word "spontaneously" here means no other effort has been made by a third party, or one that is neither the hotter nor colder object.[12]

See also College Physics §15.6 Entropy and the Second Law of Thermodynamics and University Physics Volume 2 §4.6 Entropy.

Finally, suppose X and Y are in thermal equilibrium, and Y and Z are in thermal equilibrium as well. As shown above, we have $T = T' = T''$. Consider the following wall removal:

$$((T; X) \mid (T; Z)) \xrightarrow{\text{a}} \left(\widetilde{T}; X \oplus Z\right). \tag{1.238}$$

The heat transfer $Q_{X \leftarrow Z}$ from Z to X is

$$Q_{X \leftarrow Z} = U\left(\widetilde{T}; X\right) - U(T; X) = U(T; Z) - U\left(\widetilde{T}; Z\right). \tag{1.239}$$

If $T < \widetilde{T}$, by Lemma 1.2.2, we have

$$\begin{aligned} U\left(\widetilde{T}; X\right) - U(T; X) &> 0 \\ U(T; Z) - U\left(\widetilde{T}; Z\right) &< 0, \end{aligned} \tag{1.240}$$

which is absurd; if $\widetilde{T} < T$, the signs reverse, again a contradiction:

$$\begin{aligned} U\left(\widetilde{T}; X\right) - U(T; X) &< 0 \\ U(T; Z) - U\left(\widetilde{T}; Z\right) &> 0, \end{aligned} \tag{1.241}$$

Thus, $T = \widetilde{T}$, so $Q_{X \leftarrow Z} = 0$ holds. ∎

Remark 18 (Zeroth Law of Thermodynamics). The final property is known as the zeroth law of thermodynamics. From a mathematical perspective, the relation of thermal equilibrium defines an equivalence relation on the set of thermodynamic states:

- Reflexivity

  For any state $(T; X)$, we have $(T; X) \sim (T; X)$.

- Symmetry

  If $(T; X) \sim (T'; Y)$, then $(T'; Y) \sim (T; X)$.

- Transitivity

  If $(T; X) \sim (T'; Y)$ and $(T'; Y) \sim (T''; Z)$, then $(T; X) \sim (T''; Z)$.

For further discussion, see College Physics 2e §13.1 Temperature and University Physics Volume 2 §1.1 Temperature and Thermal Equilibrium.

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[12]University Physics Volume 2 §4.1 Reversible and Irreversible Processes

1.5.4 Applications

Theorem 1.5.6 (Helmholtz's Free Energy is Complete Thermodynamic Function). *Suppose Helmholtz's free energy is differentiable at $(T; X)$. Then*

$$S(T; X) = -\frac{\partial F[T; X]}{\partial T}$$

$$U(T; X) = -T^2 \frac{\partial}{\partial T} \left(\frac{F[T; X]}{T} \right) \tag{1.242}$$

That is if F is known as a function of states, $[T; X]$, both the entropy S and the internal energy U can be obtained from it. Hence, as a function of $[T; X]$, F is sometime called a complete thermodynamic function.

Remark 19 (The Heat Capacity). Recalling Definition 1.2.4 and Remark 15, we obtain

$$C_V(T; X) = -T \frac{\partial^2 F[T; X]}{\partial T^2}. \tag{1.243}$$

Proof. By Definition 1.5.1 and Theorem 1.5.1,

$$\begin{aligned}
\frac{\partial F[T; X]}{\partial T} &= \frac{\partial \left(U(T; X) - TS(T; X) \right)}{\partial T} \\
&= \frac{\partial U(T; X)}{\partial T} - S(T; X) - T \frac{\partial S(T; X)}{\partial T} \\
&= -S(T; X).
\end{aligned} \tag{1.244}$$

Similarly,

$$\begin{aligned}
-T^2 \frac{\partial}{\partial T} \left(\frac{F[T; X]}{T} \right) &= -T^2 \frac{\partial}{\partial T} \left(\frac{U(T; X)}{T} - S(T; X) \right) \\
&= -T^2 \left(\frac{1}{T} \frac{\partial U(T; X)}{\partial T} - \frac{U(T; X)}{T^2} - \frac{\partial S(T; X)}{\partial T} \right) \\
&= U(T; X) + T \left(T \frac{\partial S(T; X)}{\partial T} - \frac{\partial U(T; X)}{\partial T} \right) \\
&= U(T; X).
\end{aligned} \tag{1.245}$$

■

Definition 1.5.4 (Chemical Potential of Fluid). As in Example 1.1.1 and Example 1.3.1, consider a $\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)$ with a variation of the particle number $N \mapsto N + \Delta N$. We define the chemical potential μ by

$$\mu \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) := \frac{\partial F \left[T; \begin{pmatrix} V \\ N \end{pmatrix} \right]}{\partial N}. \tag{1.246}$$

Example 1.5.4 (The Chemical Potential of Ideal Gas). Using the expression for F in Example 1.5.1, the chemical potential of an ideal gas is computed as follows:

$$
\begin{aligned}
\mu\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) &= \frac{\partial}{\partial N}\left(-NRT\ln\left(\left(\frac{T}{T_*}\right)^c \frac{V}{v_* N}\right) + Nu\right) \\
&= RT - RT\ln\left(\left(\frac{T}{T_*}\right)^c \frac{V}{v_* N}\right) + u
\end{aligned}
\tag{1.247}
$$

Example 1.5.5 (Maxwell's Relations – Energy Equation and Ideal Gas). For simplicity, consider a fluid in the state $\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)$. Assume F is sufficiently smooth, in particular twice continuously differentiable. Then the following derivatives commute:

$$
\frac{\partial}{\partial V}\frac{\partial F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right]}{\partial T} = \frac{\partial}{\partial T}\frac{\partial F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right]}{\partial V}
\tag{1.248}
$$

Using Theorem 1.5.6 and (1.71), we obtain the Maxwell relation

$$
\frac{\partial S\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)}{\partial V} = \frac{\partial p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)}{\partial T}.
\tag{1.249}
$$

Since $U = TS + F$ by Definition 1.5.1, the differentiation with respect to V yields the following equation:

$$
\begin{aligned}
\frac{\partial U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)}{\partial V} &= \frac{\partial}{\partial V}\left(TS\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) + F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right]\right) \\
&= T\frac{\partial p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)}{\partial T} - p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)
\end{aligned}
\tag{1.250}
$$

If we apply this energy equation to the state equation $p = \frac{NRT}{V}$ of an ideal gas, see Example 1.3.2, we obtain

$$
\frac{\partial U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)}{\partial V} = T\frac{\partial p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)}{\partial T} - p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) = T\frac{\partial}{\partial T}\left(\frac{NRT}{V}\right) - \frac{NRT}{V} = 0
\tag{1.251}
$$

Thus, the internal energy of an ideal gas does not depend on the volume – Joule's law.

Example 1.5.6 (Adiabatic Expansion). Consider an adiabatic expansion of the fluid $\begin{pmatrix} V \\ N \end{pmatrix}$ from Example 1.1.1. Let the volume increase $V \mapsto V + \Delta V$ by $\Delta V > 0$:

$$
\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) \xrightarrow{\text{a}} \left(T'; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix}\right),
\tag{1.252}
$$

where T' is the final temperature. We claim that

$$S\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) < S\left(T'; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix}\right). \qquad (1.253)$$

To show this, consider the following quasistatic adiabatic compression

$$\left(T'; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix}\right) \xrightarrow{\text{qa}} \left(T''; \begin{pmatrix} V \\ N \end{pmatrix}\right) \qquad (1.254)$$

which returns the system to its original volume, where T'' is a priori unknown. Since the pressure of the fluid is always positive during this compression, positive work is done on the system:

$$U\left(T'; V + \Delta V, N\right) \xdashrightarrow{\Downarrow W_{\text{external}} > 0} U\left(T''; V, N\right) \qquad (1.255)$$

Combining this with the above adiabatic expansion, we have

$$U\left(T; V, N\right) \xdashrightarrow{\Downarrow W_{\text{external}} > 0} U\left(T''; V, N\right) \quad U\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) + W = U\left(T''; \begin{pmatrix} V \\ N \end{pmatrix}\right), \qquad (1.256)$$

so that $U\left(T''; V, N\right) - U\left(T; V, N\right) = W > 0$. Hence,

$$U\left(T; V, N\right) < U\left(T''; V, N\right). \qquad (1.257)$$

By Lemma 1.2.2, this implies $T < T''$. Then, by Theorem 1.5.1,

$$S\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) < S\left(T''; \begin{pmatrix} V \\ N \end{pmatrix}\right) = S\left(T'; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix}\right). \qquad (1.258)$$

Thus, such an adiabatic expansion is irreversible, by Theorem 1.5.2. See University Physics Volume 2 §4.7 Entropy on a Microscopic Scale.

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