

Thermodynamics
À la Manière de TAsAKI

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Chapter 0

Introduction

This note is an introduction to thermodynamics, a classical macroscopic theory about the interconversion of heat and work. Following closely [Tas01], we adopt an axiomatic approach. Here is a list of postulates:

- (Definition 1.1.5) A thermodynamic system is expressed by a single intensive parameter “temperature” and a finite set of extensive parameters when in thermal equilibrium.
- (Definition 1.2.2) Joule’s Experiment – at least one adiabatic process keeps the extensive parameters of a state constant, but the “temperature” increases. Within this “temperature” increasing process, some 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 both initial and final states.
- (Definition 1.2.6) Planck’s Statement – The above-mentioned “temperature” increasing Joule’s experiment is irreversible.
- (Definition 1.3.2) Thermal interactions between systems behave “well.”
- (Definition 1.4.2) Adiabatic Expansion – For any state, there is a lower temperature state which is accessible via an adiabatic process.

We assume working knowledge of both mathematics and physics, in particular Newton’s mechanics.

Chapter 1

Thermodynamics

Thermodynamics is a branch of classical and macroscopic physics. A typical target – a tablespoon of water – contains some Avogadro number $\sim 10^{23}$ of chemical components and it is impossible to trace their motions by solving 10^{23} equations of motion! Our macroscopic observations and experiments are based on their averages; surprisingly small numbers of parameters survive and they determine the macroscopic state of substances.

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 neglected, and that are not acted on by electric, magnetic, or gravitational fields [Cal60].

1.1 Equilibrium States

We consider physical systems under certain, special, states – equilibrium states.

1.1.1 Extensive Parameters

In short, a thermodynamic system is a black box with some mechanically accessible channel – we can measure work, energy, and the like through such mechanical handles, to reveal both mechanical and non-mechanical properties of thermodynamic systems. Let us consider a single kind of substance as a simple system. Such a thermodynamic system, say X , can have several different states; here, our focus is on the macroscopically unchanged equilibrium states. Some finite parameters fully characterize such an equilibrium state of a system:

Definition 1.1.1 (Extensive Variables). Let X be a thermodynamic system. We suppose that its equilibrium state is fully determined by specifying some

finite, non-negative, parameters, say

$$\begin{pmatrix} X^1 \\ \vdots \\ X^n \end{pmatrix} \in \mathbb{R}_{\geq 0}^n \quad (1.1)$$

s.t., for any scalar $\lambda > 0$:

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

Such parameters are called extensive parameters.

Example 1.1.1 (Fluids). Consider a fixed volume, say a cylinder V of fluid; let m be its mass. Its macroscopic state is represented as

$$\begin{pmatrix} V \\ m \end{pmatrix}. \quad (1.3)$$

Consider $\lambda = 2$ case. The left-hand side:

$$2 \begin{pmatrix} V \\ m \end{pmatrix} \quad (1.4)$$

means we set two identical cylinders of fluids and recognize them as a single system. The right-hand side:

$$\begin{pmatrix} 2V \\ 2m \end{pmatrix} \quad (1.5)$$

is a system that has double volume $2V$ with double mass $2m$. The assumption states that we identify these two systems.

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

$$n(X) := \frac{m}{M(X)}, \quad (1.6)$$

where $M(X)$ is an arbitrary constant. As we can verify, $n(X)$ is also an extensive parameter. Since $M(X)$ is arbitrary, we may set:

- $M(X) = 1$

We may use the mass as the amount of substance.

- $M(X)$ is the “atomic weight” of X

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

$$A_r(X) := \frac{m(X)}{\frac{m(^{12}\text{C})}{12}} \quad (1.7)$$

see Atomic Weights and Isotopic Compositions - Column Descriptions.¹

You can use a table of Standard Atomic Weights² or through some classical gravimetric analysis to choose $M(X)$.

For a multiple-component system, $X = \{X_i \mid i \in I\}$ of some index I , if X is chemically unchanged, we may apply

$$n(X_i) := \frac{m_i}{M(X_i)} \quad (1.8)$$

for $i \in I$. Then the total amount $n(X)$ is given by their sum: $\sum_{i \in I} n(X_i)$.

So, having a table of atomic masses, we can determine the compositional formula for a multiple-component system X . For example, the following substances have CH as their chemical – empirical – formula:

- acetylene (C_2H_2)
- benzene (C_6H_6)

If Boyle-Charles law is a good approximation, namely if “temperature” is relatively high and the density is relatively low, we may determine, for any gas:

$$R := \frac{pV}{mT} \quad (1.9)$$

where p stands for pressure, V is the volume, m is the mass, and T is absolute “temperature,” which will be introduced later, see Definition 1.4.3, of a given gas. Then, as an experimental fact, we have

$$R_{\text{acetylene}} \approx 3R_{\text{benzene}} \quad (1.10)$$

So, if we set $M(\text{acetylene})$ and $M(\text{benzene})$ s.t.,

$$\frac{M(\text{acetylene})}{M(\text{benzene})} \approx 3 \quad (1.11)$$

then we establish, as a good approximation:

$$\frac{pV}{nT} = \text{constant}, \quad (1.12)$$

between acetylene and benzene. I.e., if we choose acetylene = C_kH_l with some numbers k and l , then benzene = $C_{3k}H_{3l}$. Such an equation is called an equation of state, see Example 1.3.1.

Exercise 1.1.1. Find the definition of molar gas constant R from CODATA.³

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

²<https://www.nist.gov/pml/periodic-table-elements>

³<https://physics.nist.gov/cuu/Constants/>

We use the amount N of substance as an extensive parameter of a system:

$$\begin{pmatrix} V \\ N \end{pmatrix} \quad (1.13)$$

Definition 1.1.2 (Juxtaposition). We can consider two systems X and Y as a single system:

$$X \oplus Y = \begin{pmatrix} X^1 \\ \vdots \\ X^n \end{pmatrix} \oplus \begin{pmatrix} Y^1 \\ \vdots \\ Y^m \end{pmatrix} \quad (1.14)$$

Note that these two systems have, in general, different number of “components.” Since $X \oplus Y$ forms another system, for $\lambda > 0$,

$$\lambda(X \oplus Y) = (\lambda X) \oplus (\lambda Y). \quad (1.15)$$

1.1.2 Walls

Some extensive parameter of a system has mechanical access, e.g., a cylinder-full of gas with a movable piston.

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

$$X \mapsto \lambda X \oplus (1 - \lambda)X. \quad (1.16)$$

This can be done, experimentally, by inserting a thin impermeable wall that does not allow to matter go through.

We suppose that for an equilibrium state of a system, both insertion and removal of a wall require no mechanical work.

Example 1.1.2. Let X be a system in Example 1.1.1, $\begin{pmatrix} V \\ N \end{pmatrix}$. Suppose L is a typical length scale of the system X . Then the volume V is L^3 order:

$$V \in \Theta(L^3) \quad (1.17)$$

Any wall has L^2 order surface area. Hence, the work W to insert/remove a wall is L^2 order:

$$W \in \Theta(L^2). \quad (1.18)$$

Then for any permissible error $\epsilon > 0$, we may choose a sufficiently large $L > 0$ s.t.,

$$\left| \frac{W}{V} \right| < \epsilon. \quad (1.19)$$

That is, the ratio $\frac{W}{V}$ behaves like $1/L$ so that as $L \rightarrow \infty$, $\frac{W}{V} \rightarrow 0$. Hence, as a thermodynamic limit $L \rightarrow +\infty$, we may suppose that no cost is required for wall insertion/removal for an equilibrium state of a system.

Remark 2. If a wall separates two different systems, for instance, between X and Y in $X \oplus Y$, to keep the removal process “quasistatic,” both states must be “balanced.”

Definition 1.1.4 (Adiabatic Walls and Isolated Systems). A wall is called an adiabatic wall iff it does not allow any “heat” transfer. Since “heat” is not yet introduced, let us define adiabatic walls as a special constraint between the system and its complement – environment. A system is called isolated iff it does not interact with its environment. Such an isolated system is, experimentally, achieved by enclosing it in adiabatic walls, e.g., a double-walled thermos.

Definition 1.1.5 (Postulate: Equilibrium States of Adiabatic Systems). Let X be a thermodynamic system. With adiabatic walls, we may isolate X from the environment. I.e., X is an adiabatic system. Fixing its extensive parameters $\{X^1, \dots, X^n\}$, we suppose that the system will eventually become an equilibrium state:

$$\left(T; \begin{pmatrix} X^1 \\ \vdots \\ X^n \end{pmatrix} \right), \quad (1.20)$$

where T of the equilibrium “temperature” is some parameter. Such a final equilibrium “temperature” depends solely on the initial state of the system X . Note that the existence of equilibrium states is sometimes called “minus first law.”

We also assume that the “temperature” of the equilibrium state is an intensive parameter, namely if we consider $\lambda X, \lambda > 0$ of a scaled system, it will eventually become:

$$\left(T; \begin{pmatrix} \lambda X^1 \\ \cdot \\ \lambda X^n \end{pmatrix} \right). \quad (1.21)$$

That is, under $X \mapsto \lambda X$, the “temperature” does not change.

Remark 3 (Positive “Temperature”). If you use the degree Celsius, add 273.15; if you use the degree Fahrenheit, add 459.67, so that $T > 0$. See SI Units – Temperature.⁴

1.2 Adiabatic Processes

We consider processes, keeping systems isolated from the external 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 some system. If we enclose the system in

⁴<https://www.nist.gov/pml/owm/si-units-temperature>

adiabatic walls, we can “thermally” isolate the system from the environment. Under such an adiabatic condition, the thermodynamic states transition as follows:

$$(T_1; X_1) \xrightarrow{a} (T_2; X_2), \quad (1.22)$$

where both initial and final states are in equilibrium. Note that, for a given initial “temperature” T_1 , the initial equilibrium state $(T_1; X_1)$, and the final equilibrium state X_2 , the final “temperature” is fully determined by the state X_2 itself along with this 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 the intermediate states are in equilibrium, then such a virtual process is called quasistatic. We use

$$(T_1; X_1) \xrightarrow{qa} (T_2; X_2) \quad (1.23)$$

for a quasistatic adiabatic process.

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 final “temperature” of an quasistatic adiabatic process $(T_1; X_1) \xrightarrow{qa} (T_2; X_2)$ is continuous with respect to X_2 :

$$X_2 \dashrightarrow X_1 \Rightarrow T_2 \dashrightarrow T_1. \quad (1.24)$$

In other words, $t(X_2) = T_2$ satisfies $\lim_{X_2 \rightarrow X_1} t(X_2) = t(X_1) = T_1$.

- A quasistatic adiabatic process $(T_1; X_1) \xrightarrow{qa} (T_2; X_2)$ has its inverse: $(T_1; X_1) \xleftarrow{qa} (T_2; X_2)$.

It is worth mentioning that both a quasistatic adiabatic process and its inverse are quasistatic adiabatic processes:

$$(T_1; X_1) \xleftrightarrow{qa} (T_2; X_2) \quad (1.25)$$

⁵Elliott H. Lieb and Jakob Yngvason “A Guide to Entropy and the Second Law of Thermodynamics”

⁶University Physics Volume 2 §3.4 Thermodynamic Processes

Remark 4. We will soon give a characterization of an adiabatic process in Definition 1.2.3 in terms of energy.

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

$$(T_1; X) \xrightarrow{a} (T_2; X). \quad (1.26)$$

Within this process, some positive work must be done on the system. That is, the work done by the system is negative.

Remark 5. See, for example, December 1840: Joule’s abstract on converting mechanical power into heat⁷, 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 are some operations $X_1 \mapsto X_2$ and $X_2 \mapsto X_1$. Then, for arbitrary $T_1, T_2 > 0$, either*

$$(T_1; X_1) \xrightarrow{a} (T_2; X_2) \quad (1.27)$$

or

$$(T_1; X_1) \xleftarrow{a} (T_2; X_2) \quad (1.28)$$

exists.

Proof. By assumption, there exists a quasistatic adiabatic process

$$(T_1; X_1) \xrightarrow{qa} (T'; X_2), \quad (1.29)$$

where T' is an unknown final “temperature” of this process.

- $T' < T_2$ case

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

$$(T'; X_2) \xrightarrow{a} (T_2; X_2). \quad (1.30)$$

Hence their combination is the desired process:

$$(T_1; X_1) \xrightarrow{qa} (T'; X_2) \xrightarrow{a} (T_2; X_2). \quad (1.31)$$

- $T' \geq T_2$ case

If $T' = T_2$, nothing has to be shown:

$$(T_1; X_1) \xrightarrow{qa} (T' = T_2; X_2). \quad (1.32)$$

So we may suppose $T' > T_2$. By Definition 1.2.1, there exists

$$(T_1; X_1) \xleftarrow{qa} (T'; X_2). \quad (1.33)$$

Recalling $T_2 < T'$, we obtain the desired process:

$$(T_2; X_2) \xrightarrow{a} (T'; X_2) \xrightarrow{qa} (T_1; X_1). \quad (1.34)$$

⁷<https://www.aps.org/publications/apsnews/200912/physicshistory.cfm>

Thus either $(T_1; X_1) \xrightarrow{a} (T_2; X_2)$ or $(T_1; X_1) \xleftarrow{a} (T_2; X_2)$ exists. ■

Definition 1.2.3 (Postulate: First Law of Thermodynamics). We assume, as a characterization of an adiabatic process, that the work done by the system during an adiabatic process depends only on the initial and final states.

In other words, as the work is “flow,” there exists a corresponding “stock,” the internal energy U , of the system:

$$U(T_1; X_1) \xrightarrow[\Downarrow W_{\text{ad}}]{} U(T_2; X_2) \quad W_{\text{ad}} = U(T_1; X_1) - U(T_2; X_2). \quad (1.35)$$

For a system, we choose a reference equilibrium state $(T_*; X_*)$, where X_* is some physically accessible state. If we consider λX , $\lambda > 0$, then $(T_*, \lambda X_*)$ is the corresponding reference point for the scaled system. By Lemma 1.2.1, there is either $(T_*, \lambda X_*) \xrightarrow{a} (T; \lambda X)$ or $(T_*, \lambda X_*) \xleftarrow{a} (T; \lambda X)$, we choose

$$U(T; \lambda X) := \begin{cases} -W_{\text{ad}} \left((T_*, \lambda X_*) \xrightarrow{a} (T; \lambda X) \right) & \text{if } (T_*, \lambda X_*) \xrightarrow{a} (T; \lambda X) \text{ exists} \\ W_{\text{ad}} \left((T_*, \lambda X_*) \xleftarrow{a} (T; \lambda X) \right) & \text{otherwise} \end{cases} \quad (1.36)$$

We assume, for later analysis, some good analytical properties. For example, U is continuous:

$$(T_1; X_1) \dashrightarrow (T_2; X_2) \Rightarrow U(T_1; X_1) \dashrightarrow U(T_2; X_2). \quad (1.37)$$

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. *The internal energy for a fixed system X is an increasing function of “temperature.” That is,*

$$T_1 < T_2 \Rightarrow U(T_1; X) < U(T_2; X). \quad (1.38)$$

Proof. For the adiabatic process in Definition 1.2.2:

$$(T_1; X) \xrightarrow{a} (T_2; X), T_1 < T_2, \quad (1.39)$$

the work W done by the system is negative:

$$U(T_1; X) \xrightarrow[\Downarrow W < 0]{} U(T_2; X) \quad (1.40)$$

That is,

$$W = U(T_1; X) - U(T_2; X) < 0. \quad (1.41)$$

Hence, if $T_1 < T_2$, along with the corresponding adiabatic process, we have $U(T_1; X) < U(T_2; X)$. ■

Definition 1.2.4 (Heat Capacity at Constant Volume). The following quantity is called the heat capacity at constant volume:

$$C_V(T; X) := \frac{\partial U(T; X)}{\partial T}. \quad (1.42)$$

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

$$(T_1; X_1) \xrightarrow{a} (T_2; X_2) \quad (1.43)$$

is called reversible iff there exists an adiabatic process:

$$(T_1; X_1) \xleftarrow{a} (T_2; X_2). \quad (1.44)$$

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

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

Definition 1.2.6 (Postulate: Planck’s Statement). The “temperature” increasing adiabatic process in Definition 1.2.2:

$$(T_1; X) \xrightarrow{a} (T_2; X), T_1 < T_2, \quad (1.45)$$

is irreversible; if $(T_1; X) \xrightarrow{a} (T_2; X)$ exists, $T_1 \leq T_2$.

1.3 Isothermal Processes

We will consider processes under a constant “temperature” condition, from $(T; X_1)$ to $(T; X_2)$, for instance. Experimentally, it is achieved by keeping thermal contact with some “temperature” reservoir – a.k.a., a “heat” bath and/or a thermostat – such as the atmosphere and the sea of the Earth. The nature 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

1.3.0 Heat Bath – Construction

Let X_1, X_2 be states of a system, Y be a state, and $\lambda > 0$. Consider $X_1 \oplus \lambda Y$ and a fixed process $X_1 \mapsto X_2$. If we keep the system $X_1 \oplus \lambda Y$ isolated from their environment, we have the following:

$$(T; X_1 \oplus \lambda Y) \xrightarrow{a} (T_\lambda; X_2 \oplus \lambda Y), \quad (1.46)$$

⁸University Physics Volume 2 §3.4 Thermodynamic Processes

where T_λ is some unknown final “temperature.” The final “temperature” and the work W_λ done by the system during this adiabatic process:

$$U(T; X_1 \oplus \lambda Y) \xrightarrow{\dots\dots\dots} U(T_\lambda; X_2 \oplus \lambda Y) \quad (1.47)$$

$\Downarrow W_\lambda$

are both functions of the scale $\lambda > 0$.

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

$$Q_\lambda := U(T; \lambda Y) - U(T_\lambda; \lambda Y) = \lambda(U(T; Y) - U(T_\lambda; Y)). \quad (1.48)$$

I.e., the heat transfer is defined via the following:

$$\left\{ \begin{array}{ccc} U(T; \lambda Y) & \xrightarrow{\dots\dots\dots} & U(T_\lambda; \lambda Y) \\ & \Downarrow Q_\lambda & \\ U(T; X_1) & \xrightarrow{\dots\dots\dots} & U(T_\lambda; X_2) \\ & \Downarrow W_X & \end{array} \right. \quad (1.49)$$

where the work done by the system W_X is defined by

$$U(T; X_1) \xrightarrow{\dots\dots\dots} U(T_\lambda; X_2) \quad (1.50)$$

$\Downarrow W_X$

Lemma 1.3.1. *If we write*

$$W_\lambda := W_X + Q_\lambda = U(T; X_1) - U(T_\lambda; X_2) + Q_\lambda \quad (1.51)$$

then Q_λ can be seen as the total heat transfer from the finite size “heat bath” λY to X_1 .

Remark 6. It is worth mentioning that, in our formulation, the mechanical equivalence of heat and energy is built-in; 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. Let us introduce a notation for an adiabatic wall:

$$((T; X) | (T'; \lambda Y)) \quad (1.52)$$

i.e., two system X and λY are separated by an adiabatic wall $|$. If we enclose the entire system into adiabatic walls, by replacing the adiabatic wall $|$ into a diathermal wall slowly, we obtain the corresponding adiabatic process:

$$((T; X) | (T'; \lambda Y)) \xrightarrow{a} (\tilde{T}; X \oplus \lambda Y). \quad (1.53)$$

Since no work is done under this process, see Definition 1.1.3, we may apply Definition 1.2.3 of energy conservation:

$$U(T; X) + U(T'; \lambda Y) = U(\tilde{T}; X \oplus \lambda Y) = U(\tilde{T}; X) + U(\tilde{T}; \lambda Y) \quad (1.54)$$

Then

$$U(\tilde{T}; X) - U(T; X) = U(T'; \lambda Y) - U(\tilde{T}; \lambda Y) \quad (1.55)$$

is the transferred energy from λY to X . Hence, for the process in (1.49), Q_λ is indeed the transferred heat from λY to X_1 . ■

To build a heat bath as a constant T -reservoir, we insist the following assertion on the thermal interaction between systems:

Definition 1.3.2 (Postulate: Finite Heat Transfer in Thermodynamic Limit). We assume $\lim_{\lambda \rightarrow \infty} Q_\lambda$ exists. I.e., even we take $\lambda \rightarrow \infty$ limit, Q_λ does not diverge. In other words, the thermal interaction between systems X and λY behaves well.

Lemma 1.3.2. *Along with the thermodynamic limit $\lambda \rightarrow \infty$, the final “temperature” of the composite system remains constant, $\lim_{\lambda \rightarrow \infty} T_\lambda = T$.*

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

$$\lambda \geq \lambda_\epsilon \Rightarrow |t_\lambda - t| < \epsilon. \quad (1.56)$$

Suppose for contradiction that $T \neq \lim_{\lambda \rightarrow \infty} T_\lambda$. Then, for any $\lambda > 0$, there exists $\delta > 0$ with $|T_\lambda - T| \geq \delta$. By Lemma 1.2.2, $T \mapsto U(T; Y)$ is an increasing function. Hence, if $T_\lambda \neq T$,

$$U(T; Y) - U(T_\lambda; Y) \neq 0, \quad (1.57)$$

i.e., there exists some $\delta' > 0$ with

$$|U(T; Y) - U(T_\lambda; Y)| \geq \delta'. \quad (1.58)$$

Hence, as $\lambda \rightarrow +\infty$,

$$|Q_\lambda| = \lambda |U(T; Y) - U(T_\lambda; Y)| \geq \lambda \delta' \rightarrow +\infty, \quad (1.59)$$

which is absurd. Therefore, $\lim_{\lambda \rightarrow \infty} T_\lambda = T$. ■

Under $\lambda \rightarrow \infty$ limit, the attached system λY behaves like an ambient environment, keeping the “temperature” of the system X constant. This property is nothing but T -reservoir, i.e., a heat bath. The processes under such constant T environment is called isothermal processes:

1.3.1 Isothermal Process and Heat

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 $\lambda \rightarrow +\infty$ is called a heat bath or T -reservoir. Then (1.51) converges, i.e.,

$$W := \lim_{\lambda \rightarrow \infty} W_\lambda = \lim_{\lambda \rightarrow \infty} U(T; X_1) - U(T_\lambda; X_2) + Q_\lambda = U(T; X_1) - U(T; X_2) + Q. \quad (1.60)$$

Moreover, it represents the energy conservation for an isothermal process from X_1 to X_2 under a constant T :

$$U(T; X_1) \xrightarrow[\Downarrow W]{\Downarrow Q} U(T; X_2) \quad (1.61)$$

It 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 consequence, there exists no perpetual motion machine of the first kind – an “engine” that provides positive work with no external energy source: violation of energy conservation.

It is worth mentioning that $Q - W = U(T; X_2) - U(T; X_1)$ does not depend on the thermodynamic 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 we established in Definition 1.3.3, we call an operation $X_1 \mapsto X_2$ under constant “temperature” T an isothermal process:

$$(T; X_1) \xrightarrow{i} (T; X_2). \quad (1.62)$$

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:

$$(T; X_1) \xrightarrow{qi} (T; X_2). \quad (1.63)$$

Any quasistatic isothermal process has the inverse

$$(T; X_1) \xleftarrow{qi} (T; X_2), \quad (1.64)$$

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:*

$$W_{cyc} \leq 0. \quad (1.65)$$

Proof. Let X and Y be systems and $\lambda > 0$. For a cyclic operation $X \mapsto X$, let us consider the corresponding adiabatic process:

$$(T; X \oplus \lambda Y) \xrightarrow{a} (T_\lambda; X \oplus \lambda Y). \quad (1.66)$$

By Definition 1.2.6, we obtain

$$T \leq T_\lambda. \quad (1.67)$$

Hence, by Lemma 1.2.2,

$$\begin{aligned} U(T; X) &\leq U(T_\lambda; X) \\ U(T; Y) &\leq U(T_\lambda; Y) \end{aligned} \quad (1.68)$$

Since the transferred heat Q_λ in Definition 1.3.1 is

$$Q_\lambda = \lambda(U(T; Y) - U(T_\lambda; Y)) \leq 0, \quad (1.69)$$

we conclude

$$W_\lambda := U(T; X) - U(T_\lambda; X') + Q_\lambda \leq 0. \quad (1.70)$$

If we take $\lambda \rightarrow +\infty$ limit, we obtain the desired result:

$$W := \lim_{\lambda \rightarrow \infty} W_\lambda \leq 0 \quad (1.71)$$

since $T_\lambda \rightarrow T$ if $\lambda \rightarrow \infty$ and, hence, the transition $X \mapsto X'$ becomes an isothermal cyclic process. ■

Remark 8 (Impossibility of Perpetual Motion Machine of Second Kind). There is no perpetual motion machine of the second kind – no cycle under constant “temperature” provides positive work outside.

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

Proof. Let $(T; X) \xrightarrow{q_i} (T; X)$ be a quasistatic isothermal cycle and W be the work done through this cycle. By Theorem 1.3.1, such the work along a cycle must be non-positive $W \leq 0$. By Definition 1.3.4, there exists its inverse process $(T; X) \xleftarrow{q_i} (T; X)$. This inverse process is cyclic as well. The work done by this inverse cycle is $-W$; By Theorem 1.3.1 again, $-W \leq 0$. Hence, $W = 0$. ■

1.3.2 Maximum Work and Helmholtz’ Free Energy

One of the fundamental goals of thermodynamics is to examine the conditions to obtain maximum available, obtainable, energy from a system, a.k.a., “exergy” of the useful work “potential.”

Maximum Work

Definition 1.3.6 (Maximum Work). Let X_1, X_2 be states of some system. Define:

$$W_{\max}(T; X_1 \mapsto X_2) := \max \left\{ W \mid U(T; X_1) \begin{array}{c} \xrightarrow{\downarrow Q} \\ \xrightarrow{\downarrow W} \end{array} U(T; X_2) \right\}, \quad (1.72)$$

where the processes under max run all isothermal processes.

Theorem 1.3.2 (Principle of Maximum Work). *The maximum work is the work done during a quasistatic process:*

$$(T; X_1) \xrightarrow{q_i} (T; X_2). \quad (1.73)$$

Proof. Let W, W' be the works done by the system during a quasistatic isothermal process and an arbitrary isothermal process, respectively. We will show $W' \leq W$. By Definition 1.3.4, there exists $(T; X_1) \xleftarrow{\text{qi}} (T; X_2)$. Since

$$(T; X_1) \begin{array}{c} \xrightarrow{i} \\ \xleftarrow{\text{qi}} \end{array} (T; X_2) \quad (1.74)$$

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:

$$-W + W' \leq 0. \quad (1.75)$$

As W' is the work done through an arbitrary isothermal process, we obtain the desired maximum property $W' \leq W$. ■

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 given by a quasistatic isothermal process, so it suffices to show the work done by quasistatic processes are the same. Consider two quasistatic isothermal processes:

$$(T; X_1) \begin{array}{c} \xrightarrow{\text{qi}} \\ \xrightarrow{\text{qi}} \end{array} (T; X_2) \quad (1.76)$$

The combination of one and the inverse of the other forms a quasistatic isothermal cycle:

$$(T; X_1) \begin{array}{c} \xrightarrow{\text{qi}} \\ \xleftarrow{\text{qi}} \end{array} (T; X_2) \quad (1.77)$$

By Lemma 1.3.3, the net work done by such a cycle is zero, hence we conclude the work done by two quasistatic processes coincide. ■

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

1. For $\lambda > 0$,

$$W_{\max}(T; \lambda X_2 \mapsto \lambda X_1) = \lambda W_{\max}(T; X_1 \mapsto X_2). \quad (1.78)$$

- 2.

$$W_{\max}(T; X_2 \mapsto X_1) = -W_{\max}(T; X_1 \mapsto X_2) \quad (1.79)$$

- 3.

$$W_{\max}(T; X_1 \mapsto X_3) = W_{\max}(T; X_1 \mapsto X_2) + W_{\max}(T; X_2 \mapsto X_3). \quad (1.80)$$

4. For the following two processes:

$$\begin{aligned} (T; X_1) &\xrightarrow{\text{qi}} (T; X_2) \\ (T; Y_1) &\xrightarrow{\text{qi}} (T; Y_2) \end{aligned} \tag{1.81}$$

i.e., through $(T; X_1 \oplus Y_1) \xrightarrow{\text{qi}} (T; X_2 \oplus Y_2)$, the maximum work satisfies:

$$W_{\max}(T; X_1 \oplus Y_1 \mapsto X_2 \oplus Y_2) = W_{\max}(T; X_1 \mapsto X_2) + W_{\max}(T; Y_1 \mapsto Y_2) \tag{1.82}$$

Helmholtz' Free Energy

By Corollary 1.3.2.1, we may define, as the corresponding stock:

Definition 1.3.7 (Helmholtz's Free Energy). Thanks to Corollary 1.3.2.1, the maximum work $W_{\max}(T; X_1 \mapsto X_2)$ does not depend on any specific path from $(T; X_1)$ to $(T; X_2)$ transition. Hence, we can define, as a corresponding stock, Helmholtz's free energy F via the following stock-flow diagram:

$$F[T; X_1] \begin{array}{c} \xrightarrow{\text{.....}} \\ \downarrow W_{\max} \end{array} F[T; X_2] \tag{1.83}$$

I.e., Helmholtz's free energy is defined via the maximum availability of the work at a constant "temperature." Sometimes, it is also called the principle of maximum work: any isothermal process can not extract more work from the system than the loss of Helmholtz's free energy.

As we did for internal energy Definition 1.2.3, we choose a reference point (T_*, X_*) that is physically accessible to the states we consider; for a scaled system $(T; \lambda X)$, $\lambda > 0$, we set $(T_*; \lambda X_*)$:

$$F[T; \lambda X] := W_{\max}(T; \lambda X \mapsto \lambda X_*). \tag{1.84}$$

We assume, for later analysis, some good analytical properties like internal energy:

$$T_1 \dashrightarrow T_2 \Rightarrow F[T_1; X] \dashrightarrow F[T_2; X]. \tag{1.85}$$

1.3.3 Equation of State and Pressure

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

Example 1.3.1 (Fluids – Pressure). Let $V = Al$ be a cylinder with cross-section A and length l with a movable piston. Under the following quasistatic isothermal process:

$$\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) \rightarrow \left(T; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix} \right), \tag{1.86}$$

where $V + \Delta V = A(l + \Delta l)$, consider the mechanical work W done by the system. Let F be the force provided by the system. If Δl is sufficiently small, up to $(\Delta l)^2$ order,

$$W = F\Delta l = \frac{F}{A}A\Delta l = p\Delta V, \quad (1.87)$$

where $p = \frac{F}{A}$ stands for the pressure. As the process is quasistatic isothermal, $W = W_{\max}$, hence, as an equation of the thermodynamic system, we obtain:

$$\begin{aligned} p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) &:= \lim_{\Delta V \rightarrow +0} \frac{W_{\max}\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \mapsto \begin{pmatrix} V + \Delta V \\ N \end{pmatrix}\right)}{\Delta V} \\ &= - \lim_{\Delta V \rightarrow +0} \frac{F\left[T; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix}\right] - F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right]}{\Delta V} \\ &= - \frac{\partial F\left[T; \begin{pmatrix} V \\ N \end{pmatrix}\right]}{\partial V}. \end{aligned} \quad (1.88)$$

That is, the pressure of the system is given by the following function:

$$\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) \mapsto p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) \quad (1.89)$$

Such one is called the equation of state.

Exercise 1.3.2 (Intensive Property). Show that pressure is an intensive parameter:

$$p\left(T; \lambda \begin{pmatrix} V \\ N \end{pmatrix}\right) = p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) \quad (1.90)$$

for $\lambda > 0$.

Example 1.3.2 (Ideal Gas). As we examined in Remark 1,

$$p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) \approx \frac{NRT}{V}, \quad (1.91)$$

where T stands for the absolute “temperature.” So, we may consider, as a toy model of gas, an ideal gas whose pressure is exactly the right-hand side of the above equation. Moreover, we also require the heat capacity of an ideal gas to be proportional to the amount of substance only. So the following equations are the characteristics of an ideal gas:

$$\begin{aligned} p\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) &= \frac{NRT}{V} \\ C_V\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) &= cNR, \end{aligned} \quad (1.92)$$

where C_V is the heat capacity, defined in Definition 1.2.4. See College Physics §13.3 The Ideal Gas Law and University Physics Volume 2 §3.5 Heat Capacities of an Ideal Gas. It is worth mentioning that C_V has no T -dependence – Regnault’s law.

Recalling (1.88), we may obtain Helmholtz’s free energy of the ideal gas:

$$F \left[T; \left(\frac{V}{N} \right) \right] - F \left[T; \left(\frac{V_*}{N} \right) \right] = - \int_{V_*}^V \frac{NRT}{V'} dV' = -NRT \ln \frac{V}{V_*}, \quad (1.93)$$

where V_* is some initial volume, see Definition 1.3.7:

$$F \left[T; \left(\frac{V_*}{N} \right) \right] = 0. \quad (1.94)$$

Note that $\ln = \log$, see Algebra and Trigonometry 2e §6.3 Logarithmic Functions and Algebra and Trigonometry 2e §6.5 Logarithmic Properties. If we choose an initial condition, namely at $V_* = v(T)N$, where v is a function of absolute “temperature” and N of the amount of substance as a normalization factor then:

$$F \left[T; \left(\frac{V}{N} \right) \right] = -NRT \ln \frac{V}{v(T)N}. \quad (1.95)$$

Exercise 1.3.3. Plot $x \mapsto -\ln(x)$ and show $V \mapsto F \left[T; \left(\frac{V}{N} \right) \right]$ is a decreasing function. I.e., for the same amount of ideal gas, the smaller the volume V is, the more work can be done by the system.

By Definition 1.2.4,

$$U \left(T; \left(\frac{V}{N} \right) \right) - U \left(T_*; \left(\frac{V}{N} \right) \right) = \int_{T_*}^T cNR dT' = cNR(T - T_*) \quad (1.96)$$

where we set:

$$U \left(T_*; \left(\frac{V}{N} \right) \right) = 0, \quad (1.97)$$

see Definition 1.2.3. Hence we may write:

$$U \left(T; \left(\frac{V}{N} \right) \right) = cNRT + Nu, \quad (1.98)$$

where $u = -cRT_*$. Note that the internal energy of the ideal gas does not change under isothermal processes.

As we obtain the internal energy of ideal gas, let us consider a quasistatic adiabatic process:

$$\left(T; \left(\frac{V}{N} \right) \right) \xrightarrow{\text{qa}} \left(T'; \left(\frac{V'}{N} \right) \right) \quad (1.99)$$

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

$$\Delta W = p\Delta V = \frac{NRT}{V} \Delta V, \quad (1.100)$$

where we use the equation of state. By energy conservation:

$$U(T; V, N) \xrightarrow[\Downarrow \Delta W]{\dots\dots\dots} U(T'; V', N) \quad (1.101)$$

we have

$$\Delta W = U\left(T; \left(\frac{V}{N}\right)\right) - U\left(T'; \left(\frac{V'}{N}\right)\right) = -cNR\Delta T. \quad (1.102)$$

Hence, we obtain the following differential equation:

$$\frac{NRT}{V} dV = -cNRdT. \quad (1.103)$$

Separating the variables:

$$c \int \frac{dT}{T} = - \int \frac{dV}{V} \quad (1.104)$$

we obtain the Poisson equation for an ideal gas:

$$T^c V = \text{constant under an adiabatic process} \quad (1.105)$$

1.4 Heat and Carnot's Theorem

Definition 1.4.1 (Maximum Heat Transfer From Heat Bath). For an isothermal process:

$$(T; X_1) \xrightarrow{i} (T; X_2), \quad (1.106)$$

let us define the maximum heat transfer $Q_{\max}(T; X_1 \mapsto X_2)$ from the T -reservoir to the system:

$$Q_{\max}(T; X_1 \mapsto X_2) := \max \left\{ Q \mid U(T; X_1) \xrightarrow[\Downarrow W]{\dots\dots\dots Q} U(T; X_2) \right\} \quad (1.107)$$

It follows, by Definition 1.3.6 and Definition 1.3.7,

$$\begin{aligned} Q_{\max}(T; X_1 \mapsto X_2) &= W_{\max}(T; X_1 \mapsto X_2) + U(T; X_2) - U(T; X_1) \\ &= U(T; X_2) - F[T; X_2] - U(T; X_1) + F[T; X_1] \end{aligned} \quad (1.108)$$

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 Process

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

Theorem 1.4.1 (Generalized Isothermal Process). *Let us consider the following processes:*

$$((T; X_1) | (T'; \lambda Y)) \xrightarrow{a} (\tilde{T}; X_1 \oplus \lambda Y) \xrightarrow{a} (T'_\lambda; X_2 \oplus \lambda Y), \quad (1.109)$$

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

$$(T; X_1) \xrightarrow{i'} (T'; X_2). \quad (1.110)$$

Proof. The corresponding state transitions are the following, see (1.49):

$$\left\{ \begin{array}{ccc} U(T'; \lambda Y) & \cdots \cdots \cdots & U(T'_\lambda; \lambda Y) \\ & \Downarrow Q'_\lambda & \\ U(T; X_1) & \cdots \cdots \cdots & U(T'_\lambda; X_2) \\ & \Downarrow W'_X & \end{array} \right. \quad (1.111)$$

By Definition 1.3.2 and its consequence in Lemma 1.3.2, both heat transfer Q'_λ and the work done by the system $W'_\lambda := U(T; X_1) - U(T; T_2) + Q'_\lambda$ have $\lambda \rightarrow +\infty$ limits:

$$U(T; X_1) \xrightarrow[\Downarrow W']{\Downarrow Q'} U(T'; X_2) \quad (1.112)$$

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

Remark 9 (Wall-Removal i' -Process). If we set $X_2 = X_1$:

$$(T; X_1) \xrightarrow{i'} (T'; X_1) \quad (1.113)$$

since the state stays X_1 , such i' -process provides zero work. As mentioned in Definition 1.1.3, such wall-removal i' -process requires no work as well.

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

$$(T; X_1) \xrightarrow{qa} (T'; X_3) \xrightarrow{qi} (T'; X_2). \quad (1.114)$$

Similarly, the maximum heat transfer from the environment is also given by the above quasistatic process.

Proof. Let W' be the work done by an arbitrary generalized isothermal process $(T; X) \xrightarrow{i'} (T'; X')$ under T' . Compare the following two processes:

$$(T; X_1) \xrightarrow[\text{qa}]{\text{i'}} (T'; X_3) \xrightarrow{\text{qi}} (T'; X_2) \quad (1.115)$$

The work W'_{qa} done by the quasistatic adiabatic process is given by the following energy conservation:

$$U(T; X_1) \xrightarrow{\downarrow W'_{\text{qa}}} U(T'; X_3) \quad (1.116)$$

The quasistatic isothermal process is expressed as:

$$U(T; X_3) \xrightarrow{\downarrow W'_{\text{qi}}} U(T'; X_2) \quad (1.117)$$

I.e., the work W_{q} done by these quasistatic processes is $W_{\text{q}} = W'_{\text{qa}} + W'_{\text{qi}}$.

Reverting quasistatic processes, consider the following cycle:

$$(T; X_1) \xrightarrow{\text{i}} (T'; X_2) \xrightarrow{\text{qi}} (T'; X_3) \xrightarrow{\text{qa}} (T; X_1) \quad (1.118)$$

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

$$W_{\text{cyc}} = W' - W_{\text{q}}. \quad (1.119)$$

By Theorem 1.3.1, $W_{\text{cyc}} \leq 0$ since the whole cycle is under T' -reservoir. In other words, it is an isothermal cycle, hence

$$W' \leq W_{\text{q}}. \quad (1.120)$$

Moreover, with the heat transfer Q' from T' -reservoir through $(T; X_1) \xrightarrow{\text{i}} (T'; X_2)$, see (1.112), we obtain:

$$\begin{aligned} 0 \geq W_{\text{cyc}} &= (Q' - U(T'; X_2) + U(T; X_1)) \\ &\quad - (U(T; X_1) - U(T'; X_3) + F[T'; X_3] - F[T'; X_2]) \\ &= Q' + F[T'; X_2] - F[T'; X_3] + U(T'; X_3) - U(T'; X_2) \\ &= Q' + Q_{\text{max}}(T' : X_2 \mapsto X_3). \end{aligned} \quad (1.121)$$

Hence, we conclude:

$$Q' \leq -Q_{\text{max}}(T' : X_2 \mapsto X_3) = Q'_{\text{qi}}. \quad (1.122)$$

■

Definition 1.4.2 (Postulate: Adiabatic Accessible Lower “Temperature” State). Let $T > 0$, and X_0 be a state. We assume that there exist $(T'; X_1)$ and a quasistatic adiabatic process:

$$(T; X_0) \xrightarrow{\text{qa}} (T'; X_1) \quad (1.123)$$

with $0 < T' < T$.

Experimentally, through adiabatic expansion of gas, the system provides positive work outside and “temperature” drops, 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 check “adiabatic expansion process.”

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

$$Q_{\max}(T; X_0 \mapsto X_1) > 0. \quad (1.124)$$

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

$$(T; X_1) \xrightarrow{\text{qi}} (T; X_0) \xrightarrow{\text{qa}} (T'; X_1) \xrightarrow{\text{i}} (T; X_1) \quad (1.125)$$

where the process $(T'; X_1) \xrightarrow{\text{i}} (T; X_1)$ is the generalized isothermal process under T -reservoir – not T' ! – in Theorem 1.4.1, and $T' > 0$ is that of Definition 1.4.2:

$$0 < T' < T. \quad (1.126)$$

Let W_{cyc} be the work done by the above isothermal cycle under T . By 1.3.1, $W_{\text{cyc}} \leq 0$:

$$\begin{aligned} 0 &\geq W_{\text{cyc}} = W_{\text{qi}} + W_{\text{qa}} + W_{\text{i}} \\ &= F[T; X_1] - F[T; X_0] + U(T; X_0) - U(T'; X_1) + 0 \\ &> F[T; X_1] - F[T; X_0] + U(T; X_0) - U(T(> T'); X_1) \\ &= -Q_{\max}(T; X_0 \mapsto X_1), \end{aligned} \quad (1.127)$$

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 $(T; X) \xrightarrow{\text{qi}} (T'; X')$ be a quasistatic isothermal process. If $Q_{\max}(T; X \mapsto X') = 0$, then there exists the corresponding quasistatic adiabatic process: $(T; X) \xrightarrow{\text{qa}} (T'; X')$.*

Proof. By Lemma 1.2.1 of $T' = T$ 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, we can replace X and X' , see Remark 10 for this complementary part. For the corresponding operation $X \mapsto X'$, we have a quasistatic adiabatic process:

$$(T; X) \xrightarrow{\text{qa}} (T'; X'), \quad (1.128)$$

where the final “temperature” T' is unknown. We will show that T' is indeed T and it is the desired quasistatic adiabatic process.

If we suppose $T' > T$, then we have the following adiabatic process:

$$(T; X) \xleftarrow{\text{qa}} (T'; X') \xrightarrow{\text{a}} (T; X) \quad (1.129)$$

By Definition 1.2.6, no such a “temperature” decreasing adiabatic process exists, hence we conclude $T' \leq T$. To show $T' = T$, suppose $T' < T$ for contradiction. By Lemma 1.2.2, we have $U(T'; X') < U(T; X')$. Now, we obtain the following cycle:

$$(T; X) \xrightarrow{\text{qa}} (T'; X') \xrightarrow{\text{i}} (T; X') \xleftarrow{\text{qi}} (T; X) \quad (1.130)$$

where $(T'; X') \xrightarrow{\text{i}} (T; X')$ is a generalized isothermal process under T -reservoir. That is, the whole cycle is isothermal, and, by Theorem 1.3.1, the work done by the cycle W_{cyc} is non-positive:

$$0 \geq W_{\text{cyc}} = U(T; X') - U(T; X) + Q_{\text{max}}(T; X \mapsto X') + U(T; X) - U(T'; X'). \quad (1.131)$$

Recalling the hypothesis $Q_{\text{max}}(T; X \mapsto X') = 0$, we obtain $U(T; X') - U(T'; X') \leq 0$, which is absurd. Hence, we establish $T' = T$. ■

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

$$(\tilde{T}; X) \xleftarrow{\text{qa}} (T; X') \quad (1.132)$$

If $\tilde{T} > T$ were the case, then we would have the following “temperature” decreasing adiabatic process:

$$(T; X) \xleftarrow{\text{a}} (T; X') \xleftarrow{\text{qa}} (\tilde{T}; X') \quad (1.133)$$

which contradicts with Definition 1.2.6, hence $\tilde{T} \leq T$. If we suppose $\tilde{T} < T$, to show $\tilde{T} = T$ by proof by contradiction, then we can form the following isothermal cycle:

$$(T; X) \xrightarrow{\text{qi}} (T; X') \xrightarrow{\text{qa}} (\tilde{T}; X) \xleftarrow{\text{i}'} (T; X) \quad (1.134)$$

where i' -process is under T -reservoir and by Lemma 1.2.2, $U(T; X) > U(\tilde{T} < T; X)$ as $T > \tilde{T}$. The total work done by this cycle W becomes

$$\begin{aligned} W &= U(T; X) - U(T; X') \\ &\quad + Q_{\text{max}}(T; X \mapsto X') + U(T; X') - U(\tilde{T}; X) + 0 \\ &= U(T; X) - U(\tilde{T}; X). \end{aligned} \quad (1.135)$$

By Theorem 1.3.1, $W \leq 0$ i.e., $U(T; X) \leq U(\tilde{T}; X)$, contradiction. Hence $\tilde{T} = T$ holds.

Theorem 1.4.2 (The Universality of Q_{\max} (Carnot)). Let $(T_L; X_0)$ and X_1 s.t., $Q_{\max}(T_L; X_0 \mapsto X_1) > 0$, see Lemma 1.4.1. For T_H , let us consider $Q_{\max}(T_H; X'_0 \mapsto X'_1)$, where $(T_H; X'_0)$ and $(T_H; X'_1)$ are some states s.t., the following quasistatic adiabatic processes exist:

$$\begin{array}{ccc} (T_H; X'_0) & & (T_H; X'_1) \\ \uparrow \text{qa} & & \uparrow \text{qa} \\ (T_L; X_0) & & (T_L; X_1) \end{array} \quad (1.136)$$

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 on neither a specific choice of thermodynamic systems nor the states, but solely on the “temperatures” T_L and T_H :

$$f_C(T_H, T_L) := \frac{Q_{\max}(T_H; X'_0 \mapsto X'_1)}{Q_{\max}(T_L; X_0 \mapsto X_1)} \quad (1.137)$$

We call f_C the Carnot function.

Definition 1.4.3 (Absolute Temperature). Before we state the proof of Theorem 1.4.2, let us define absolute temperatures that we have already used in Remark 1 and Example 1.3.2. Observe:

$$f_C(T_H, T_L) = \frac{Q_{\max}(T_H; \sim)}{Q_{\max}(T_M; \sim)} \frac{Q_{\max}(T_M; \sim)}{Q_{\max}(T_L; \sim)} = \frac{f_C(T_H, T_M)}{f_C(T_L, T_M)}, \quad (1.138)$$

where T_M is an arbitrary temperature and \sim stands for the corresponding transitions under given temperatures. As $f_C(T_H, T_L)$ depends solely on T_H and T_L , so as $\frac{f_C(T_H, T_M)}{f_C(T_L, T_M)}$. This motivates us to introduce absolute temperatures; a temperature scale is called absolute, for instance Kelvin or Rankine, iff the Carnot function coincides with the ratio of temperatures:

$$f_C(T_H, T_L) = \frac{T_H}{T_L}. \quad (1.139)$$

We use an absolute temperature – in stead of some 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.

Definition 1.4.4 (Carnot Cycle and Heat Engine). Let us define one of the most important concepts in Thermodynamics, Carnot cycle. The following cycle – a heat “engine” – is called Carnot cycle:

$$\begin{array}{ccc} (T_H; X'_0) & \xrightarrow{\text{qi}} & (T_H; X'_1) \\ \uparrow \text{qa} & & \downarrow \text{qa} \\ (T_L; X_0) & \xleftarrow{\text{qi}} & (T_L; X_1) \end{array} \quad (1.140)$$

The work W_{cyc} done by the above Carnot cycle is:

$$\begin{aligned}
W_{\text{cyc}} &= W_{\text{max}}(T_{\text{H}}; X'_0 \mapsto X'_1) + U(T_{\text{H}}; X'_1) - U(T_{\text{L}}; X_1) \\
&\quad + W_{\text{max}}(T_{\text{L}}; X_1 \mapsto X_0) + U(T_{\text{L}}; X_0) - U(T_{\text{H}}; X'_0) \\
&= W_{\text{max}}(T_{\text{H}}; X'_0 \mapsto X'_1) + U(T_{\text{H}}; X'_1) - U(T_{\text{H}}; X'_0) \\
&\quad - (W_{\text{max}}(T_{\text{L}}; X_0 \mapsto X_1) + U(T_{\text{H}}; X'_0) - U(T_{\text{L}}; X_0)) \\
&= Q_{\text{max}}(T_{\text{H}}; X'_0 \mapsto X'_1) - Q_{\text{max}}(T_{\text{L}}; X_0 \mapsto X_1),
\end{aligned} \tag{1.141}$$

where we have used Definition 1.4.1.

By Definition 1.4.1, $Q_{\text{max}}(T_{\text{H}}; X'_0 \mapsto X'_1)$ is the heat transfer from T_{H} -reservoir to the system and $Q_{\text{max}}(T_{\text{H}}; X_1 \mapsto X_0) = -Q_{\text{max}}(T_{\text{H}}; X_0 \mapsto X_1) < 0$ is the heat transfer from T_{L} -reservoir to the system along with $X_1 \mapsto X_0$, i.e., along with $X_1 \mapsto X_0$ $Q_{\text{max}}(T_{\text{H}}; X_0 \mapsto X_1) > 0$ is the heat transfer from the system to T_{L} -reservoir. Such an energy transformer – from heat to work – 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 us consider a state Y_0 of an arbitrary system. By Lemma 1.4.1, there exists Y_1 with

$$Q_{\text{max}}(T_{\text{L}}; Y_0 \mapsto Y_1) > 0. \tag{1.142}$$

For the following Carnot cycle:

$$\begin{array}{ccc}
(T_{\text{H}}; Y'_0) & \xrightarrow{\text{qi}} & (T_{\text{H}}; Y'_1) \\
\text{qa} \uparrow & & \downarrow \text{qa} \\
(T_{\text{L}}; Y_0) & \xleftarrow{\text{qi}} & (T_{\text{L}}; Y_1)
\end{array} \tag{1.143}$$

and given $Q_{\text{max}}(T_{\text{L}}; X_0 \mapsto X_1) > 0$, let us define a positive size parameter:

$$\lambda := \frac{Q_{\text{max}}(T_{\text{L}}; Y_0 \mapsto Y_1)}{Q_{\text{max}}(T_{\text{L}}; X_0 \mapsto X_1)} > 0. \tag{1.144}$$

Consider the following scaled but opposite Carnot cycle of λX and (1.143):

$$\begin{array}{ccc}
(T_{\text{H}}; \lambda X'_1) & \xrightarrow{\text{qi}} & (T_{\text{H}}; \lambda X'_0) & (T_{\text{H}}; Y'_0) & \xrightarrow{\text{qi}} & (T_{\text{H}}; Y'_1) \\
\text{qa} \uparrow & & \downarrow \text{qa} & \text{qa} \uparrow & & \downarrow \text{qa} \\
(T_{\text{L}}; \lambda X_1) & \xleftarrow{\text{qi}} & (T_{\text{L}}; \lambda X_0) & (T_{\text{L}}; Y_0) & \xleftarrow{\text{qi}} & (T_{\text{L}}; Y_1)
\end{array} \tag{1.145}$$

They can be processed simultaneously since they share the same temperature profiles:

$$\begin{array}{ccc}
(T_{\text{H}}; \lambda X'_1 \oplus Y'_0) & \xrightarrow{\text{qi}} & (T_{\text{H}}; \lambda X'_0 \oplus Y'_1) \\
\text{qa} \uparrow & & \downarrow \text{qa} \\
(T_{\text{L}}; \lambda X_1 \oplus Y_0) & \xleftarrow{\text{qi}} & (T_{\text{L}}; \lambda X_0 \oplus Y_1)
\end{array} \tag{1.146}$$

The bottom quasistatic isothermal process satisfies:

$$\begin{aligned}
& Q_{\max}(T_L; \lambda X_0 \oplus Y_1 \mapsto \lambda X_1 \oplus Y_0) \\
&= \lambda Q_{\max}(T_L; X_0 \mapsto X_1) - Q_{\max}(T_L; Y_0 \mapsto Y_1) \\
&= 0,
\end{aligned} \tag{1.147}$$

where we have used Definition 1.4.4 and the very definition of λ in (1.144). Hence we may apply Lemma 1.4.2, i.e., there exists a corresponding quasistatic adiabatic process. Replacing the bottom process, we obtain the following cycle:

$$\begin{array}{ccc}
(T_H; \lambda X'_1 \oplus Y'_0) & \xrightarrow{\text{qi}} & (T_H; \lambda X'_0 \oplus Y'_1) \\
\text{qa} \uparrow & & \downarrow \text{qa} \\
(T_L; \lambda X_1 \oplus Y_0) & \xleftarrow{\text{qa}} & (T_L; \lambda X_0 \oplus Y_1)
\end{array} \tag{1.148}$$

By construction, it is given by three adiabatic processes with an isothermal process under T_H -reservoir. That is, it is an isothermal cycle; since each process is quasistatic, by Theorem 1.3.1, the total work done is zero. Recalling Definition 1.4.4 and (1.141), we obtain:

$$\begin{aligned}
0 &= -\lambda(Q_{\max}(T_H; X'_0 \mapsto X'_1) - Q_{\max}(T_L; X_0 \mapsto X_1)) \\
&\quad + Q_{\max}(T_H; Y'_0 \mapsto Y'_1) - Q_{\max}(T_L; Y_0 \mapsto Y_1) \\
&= -\frac{Q_{\max}(T_L; Y_0 \mapsto Y_1)}{Q_{\max}(T_L; X_0 \mapsto X_1)}(Q_{\max}(T_H; X'_0 \mapsto X'_1) - Q_{\max}(T_L; X_0 \mapsto X_1)) \\
&\quad + Q_{\max}(T_H; Y'_0 \mapsto Y'_1) - Q_{\max}(T_L; Y_0 \mapsto Y_1) \\
&= -Q_{\max}(T_L; Y_0 \mapsto Y_1) \frac{Q_{\max}(T_H; X'_0 \mapsto X'_1)}{Q_{\max}(T_L; X_0 \mapsto X_1)} + Q_{\max}(T_H; Y'_0 \mapsto Y'_1)
\end{aligned} \tag{1.149}$$

Since $Q_{\max}(T_L; Y_0 \mapsto Y_1) > 0$ and the system Y is arbitrary, we establish:

$$f_C := \frac{Q_{\max}(T_H; X'_0 \mapsto X'_1)}{Q_{\max}(T_L; X_0 \mapsto X_1)} = \frac{Q_{\max}(T_H; Y'_0 \mapsto Y'_1)}{Q_{\max}(T_L; Y_0 \mapsto Y_1)} \tag{1.150}$$

the universality – independence of the physical systems – of Carnot function f_C . ■

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 engines⁹.

⁹<https://www.aps.org/publications/apsnews/200906/physicshistory.cfm>

1.4.3 Efficiency of Heat Engines

Definition 1.4.5 (Efficiency of Heat Engines). Let $0 < T_L < T_H$. If a heat engine takes $Q_H > 0$ of heat from T_H -reservoir, gives $Q_L > 0$ to T_L -reservoir, the work W done by the engine is defined via:

$$E \begin{array}{c} \cdots \downarrow Q_H \cdots \\ \downarrow W \quad \downarrow Q_L \end{array} \rightarrow E \quad W = Q_H - Q_L. \quad (1.151)$$

The efficiency ε of this heat engine is:

$$\varepsilon := \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H}. \quad (1.152)$$

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). *As a heat engine, the efficiency of the Carnot cycle in Definition 1.4.4 is*

$$\varepsilon_C = 1 - \frac{T_L}{T_H}, \quad (1.153)$$

where T_L, T_H are absolute temperatures of reservoirs.

Proof. By Definition 1.4.3,

$$f_C(T_H, T_L) = \frac{T_H}{T_L} = \frac{Q_{\max}(T_H; X'_0 \mapsto X'_1)}{Q_{\max}(T_L; X_0 \mapsto X_1)} \quad (1.154)$$

and

$$W_{\text{cyc}} = Q_{\max}(T_H; X'_0 \mapsto X'_1) - Q_{\max}(T_L; X_0 \mapsto X_1), \quad (1.155)$$

we obtain the desired result:

$$1 - \frac{Q_{\max}(T_L; X_0 \mapsto X_1)}{Q_{\max}(T_H; X'_0 \mapsto X'_1)} = 1 - \frac{T_L}{T_H}, \quad (1.156)$$

■

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. It means that for any heat engine between two heat baths $T_L < T_H$, its efficiency is always smaller than, or equal to, that of Carnot's cycle:

Exercise 1.4.2. Carnot showed that no heat engine with greater efficiency than that of Carnot's cycle. Let's us show his claim.

Consider an arbitrary heat engine:

$$e \begin{array}{c} \cdots \downarrow q_H \cdots \\ \downarrow w \quad \downarrow q_L \end{array} \rightarrow e \quad (1.157)$$

1. Define the efficiency ε' of this process.
2. Let $\lambda := \frac{q_H}{Q_H}$ and consider the inverse of the λ -scaled Carnot cycle in Lemma 1.4.3.
3. If we combine these two processes – (1.157) and the scaled inverse Carnot process in Lemma 1.4.3 – we have another heat engine:

$$E' \begin{array}{c} \xrightarrow{\downarrow Q'_H} \\ \downarrow W' \quad \downarrow Q'_L \end{array} E' \quad (1.158)$$

Find 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, we may apply Theorem 1.3.1. Then, conclude $\varepsilon' \leq \varepsilon_C$.

We can show his theorem under milder conditions with mathematical rigor, see Theorem 1.5.4.

1.5 Entropy

Heat cannot be completely converted to mechanical work and always involves loss. The quantity that gives an analytical expression to this tendency toward loss of availability is entropy.

1.5.1 Entropy

Definition 1.5.1 (Entropy). We define, for an equilibrium state $(T; X)$,

$$S(T; X) := \frac{U(T; X) - F[T; X]}{T}. \quad (1.159)$$

We call $S(T; X)$ the entropy of the state $(T; X)$. For a quasistatic isothermal process, $(T; X_1) \xrightarrow{\text{qi}} (T; X_2)$, recalling Definition 1.4.1, the heat transfer $Q_{\max}(T; X_1 \mapsto X_2)$ from T -reservoir is:

$$Q_{\max}(T; X_1 \mapsto X_2) = U(T; X_2) - F[T; X_2] - (U(T; X_1) - F[T; X_1]) \quad (1.160)$$

Hence, entropy S satisfies:

$$S(T; X_1) \begin{array}{c} \xrightarrow{\downarrow Q_{\max}/T} \\ \end{array} S(T; X_2) \quad S(T; X_2) - S(T; X_1) = \frac{Q_{\max}(T; X_1 \mapsto X_2)}{T} \quad (1.161)$$

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 $S(T; X)$ is 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. Find 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 Prefixes¹¹.

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

$$\begin{array}{ccc} (T_H; X'_0) & & (T_H; X'_1) \\ \uparrow qa & & \uparrow qa \\ (T_L; X_0) & & (T_L; X_1) \end{array} \quad (1.162)$$

the change in entropy is invariant:

$$S(T_H; X'_0) - S(T_L; X_0) = S(T_H; X'_1) - S(T_L; X_1). \quad (1.163)$$

Proof. By Theorem 1.4.2 and Definition 1.4.3, along with the given quasistatic adiabatic processes,

$$\frac{T_H}{T_L} = \frac{Q_{\max}(T_H; X'_0 \mapsto X'_1)}{Q_{\max}(T_L; X_0 \mapsto X_1)} \quad (1.164)$$

holds. Hence:

$$\begin{aligned} S(T_H; X'_1) - S(T_H; X'_0) &= \frac{Q_{\max}(T_H; X'_0 \mapsto X'_1)}{T_H} \\ &= \frac{Q_{\max}(T_L; X_0 \mapsto X_1)}{T_L} \\ &= S(T_L; X_1) - S(T_L; X_0) \end{aligned} \quad (1.165)$$

■

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 s.t., the entropy itself is invariant under quasistatic adiabatic processes. We choose a reference point $(T_*, \lambda X_*)$, $\lambda > 0$ and the corresponding entropy value λS_* for a scaled system with:

$$S(T_*; \lambda X_*) := \lambda S_* \quad (1.166)$$

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

¹¹Chapter 4 of <https://www.nist.gov/pml/special-publication-811>

and for any $(T; \lambda X)$ with $(T; \lambda X) \xleftrightarrow{\text{qa}} (T_*; \lambda X_*)$,

$$S(T; \lambda X) := \lambda S_*. \quad (1.167)$$

If we choose $(T_L; X_0)$ as the reference point $(T_*; X_*)$, we obtain $0 = S(T_H; X'_1) - S(T_L; X_1)$. That is, along with a quasistatic adiabatic process, say $(T_L; X_1) \xrightarrow{\text{qa}} (T_H; X'_1)$, entropy does not change:

$$S(T_L; X_1) = S(T_H; X'_1). \quad (1.168)$$

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 $(T; X)$:*

$$\frac{\partial U(T; X)}{\partial T} = T \frac{\partial S(T; X)}{\partial T}. \quad (1.169)$$

Proof. Let T_1, T_2 s.t., $0 < T_1 < T_2$, and X_1 be an arbitrary state of some system, and X_2, X_3 be states with

$$\begin{aligned} (T_2; X_1) &\xleftrightarrow{\text{qa}} (T_1; X_2) \\ (T_1; X_1) &\xleftrightarrow{\text{qa}} (T_2; X_3). \end{aligned} \quad (1.170)$$

Then we consider the following two cycles:

$$\begin{array}{ccc} (T_2; X_1) & \xrightarrow{\text{qi}} & (T_2; X_3) \\ \uparrow \text{qa} & \searrow \text{i}' & \downarrow \text{qa} \\ (T_1; X_2) & \xleftarrow{\text{qi}} & (T_1; X_1) \end{array} \quad (1.171)$$

Along with the left cycle, as $(T_2; X_1) \xrightarrow{\text{i}'} (T_1; X_1)$ is a T_1 -isothermal process with no work, see Remark 9, we may apply Theorem 1.3.1 for the total work done by the cycle:

$$\begin{aligned} 0 &\geq W_{\max}(T_1; X_1 \mapsto X_2) + W_{\text{ad}}((T_1; X_2) \rightarrow (T_2; X_2)) + 0 \\ &= F[T_1; X_1] - F[T_1; X_2] + U(T_1; X_2) - U(T_2; X_1) \\ &= F[T_1; X_1] - F[T_1; X_2] + U(T_1; X_2) - U(T_2; X_1) - U(T_1; X_1) + U(T_1; X_1) \\ &= T_1(S(T_1; X_2) - S(T_1; X_1)) - U(T_2; X_1) + U(T_1; X_1) \end{aligned} \quad (1.172)$$

As in Remark 14, the entropy is invariant under quasistatic adiabatic processes. So, we have $S(T_1; X_2) = S(T_2; X_1)$. We obtain

$$T_1(S(T_2; X_1) - S(T_1; X_1)) - U(T_2; X_1) + U(T_1; X_1) \leq 0 \quad (1.173)$$

i.e.,

$$S(T_2; X_1) - S(T_1; X_1) \leq \frac{U(T_2; X_1) - U(T_1; X_1)}{T_1}. \quad (1.174)$$

Similarly, along with the right cycle, an isothermal cycle under T_2 , the total work W' done by the cycle satisfies:

$$\begin{aligned}
0 &\geq W_{\max}(T_2; X_1 \mapsto X_3) + W_{\text{ad}}((T_2; X_3) \rightarrow (T_1; X_1)) + 0 \\
&= F[T_2; X_1] - F[T_2; X_3] + U(T_2; X_3) - U(T_1; X_1) - U(T_2; X_1) + U(T_2; X_1) \\
&= T_2(S(T_2; X_3) - S(T_2; X_1)) - U(T_1; X_1) + U(T_2; X_1) \\
&= T_2(S(T_1; X_1) - S(T_2; X_1)) - U(T_1; X_1) + U(T_2; X_1)
\end{aligned} \tag{1.175}$$

Hence, we obtain:

$$\frac{U(T_2; X_1) - U(T_1; X_1)}{T_2} \leq S(T_2; X_1) - S(T_1; X_1). \tag{1.176}$$

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

$$S(T_1; X_1) < S(T_2; X_1). \tag{1.177}$$

Combining the outcomes, we have:

$$\frac{1}{T_2} \frac{U(T_2; X_1) - U(T_1; X_1)}{T_2 - T_1} \leq \frac{S(T_2; X_1) - S(T_1; X_1)}{T_2 - T_1} \leq \frac{1}{T_1} \frac{U(T_2; X_1) - U(T_1; X_1)}{T_2 - T_1} \tag{1.178}$$

Hence, if we take the limit: $T_1 < T_2 \rightarrow T := T_1$, we obtain the desired result:

$$\frac{1}{T} \frac{\partial U(T; X)}{\partial T} = \frac{\partial S(T; X)}{\partial T}. \tag{1.179}$$

■

Corollary 1.5.1.1. *As we choose, if two states are accessible with a quasistatic adiabatic process, say $(T_1; X_1) \xrightarrow{\text{qa}} (T_2; X_2)$, then $S(T_1; X_1) = S(T_2; X_2)$ is the case. We claim the converse is also the case, namely if $S(T_1; X_1) = S(T_2; X_2)$ then there exists a quasistatic adiabatic process to connect these two states.*

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

$$(T_1; X_1) \xrightarrow{\text{qa}} (T_3; X_2), \tag{1.180}$$

where T_3 is some unknown final temperature. We will show T_3 coincides T_2 , i.e., this is the desired quasistatic adiabatic process. Clearly, we have $S(T_1; X_1) = S(T_3; X_2)$, and hence:

$$S(T_2; X_2) = S(T_1; X_1) = S(T_3; X_2) \tag{1.181}$$

Since S is an increasing function of temperature, we conclude $T_2 = T_3$. ■

Example 1.5.1 (Entropy and Helmholtz's Free Energy of Ideal Gas). Let us fix the constant $v(T)$ in (1.95) of Example 1.3.2. Consider a state $\left(T; \left(\frac{V}{N}\right)\right)$ with a reference point:

$$\begin{aligned} \left(T; \lambda \left(\frac{V}{N}\right)\right) &\overset{\text{qa}}{\longleftrightarrow} \left(T; \lambda \left(\frac{V_*}{N}\right)\right). \\ S\left(T_*; \lambda \left(\frac{V_*}{N}\right)\right) &:= \lambda cNR, \lambda > 0. \end{aligned} \quad (1.182)$$

As shown in Example 1.3.2, we have F and S for the ideal gas, so as entropy:

$$S\left(T; \left(\frac{V}{N}\right)\right) := \frac{U\left(T; \left(\frac{V}{N}\right)\right) - F\left[T; \left(\frac{V}{N}\right)\right]}{T} = \frac{cNR T + Nu + NRT \ln \frac{V}{v(T)N}}{T} \quad (1.183)$$

As in Remark 14, the entropy remains constant under a quasistatic adiabatic process, we obtain:

$$\lambda \left(\frac{Nu}{T} + NR \ln \frac{V}{v(T)N} \right) = 0. \quad (1.184)$$

That is,

$$v(T) = \frac{V}{N} \exp\left(\frac{u}{RT}\right). \quad (1.185)$$

Recalling the Poisson equation for an ideal gas $T^c V = T_*^c V_*$ in Example 1.3.2:

$$V = \left(\frac{T_*}{T}\right)^c V_*, \quad (1.186)$$

we establish:

$$v(T) = \left(\frac{T_*}{T}\right)^c \frac{V_*}{N} \exp\left(\frac{u}{RT}\right) = \left(\frac{T_*}{T}\right)^c v_* \exp\left(\frac{u}{RT}\right). \quad (1.187)$$

We then obtain the entropy for an ideal gas:

$$\begin{aligned} S\left(T; \lambda \left(\frac{V}{N}\right)\right) &= \lambda \left(cNR + NR \ln \left(\left(\frac{T}{T_*}\right)^c \frac{V}{V_*} \right) \right) \\ &= \lambda \left(cNR + NR \ln \left(\left(\frac{T}{T_*}\right)^c \frac{V}{v_* N} \right) \right), \end{aligned} \quad (1.188)$$

and

$$F\left[T; \left(\frac{V}{N}\right)\right] = -NRT \ln \frac{V}{v(T)N} = -NRT \ln \left(\left(\frac{T}{T_*}\right)^c \frac{V}{V_*} \right) + Nu. \quad (1.189)$$

Example 1.5.2 (Ideal Gas Thermometer). Recalling Example 1.5.1, let us examine a system of ideal gas as a thermometer:

$$F\left[T; \left(\frac{V}{N}\right)\right] = -NRT \ln \left(\left(\frac{T}{T_*}\right)^c \frac{V}{V_*} \right) + Nu, \quad (1.190)$$

where the temperature is an absolute temperature in Definition 1.4.3. We will see that the temperature in (1.92) of Example 1.3.2 is indeed the absolute temperature. Consider the following Carnot cycle:

$$\begin{array}{ccc}
 (T_H; V'_0, N) & \xrightarrow{\text{qi}} & (T_H; V'_1, N) \\
 \text{qa} \uparrow & & \downarrow \text{qa} \\
 (T_L; V_0, N) & \xleftarrow{\text{qi}} & (T_L; V_1, N)
 \end{array} \tag{1.191}$$

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

$$\begin{aligned}
 f_C(T_H, T_L) &:= \frac{Q_{\max}(T_H; V'_0 \mapsto V'_1)}{Q_{\max}(T_L; V_0 \mapsto V_1)} \\
 &= \frac{F\left[T_H; \left(\frac{V'_0}{N}\right)\right] - F\left[T_H; \left(\frac{V'_1}{N}\right)\right] + U\left(T_H; \left(\frac{V'_1}{N}\right)\right) - U\left(T_H; \left(\frac{V'_0}{N}\right)\right)}{F\left[T_L; \left(\frac{V_0}{N}\right)\right] - F\left[T_L; \left(\frac{V_1}{N}\right)\right] + F\left[T_L; \left(\frac{V_1}{N}\right)\right] - F\left[T_L; \left(\frac{V_0}{N}\right)\right]} \\
 &= \frac{F\left[T_H; \left(\frac{V'_0}{N}\right)\right] - F\left[T_H; \left(\frac{V'_1}{N}\right)\right]}{F\left[T_L; \left(\frac{V_0}{N}\right)\right] - F\left[T_L; \left(\frac{V_1}{N}\right)\right]} \\
 &= \frac{NRT_H \ln\left(\frac{V'_1}{V'_0}\right)}{NRT_L \ln\left(\frac{V_1}{V_0}\right)}
 \end{aligned} \tag{1.192}$$

Poisson equation in Example 1.3.2 implies:

$$\begin{aligned}
 (T_H)^c V'_1 &= (T_L)^c V_1 \\
 (T_H)^c V'_0 &= (T_L)^c V_0.
 \end{aligned} \tag{1.193}$$

So, we obtain

$$\frac{V'_1}{V'_0} = \frac{V_1}{V_0} \tag{1.194}$$

Thus, we conclude:

$$f_C(T_H, T_L) = \frac{T_H}{T_L}. \tag{1.195}$$

That is, the temperature in the state equation of ideal gas $pV = NRT$ is indeed the absolute temperature.

Example 1.5.3 (Entropy and Heat Transfer). Along with $(T; X) \xrightarrow{\text{qi}} (T; X')$ of a quasistatic isothermal process, let

$$\begin{aligned}
 \Delta Q &:= Q_{\max}(T; X \mapsto X') \\
 \Delta S &:= S(T; X') - S(T; X)
 \end{aligned} \tag{1.196}$$

Then, by Definition 1.5.1, (1.161) becomes

$$\Delta S = \frac{\Delta Q}{T}. \quad (1.197)$$

If the transition $X \mapsto X'$ is an under quasistatic adiabatic process $(T; X) \xrightarrow{\text{qa}} (T'; X')$, as no heater transfer $\Delta Q = 0$ and $\Delta S = 0$ by Theorem 1.5.2, the above equation holds. From (T, X) to (T', X') , consider the following sequence of quasistatic isothermal and quasistatic adiabatic processes:

$$(T, X) \xrightarrow{\text{qi}} (T; X_1) \xrightarrow{\text{qa}} (T_1, X_1) \xrightarrow{\text{qi}} (T_1; X_2) \xrightarrow{\text{qa}} (T_2, X_2) \xrightarrow{\text{qi}} \dots (T', X') \quad (1.198)$$

Note that such a path from $(T; X)$ to $(T'; X')$ is not unique. Along with such a specific path, we can sum all the entropy change:

$$S(T'; X') - S(T; X) = \sum_{k=1}^n \Delta S_k = \sum_{k=1}^n \frac{\Delta Q_k}{T_k}, \quad (1.199)$$

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

$$\Delta Q_k = \Delta Q_k + 0 = Q_{\max}(T_{k-1}; X_{k-1} \mapsto X_k) + 0 \quad (1.200)$$

is the net heat transfer to the system along with $(T_{k-1}, X_{k-1}) \xrightarrow{\text{qi}} (T_{k-1}; X_k) \xrightarrow{\text{qa}} (T_k, X_k)$ for $k \in \{1, \dots, n\}$. If we formally take the limit $n \rightarrow \infty$, we obtain

$$S(T'; X') - S(T; X) = \int_{(T; X)}^{(T'; X')} \frac{dQ}{T} \quad (1.201)$$

of a Riemann integral representation of the entropy difference, 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 of some system. For $T_1, T_2 > 0$, an adiabatic process exists $(T_1; X_1) \xrightarrow{\text{a}} (T_2; X_2)$ iff*

$$S(T_1; X_1) \leq S(T_2; X_2). \quad (1.202)$$

Remark 15. As a consequence of this claim, 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 a quasistatic process is reversible by the very definition, see Definition 1.2.1 and Theorem 1.5.1.1, the entropy remains constant under quasistatic processes.

Proof. (\Rightarrow) Suppose $S(T_1, X_1) \leq S(T_2; X_2)$. Along with $X_1 \mapsto X_2$, let us consider the following quasistatic adiabatic process:

$$(T_1; X_1) \xrightarrow{\text{qa}} (T_3; X_2), \quad (1.203)$$

where T_3 is some unknown final temperature. Since

$$S(T_3; X_2) = S(T_1; X_1) \leq S(T_2; X_2) \quad (1.204)$$

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

$$(T_3; X_2) \xrightarrow{a} (T_2; X_2). \quad (1.205)$$

Hence, we obtain the desired adiabatic process:

$$(T_1; X_1) \xrightarrow{qa} (T_3; X_2) \xrightarrow{a} (T_2; X_2). \quad (1.206)$$

(\Leftarrow) Suppose there exists an adiabatic process

$$(T_1; X_1) \xrightarrow{qa} (T_2; X_2). \quad (1.207)$$

Along with $X_2 \mapsto X_1$, consider the following quasistatic adiabatic process:

$$(T_2; X_2) \xrightarrow{qa} (T_4; X_1). \quad (1.208)$$

Then we obtain:

$$(T_1; X_1) \xrightarrow{qa} (T_2; X_2) \xrightarrow{qa} (T_4; X_1). \quad (1.209)$$

By Definition 1.2.6, $T_1 \leq T_4$, hence

$$S(T_1; X_1) = S(T_2; X_2) \leq S(T_4; X_1), \quad (1.210)$$

since S is an increasing function of temperature by Theorem 1.5.1. \blacksquare

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

$$\begin{aligned} S'(T; \lambda X) &= \lambda S'(T; X) \\ S'(T; X \oplus Y) &= S'(T; X) + S'(T; Y), \end{aligned} \quad (1.211)$$

then there are $A > 0, B$ with,

$$S'(T; \lambda X) = AS(T; \lambda X) + \lambda B. \quad (1.212)$$

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:

$$A := \frac{S'(T; \lambda X_2) - S'(T; \lambda X_1)}{S(T; \lambda X_2) - S(T; \lambda X_1)} = \frac{S'(T; X_2) - S'(T; X_1)}{S(T; X_2) - S(T; X_1)}. \quad (1.213)$$

As $S(T; X_1) < S(T; X_2)$ implies $S(T; X_1) \xrightarrow{a} S(T; X_2)$ is irreversible, hence $S'(T; X_1) < S'(T; X_2)$ and we conclude:

$$A > 0. \quad (1.214)$$

Define B via:

$$\begin{aligned}
\lambda B &:= S'(T; \lambda X_2) - AS(T; \lambda X_2) \\
&= S'(T; \lambda X_1) - AS(T; \lambda X_1) \\
&= \lambda (S'(T; X_1) - AS(T; X_1)).
\end{aligned} \tag{1.215}$$

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 $S(T; X) \leq S(T; X_1)$ then define $\lambda_A \geq 0$:

$$\lambda_A := \frac{S(T; X_1) - S(T; X)}{S(T; X_2) - S(T; X_1)}. \tag{1.216}$$

i.e., $\lambda_A S(T; X_2) - \lambda_A S(T; X_1) = S(T; X_1) - S(T; X)$, hence:

$$\begin{aligned}
S(T; (\lambda_A + 1) X_1) &= (\lambda_A + 1) S(T; X_1) \\
&= \lambda_A S(T; X_2) + S(T; X) \\
&= S(T; X \oplus \lambda_A X_2).
\end{aligned} \tag{1.217}$$

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

$$(T; (\lambda_A + 1) \lambda X_1) \xrightarrow{\text{qa}} (T; \lambda X \oplus \lambda_A \lambda X_2). \tag{1.218}$$

Then

$$S'(T; (\lambda_A + 1) \lambda X_1) = S'(T; \lambda X \oplus \lambda_A \lambda X_2). \tag{1.219}$$

moreover:

$$\frac{S(T; \lambda X_1) - S(T; \lambda X)}{S(T; \lambda X_2) - S(T; \lambda X_1)} = \lambda_A = \frac{S'(T; \lambda X_1) - S'(T; \lambda X)}{S'(T; \lambda X_2) - S'(T; \lambda X_1)}. \tag{1.220}$$

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

$$\begin{aligned}
S'(T; \lambda X) - S'(T; \lambda X_1) &= \lambda_A (S'(T; \lambda X_2) - S'(T; \lambda X_1)) \\
&= \lambda_A (S(T; \lambda X) - S(T; \lambda X_1)) \\
S'(T; \lambda X) &= AS(T; \lambda X) + S'(T; \lambda X_1) - AS(T; \lambda X_1) \\
&= AS(T; \lambda X) + \lambda B.
\end{aligned} \tag{1.221}$$

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

$$\lambda'_A := \frac{S(T; X) - S(T; X_1)}{S(T; X_2) - S(T; X_1)} > 0 \tag{1.222}$$

i.e.,

$$S(T; X_1 \oplus \lambda'_A X_2) = S(T; \lambda'_A X_1 \oplus X). \tag{1.223}$$

Then

$$\frac{S(T; \lambda X) - S(T; \lambda X_1)}{S(T; \lambda X_2) - S(T; \lambda X_1)} = \lambda'_A = \frac{S(T; \lambda X) - S(T; \lambda X_1)}{S(T; \lambda X_2) - S(T; \lambda X_1)} \tag{1.224}$$

and we obtain the same result $S'(T; \lambda X) = AS(T; \lambda X) + \lambda B$. ■

1.5.3 Entropy for Composite System

Definition 1.5.2. For a composite system, say

$$\{(T_1; X_1) | \cdots | (T_n; X_n)\} \quad (1.225)$$

where $|$ is the adiabatic wall in Lemma 1.3.1, we define

$$S(\{(T_1; X_1) | \cdots | (T_n; X_n)\}) := \sum_{j=1}^n S(T_j; X_j). \quad (1.226)$$

Lemma 1.5.2 (Entropy Principle for Composite System). *Suppose that (X_1, \dots, X_n) and (X'_1, \dots, X'_m) are physically accessible. We claim there exists an adiabatic process:*

$$\{(T_1; X_1) | \cdots | (T_n; X_n)\} \xrightarrow{a} \{(T'_1; X'_1) | \cdots | (T'_m; X'_m)\} \quad (1.227)$$

iff the following inequality is the case:

$$S(\{(T_1; X_1) | \cdots | (T_n; X_n)\}) \leq S(\{(T'_1; X'_1) | \cdots | (T'_m; X'_m)\}). \quad (1.228)$$

Proof. It suffices to consider the binary case:

$$\{(T_1; X_1) | (T_2; X_2)\} \quad (1.229)$$

The entropy of this system is given by:

$$S(T_1; X_1) + S(T_2; X_2). \quad (1.230)$$

Keeping the value, say $S(T_2; X_2)$ we may change the temperature of the second component into T_1 :

$$S(T_2; X_2) = S(T_1; \widetilde{X}_2), \quad (1.231)$$

where \widetilde{X}_2 is some accessible state of X_2 . By 1.5.2, it follows that there exists a quasistatic adiabatic process:

$$(T_2; X_2) \xleftrightarrow{\text{qa}} (T_1; \widetilde{X}_2). \quad (1.232)$$

Thus, we have

$$\{(T_1; X_1) | (T_2; X_2)\} \xleftrightarrow{\text{qa}} \{(T_1; X_1) | (T_1; \widetilde{X}_2)\} \xleftrightarrow{\text{qa}} (T_1; X_1 \oplus \widetilde{X}_2) \quad (1.233)$$

where the final step is the adiabatic wall removal; since the total system is already T_1 , it can be done adiabatically and quasistatic as well.

Continuing this process, we may consider

$$S(\{(T_1; X_1) | \cdots | (T_n; X_n)\}) = S(T_1; X_1 \oplus \widetilde{X}_2 \oplus \cdots \oplus \widetilde{X}_n) \quad (1.234)$$

and

$$S(\{(T'_1; X'_1) | \cdots | (T'_m; X'_m)\}) = S\left(T'_1; X'_1 \oplus \widetilde{X}'_2 \oplus \cdots \oplus \widetilde{X}'_m\right) \quad (1.235)$$

That is,

$$\left(T_1; X_1 \oplus \widetilde{X}_2 \oplus \cdots \oplus \widetilde{X}_n\right) \xrightarrow{\text{a}} \left(T'_1; X'_1 \oplus \widetilde{X}'_2 \oplus \cdots \oplus \widetilde{X}'_m\right) \quad (1.236)$$

iff the following inequality is the case:

$$S\left(T_1; X_1 \oplus \widetilde{X}_2 \oplus \cdots \oplus \widetilde{X}_n\right) \leq S\left(T'_1; X'_1 \oplus \widetilde{X}'_2 \oplus \cdots \oplus \widetilde{X}'_m\right) \quad (1.237)$$

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

$$S(\{(T_1; X_1) | \cdots | (T_n; X_n)\}) \leq S(\{(T'_1; X'_1) | \cdots | (T'_m; X'_m)\}) \quad (1.238)$$

iff the following adiabatic process exists:

$$\begin{array}{ccc} (\{(T_1; X_1) | \cdots | (T_n; X_n)\}) & & (\{(T'_1; X'_1) | \cdots | (T'_m; X'_m)\}) \\ \text{qa} \downarrow & & \uparrow \text{qa} \\ (T_1; X_1 \oplus \widetilde{X}_2 \oplus \cdots \oplus \widetilde{X}_n) & \xrightarrow{\text{a}} & (T'_1; X'_1 \oplus \widetilde{X}'_2 \oplus \cdots \oplus \widetilde{X}'_m) \end{array} \quad (1.239)$$

■

As we examined in Remark 12 and Exercise 1.4.2, Carnot's cycles have maximum efficiency as heat engines. Here we give a more rigorous version:

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

Proof. This proof is based on [LY99].

Consider a heat engine, a cyclic process around $(T; X)$. $1 - \frac{Q_L}{Q_H}$ gives the efficiency of the following heat engine:

$$U(T; X) \begin{array}{c} \xrightarrow{\downarrow Q_H} \\ \downarrow W \quad \downarrow Q_L \end{array} U(T; X) \quad W = Q_H - Q_L. \quad (1.240)$$

Let $(T_L; L)$ and $(T_H; H)$ be the initial states of finite size heat-baths with initial temperatures $0 < T_L < T_H$. Around one cycle, the transition is represented as the following adiabatic process:

$$((T_H; H) | (T; X) | (T_L; L)) \xrightarrow{\text{a}} ((T'_H; H) | (T; X) | (T'_L; L)). \quad (1.241)$$

Through this cyclic process, T_L -reservoir receives

$$Q_L := U(T'_L; L) - U(T_L; L) \quad (1.242)$$

of heat from the cycle, and T_H -reservoir gives

$$Q_H := U(T_H; H) - U(T_H'; H) \quad (1.243)$$

of heat to the cycle.

$$\begin{array}{ccc}
 U(T_H; H) & \cdots & U(T_H'; H) \\
 & \Downarrow Q_H & \\
 U(T; X) & \cdots & U(T; X) \\
 & \Downarrow Q_L & \\
 U(T_L; L) & \cdots & U(T_L'; L)
 \end{array}
 \quad \begin{array}{l}
 \\
 W = Q_H - Q_L. \\
 \\
 \end{array}
 \quad (1.244)$$

Suppose $Q_H > 0$ and $Q_L > 0$; by 1.2.2,

$$T_L < T_L', T_H' < T_H. \quad (1.245)$$

As shown in Lemma 1.5.2,

$$S((T_H; H) | (T; X) | (T_L; L)) \leq S((T_H'; H) | (T; X) | (T_L'; L)). \quad (1.246)$$

By Definition 1.5.2,

$$S(T_H; H) + S(T_L; L) \leq S(T_H'; H) + S(T_L'; L) \quad (1.247)$$

or equivalently:

$$S(T_H; H) - S(T_H'; H) \leq S(T_L'; L) - S(T_L; L) \quad (1.248)$$

If $T \mapsto S(T; H)$ is differentiable in some neighborhood of $T_H' \leq T \leq T_H$, the left-hand side becomes

$$\begin{aligned}
 S(T_H; H) - S(T_H'; H) &= \int_{T_H'}^{T_H} \frac{\partial S(T; H)}{\partial T} dT \\
 &= \int_{T_H'}^{T_H} \frac{1}{T} \frac{\partial U(T; H)}{\partial T} dT \\
 &\geq \frac{1}{T_H} \int_{T_H'}^{T_H} \frac{\partial U(T; H)}{\partial T} dT \\
 &= \frac{1}{T_H} (U(T_H; H) - U(T_H'; H)) \\
 &= \frac{Q_H}{T_H}.
 \end{aligned}
 \quad (1.249)$$

Similarly, if $T \mapsto S(T; L)$ is differentiable in some neighborhood of $T_L' \leq T \leq T_L$, left-hand side becomes

$$\begin{aligned}
S(T_L; L) - S(T_L'; L) &= \int_{T_L}^{T_L'} \frac{\partial S(T; L)}{\partial T} dT \\
&= \int_{T_L}^{T_L'} \frac{1}{T} \frac{\partial U(T; L)}{\partial T} dT \\
&\leq \frac{1}{T_L} \int_{T_L}^{T_L'} \frac{\partial U(T; L)}{\partial T} dT \\
&= \frac{1}{T_L} (U(T_L'; L) - U(T_L; L)) \\
&= \frac{Q_L}{T_L}.
\end{aligned} \tag{1.250}$$

Thus, we obtain $\frac{Q_H}{T_H} \leq \frac{Q_L}{T_L}$:

$$1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H}. \tag{1.251}$$

This is the desired inequality since $1 - \frac{T_L}{T_H}$ gives the efficiency of the Carnot's cycle with two heat baths $T_L < T_H$. ■

Definition 1.5.3 (Thermal Contact and Thermal Equilibrium). Let

$$((T; X) | (T'; Y)) \xrightarrow{a} (\tilde{T}; X \oplus Y) \tag{1.252}$$

be the wall removal process in Lemma 1.3.1 with $\lambda = 1$. Let Q be the heat transfer from Y to X :

$$Q = U(\tilde{T}; X) - U(T; X) = U(T'; Y) - U(\tilde{T}; Y). \tag{1.253}$$

If $Q = 0$, these two systems are called in thermal equilibrium; we denote:

$$(T; X) \sim (T'; Y) \tag{1.254}$$

iff no heat transfer between X and Y along with (1.252).

Theorem 1.5.5 (Thermal Contact and Thermal Equilibrium). *For the adiabatic wall removal process in (1.252), we claim:*

- If the heat transfer between X and Y is zero, then $T = \tilde{T} = T'$.
- 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. Suppose the heat transfer along with (1.252) is zero. By Definition 1.5.3, we have

$$U(\tilde{T}; X) - U(T; X) = 0 = U(T'; Y) - U(\tilde{T}; Y). \quad (1.255)$$

By Lemma 1.2.2, we obtain $T = \tilde{T} = T'$.

If we assume $T \neq T'$, the heat transfer must be non-zero. Let

$$Q = U(\tilde{T}; X) - U(T; X) = U(T'; Y) - U(\tilde{T}; Y) \quad (1.256)$$

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

$$T < \tilde{T} < T'. \quad (1.257)$$

Then, the change in total entropy is:

$$\begin{aligned} \Delta S &:= S(\tilde{T}; X \oplus Y) - S(T; X) - S(T'; Y) \\ &= S(\tilde{T}; X) - S(T; X) - S(T'; Y) + S(\tilde{T}; Y) \\ &= \int_T^{\tilde{T}} \frac{\partial S(t; X)}{\partial t} dt - \int_{\tilde{T}}^{T'} \frac{\partial S(t; Y)}{\partial t} dt \end{aligned} \quad (1.258)$$

By Theorem 1.5.1, we obtain:

$$\begin{aligned} \Delta S &= \int_T^{\tilde{T}} \frac{1}{t} \frac{\partial U(t; X)}{\partial t} dt - \int_{\tilde{T}}^{T'} \frac{1}{t} \frac{\partial U(t; Y)}{\partial t} dt \\ &> \frac{1}{\tilde{T}} \int_T^{\tilde{T}} \frac{\partial U(t; X)}{\partial t} dt - \frac{1}{\tilde{T}} \int_{\tilde{T}}^{T'} \frac{\partial U(t; Y)}{\partial t} dt \\ &= \frac{1}{\tilde{T}} \left(U(\tilde{T}; X) - U(T; X) - U(T'; Y) + U(\tilde{T}; Y) \right) \end{aligned} \quad (1.259)$$

Since the process is adiabatic and no net work is done, the last expression is zero: $U(T; X) + U(T'; Y) = U(\tilde{T}; X \oplus Y)$. Hence we obtain the desired result:

$$\Delta S > 0. \quad (1.260)$$

Remark 16 (Second Law of Thermodynamics). This is the well-known entropy statement of the second law of thermodynamics, namely spontaneous heat transfer is always from higher temperature to lower temperature. It is referred to as the Clausius statement of the second law of thermodynamics.

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

¹²University Physics Volume 2 §4.1 Reversible and Irreversible Processes

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 $T = T' = T''$. To show $(T; X) \sim (T; Z)$, consider the following wall removal:

$$((T; X) | (T; Z)) \xrightarrow{a} (\tilde{T}; X \oplus Z). \quad (1.261)$$

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

$$Q_{X \leftarrow Z} = U(\tilde{T}; X) - U(T; X) = U(T; Z) - U(\tilde{T}; Z). \quad (1.262)$$

If $T < \tilde{T}$, since U is T -increasing by Lemma 1.2.2, we have

$$\begin{aligned} U(\tilde{T}; X) - U(T; X) &> 0 \\ U(T; Z) - U(\tilde{T}; Z) &< 0, \end{aligned} \quad (1.263)$$

which is absurd; if $\tilde{T} < T$, we have

$$\begin{aligned} U(\tilde{T}; X) - U(T; X) &< 0 \\ U(T; Z) - U(\tilde{T}; Z) &> 0, \end{aligned} \quad (1.264)$$

which is absurd, again. Hence $T = \tilde{T}$ must be the case. Then, as we desire, $Q_{X \leftarrow Z} = 0$ holds. ■

Remark 17 (Zeroth Law of Thermodynamics). The last property is called zeroth law of thermodynamics. Mathematically, the thermal equilibrium as a binary relation forms an equivalence relation:

- Reflexivity
For any state $(T; X)$, $(T; X) \sim (T; X)$ holds.
- Symmetry
If $(T; X) \sim (T'; Y)$, then $(T'; Y) \sim (T; X)$ is the case.
- Transitivity
If $(T; X) \sim (T'; Y)$ and $(T'; Y) \sim (T''; Z)$, then $(T; X) \sim (T''; Z)$.

See College Physics 2e §13.1 Temperature and University Physics Volume 2 §1.1 Temperature and Thermal Equilibrium.

1.5.4 Applications

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

$$\begin{aligned} S(T; X) &= -\frac{\partial F[T; X]}{\partial T} \\ U(T; X) &= -T^2 \frac{\partial}{\partial T} \left(\frac{F[T; X]}{T} \right) \end{aligned} \quad (1.265)$$

That is if F is known as a function of $[T; X]$, both entropy S and internal energy U can be derived – F as a function of $[T; X]$ is a complete thermodynamic function.

Proof. By Definition 1.5.1 and Theorem 1.5.1,

$$\begin{aligned} \frac{\partial F[T; X]}{\partial T} &= \frac{\partial (U(T; X) - TS(T; X))}{\partial T} \\ &= \frac{\partial U(T; X)}{\partial T} - S(T; X) - T \frac{\partial S(T; X)}{\partial T} \\ &= -S(T; X). \end{aligned} \quad (1.266)$$

Similarly,

$$\begin{aligned} -T^2 \frac{\partial}{\partial T} \left(\frac{F[T; X]}{T} \right) &= -T^2 \frac{\partial}{\partial T} \left(\frac{U(T; X)}{T} - S(T; X) \right) \\ &= -T^2 \left(\frac{1}{T} \frac{\partial U(T; X)}{\partial T} - \frac{U(T; X)}{T^2} - \frac{\partial S(T; X)}{\partial T} \right) \\ &= U(T; X) + T \left(T \frac{\partial S(T; X)}{\partial T} - \frac{\partial U(T; X)}{\partial T} \right) \\ &= U(T; X). \end{aligned} \quad (1.267)$$

Hence, if we know F as a function of $[T; X]$, the internal energy and entropy of the system can be derived. ■

Definition 1.5.4 (Chemical Potential of Fluid). As we consider in Example 1.1.1 and Example 1.3.1, let us consider the reaction of the state $\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)$ under $N \mapsto N + \Delta N$:

$$\mu \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) := \frac{\partial F \left[T; \begin{pmatrix} V \\ N \end{pmatrix} \right]}{\partial N}. \quad (1.268)$$

We call μ the chemical potential.

Example 1.5.4 (The Chemical Potential of Ideal Gas). By Example 1.5.1, we can calculate the chemical potential of an ideal gas:

$$\begin{aligned}\mu\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right) &= \frac{\partial}{\partial N} \left(-NRT \ln \left(\left(\frac{T}{T_*} \right)^c \frac{V}{v_* N} \right) + Nu \right) \\ &= RT - RT \ln \left(\left(\frac{T}{T_*} \right)^c \frac{V}{v_* N} \right) + u\end{aligned}\quad (1.269)$$

Example 1.5.5 (Maxwell's Relations – Energy Equation and Ideal Gas). For simplicity, let us consider $\left(T; \begin{pmatrix} V \\ N \end{pmatrix}\right)$ of some fluid. Suppose F is sufficiently smooth, at least continuously double differentiable:

$$\frac{\partial}{\partial V} \frac{\partial F \left[T; \begin{pmatrix} V \\ N \end{pmatrix} \right]}{\partial T} = \frac{\partial}{\partial T} \frac{\partial F \left[T; \begin{pmatrix} V \\ N \end{pmatrix} \right]}{\partial V} \quad (1.270)$$

Recalling Theorem 1.5.6 and (1.88), we conclude:

$$\frac{\partial S \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)}{\partial V} = \frac{\partial p \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)}{\partial T}. \quad (1.271)$$

Hence, as $U = TS + F$ by Definition 1.5.1, we obtain the following energy equation:

$$\begin{aligned}\frac{\partial U \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)}{\partial V} &= \frac{\partial}{\partial V} \left(TS \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) + F \left[T; \begin{pmatrix} V \\ N \end{pmatrix} \right] \right) \\ &= T \frac{\partial p \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)}{\partial T} - p \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)\end{aligned}\quad (1.272)$$

If we apply the energy equation to an ideal gas examined in Example 1.3.2, we obtain

$$\frac{\partial U \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)}{\partial V} = T \frac{\partial p \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right)}{\partial T} - p \left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) = T \frac{\partial}{\partial T} \left(\frac{NRT}{V} \right) - \frac{NRT}{V} = 0 \quad (1.273)$$

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

Example 1.5.6 (Adiabatic Expansion). Let us consider an adiabatic expansion of fluid $\left(\begin{pmatrix} V \\ N \end{pmatrix}\right)$ of Example 1.1.1. Consider the following adiabatic expansion $V \mapsto V + \Delta V, \Delta V > 0$:

$$\left(T; \begin{pmatrix} V \\ N \end{pmatrix} \right) \xrightarrow{a} \left(T'; \begin{pmatrix} V + \Delta V \\ N \end{pmatrix} \right), \quad (1.274)$$

where T' is some final temperature. We will show that

$$S\left(T; \left(\frac{V}{N}\right)\right) < S\left(T'; \left(\frac{V + \Delta V}{N}\right)\right). \quad (1.275)$$

Consider the following quasistatic adiabatic compression:

$$\left(T'; \left(\frac{V + \Delta V}{N}\right)\right) \xrightarrow{\text{qa}} \left(T''; \left(\frac{V}{N}\right)\right). \quad (1.276)$$

Since the pressure of the fluid is always positive during this compression, some positive work is done on the fluid:

$$U(T'; V + \Delta V, N) \xrightarrow{\Downarrow W_{\text{external}} > 0} U(T''; V, N) \quad (1.277)$$

With the above adiabatic process, we obtain

$$U(T; V, N) \xrightarrow{\Downarrow W_{\text{external}} > 0} U(T''; V, N) \quad U\left(T; \left(\frac{V}{N}\right)\right) + W = U\left(T''; \left(\frac{V}{N}\right)\right), \quad (1.278)$$

i.e., $U(T''; V, N) - U(T; V, N) = W > 0$:

$$U(T; V, N) < U(T''; V, N). \quad (1.279)$$

By Lemma 1.2.2, we conclude $T < T''$. Moreover, by Theorem 1.5.1,

$$S\left(T; \left(\frac{V}{N}\right)\right) < S\left(T''; \left(\frac{V}{N}\right)\right) = S\left(T'; \left(\frac{V + \Delta V}{N}\right)\right). \quad (1.280)$$

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

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