

Thermodynamics and Statistical Physics

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Chapter 1

Thermodynamics

* The key point: learn how to describe many-body systems.

1.1 Thermal equilibrium and temperature

1.1.1 Macroscopic thermodynamic state

The system considered in thermodynamics is a *macroscopic* system which consists of many “*microscopic*” particles or elements, e.g. gases, liquids, solids, plasmas, granular matter, celestial matter, human being, companies.

Thermodynamics is an *empirical* theory for the macroscopic systems, typically based on experiments or observations.

Important: the system contains “*many*” particles, e.g. 1 cm^3 gas consists of $\sim 10^{19}$ molecules.

Why not mechanics, et al.?

- Historically, one didn't know what “heat” is, also the microscopic structure of the macroscopic system.
- It is too difficult to solve the equations of motion.
- Complexity in many-body systems, compared with few-body systems.

Therefore, one introduces some macroscopic parameters, or observables, to describe the macroscopic properties of the system.

- Mechanical parameters
pressure P , volume V
- chemical parameters
density n , chemical potential μ
- Electromagnetic parameters
electric field \vec{E} , magnetic field \vec{B}
- Thermal parameters
temperature T , heat, entropy S
 T and S are exclusively from thermodynamics!

A macroscopic state is described by a “complete” set of parameters. We may construct a parameter space with the complete set of parameters x_1, x_2, \dots, x_M , then a state i can be represented by a point $(x_1^i, x_2^i, \dots, x_M^i)$ in the space. When the system changes its states, the point moves and forms a surface.

- The number of parameters in the complete set is *fixed* for a system. This is important, and should be always kept in mind. E.g., for a (dilute) gas, the number is two.
- All other parameters can be expressed as functors of the complete set of parameters.

We should find the laws governing these parameters.

Classification of the macroscopic states

{	equilibrium state:	parameters do not depend on time t , this is what we study in this course
	non-equi. state:	parameters evolves as t , or more complicated, e.g. one needs local parameters

Classification of the systems

- An isolated system
nothing is exchanged with the environment
- A thermally isolated system
no “heat” is exchange with the environment

Classification of the parameters

- Extensive parameters: $\sim V$
- Intensive parameters: independent of V

It is a good approximation that all physical parameters are either extensive or intensive.

Question: why?

Why may such a classification be useful?

e.g. for a system not too far from equilibrium, we may divide it into many pieces, then the extensive parameters can be just added up.

1.1.2 Thermal equilibrium and temperature

We can easily understand pressure, volume, density, et al, which can be defined with the knowledge in other subjects. So let us concentrate our attention on thermal observables, e.g., the temperature first.

In the daily life, we feel “hot” or “cold”, what is it? How to quantitatively describe it?

Observation: Initially, two systems are differently hot or cold, then they thermally touch each other. After a long time, they become equally hot or cold. Then we call that they are in thermal equilibrium.

The zero-th law:

If systems A and B are each in thermal equilibrium with a third system C , then A and B are in thermal equilibrium with each other.

Let us introduce a parameter T , i.e., the temperature to describe how hot or cold the system is, and *assume* the temperatures of two system in thermal equilibrium are the same.

The last assumption is very important! Otherwise we can not compare the temperatures of different systems, and T is useless.

The zero-th law is essential! Otherwise T is not unique, not well defined. In other words, the zeroth law defines the temperature.

Question: why do we feel differently when touching wood and iron at a same temperature.

Furthermore, T is a property of the macroscopic state. This is clear from the definition which does not depend on any history how the system comes to thermal equilibrium, – this is somehow also an assumption, i.e., we may have a “complete” set of parameters already even without the temperature.

As mentioned before, we may introduce many parameters to describe the macroscopic properties of a system, but not all are independent. Assuming, (x_1, x_2, \dots, x_M) is a complete set, T should be the function of (x_1, x_2, \dots, x_M) , i.e.,

$$f(T, x_1, x_2, \dots, x_M) = 0$$

This is called the *equation of state*

E.g.,

(1) The Ideal gas

$$PV = NkT$$

N : number of molecules

k : Boltzmann's constant, 1.38×10^{-16} erg/deg

T : temperature

(2) Real gases

Assuming P is not too high

$$\begin{aligned} PV &= A + BP + CP^2 + \dots \\ &= A + \frac{B'}{V} + \frac{C'}{V^2} + \dots \end{aligned}$$

$A, B(B'), C(C'), \dots$ all are functions of T .

1.1.3 Temperature scales

To define the temperature scale, we may proceed as follow:

- 1) choose a specific system
- 2) choose a specific property which depends on temperature
- 3) fix the relation between this property and T
- 4) set the unit of T

E.g. 1) water, 2) volume, 3) liner relation between V and T , 4) the transition point from liquid to solid is $T = 0$, the transition point from gas to liquid is $T = 100$.

Mathematically

$$\begin{aligned} T &= aV + b \\ 0 &= aV_i + b \\ 100 &= aV_f + b \end{aligned}$$

then

$$a = \frac{100}{V_f - V_i}, \quad b = -\frac{100V_i}{V_f - V_i}$$

To define temperature in this way, however, theoretically is not so elegant, for it depends on the system and the property we choose. It is not “universal”, and it is “difficult” to accurately measure it.

A somewhat better choice is to choose the ideal gas as the specific system. Experimentally, it is set up that at a certain (fixed) temperature

$$PV = \text{const. (depending on temperature)}$$

- Fix V , following the above procedure

$$T_V = 100 \frac{P - P_i}{P_f - P_i}$$

- Fix P ,

$$T_P = 100 \frac{V - V_i}{V_f - V_i}$$

Exercise Prove $T_V = T_P$

Hint: assume $PV = a_V T_V + b_V$ and $PV = a_P T_P + b_P$, and prove $a_V = a_P$ and $b_V = b_P$.

Proof: Since

$$PV_i = a_V 100 \frac{P - P_i}{P_f - P_i} + b_V$$

therefore,

$$a_V = \frac{P_f - P_i}{100} V_i, \quad b_V = a_V \frac{100P_i}{P_f - P_i} = P_i V_i$$

Similarly,

$$P_i V = a_P 100 \frac{V - V_i}{V_f - V_i} + b_P$$

therefore,

$$a_P = \frac{V_f - V_i}{100} P_i, \quad b_P = a_P \frac{100 V_i}{V_f - V_i} = P_i V_i$$

Since $P_f V_i = V_f P_i$ (fixed by the boiling point of water),

$$a_P = a_V \quad b_P = b_V$$

- The ideal-gas temperature scale

$$PV = NkT$$

1.2 The first law

1.2.1 Thermodynamic transformation

A change of state is a thermodynamic *transformation*. The transformation can be realized only by the *external condition*. Note that here we only consider the equilibrium state.

If the external condition changes so slowly that at any moment the system is approximately in equilibrium, the transformation is called *quasi-static*. For example, for the ideal gas, every point on the $P - V$ space represents an equilibrium state, and a quasi-static transformation is a continuous path on the $P - V$ diagram.

If not specified, we concern only quasi-static transformation.

The concept of work is taken over from mechanics. For a system described by (P, V) , the work done by the system in an infinitesimal transformation is

$$dW = PdV$$

Question: why?

e.g., in Fig. 1.1, $dW = P \cdot S \cdot dx$

For a finite process

$$\Delta W = \int dW = \int PdV$$

Important: Work is not fixed by the initial and final states, but depends on the specific process between the initial and final states.

Now, it comes another thermal concept, “heat”. “Heat” is what is absorbed by a system, if its temperature increases while no work is done.

e.g., as shown in Fig. 1.2 for $T_2 > T_1$

Obviously, the temperature of system 1 will increase therefore something should “flow” from system 2 to system 1, otherwise the temperature of system 1 will not increase.

Apparently

$$dQ = CdT$$

C is called the heat capacity, it depends on the detailed nature of the system, e.g., C_V and C_P .

Experimentally, we may fix the unit of Q with a specific system, e.g., increase the temperature of water by one degree.

$\Delta Q = \int dQ$ is also process-dependent.

1.2.2 The first law

For an arbitrary transformation given the initial and final states, let

ΔQ denote the heat absorbed by the system

ΔW denote the work done by the system

Minus sign of ΔQ and ΔW represents the opposite direction. The first law states that the quantity ΔU defined by

$$\Delta U = \Delta Q - \Delta W$$

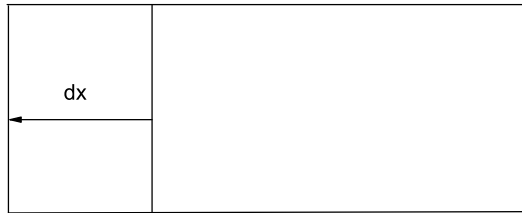


Figure 1.1:

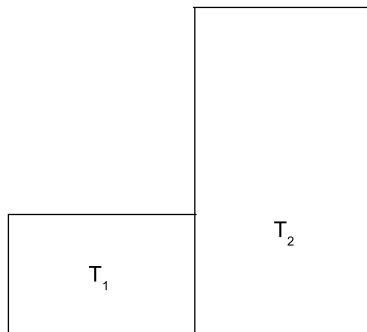


Figure 1.2:

is the same for all possible transformations, i.e. it only depends on the initial and final states.

This immediately defines a state function U , called the internal energy. Of course, it is defined only up to a constant. Experimentally, it is found that U is extensive. U being a state function means, for an infinitesimal transformation

$$dU = dQ - dW$$

is exact. That is, dU is a differential .

e.g., if

$$U = U(P, V)$$

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

dU being exact leads to

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial P}\right)_V \right]_P = \frac{\partial}{\partial P} \left[\left(\frac{\partial U}{\partial V}\right)_P \right]_V$$

Question: how to prove that dU being exact is equivalent to U being a state function?

Actually, it is also equivalent to that any loop integrals are zero, or any integrals between two states are path independent.

- If the number of independent parameters is one,

$$U = U(P)$$

$$\Delta U(P) = \int_{P_1}^{P_2} dU(P) = U(P_2) - U(P_1)$$

- If the number of independent parameters is two, as shown in Fig. 1.3,

$$U = U(P, V)$$

$$\begin{aligned}
\Delta U &= \int_{(P_1, V_1)}^{(P_2, V_2)} dU(P, V) \\
&= \int_{(P_1, V_1)}^{(P_2, V_2)} dU(P, V_C(P)) \\
&= U(P_2, V_2) - U(P_1, V_1)
\end{aligned}$$

What is the physical meaning of the first law? It states that heat is also a kind of energy, and it is feasible to convert mechanical work into heat or vice versa. When talking about energy conservation, heat should be included.

Then, what is heat?

Heat is the energy transferred through microscopic irregular motion of molecules, or particles, or elements. “Irregular” here means looking at macroscopically. Of course, the microscopic motion is still governed by the Newton’s laws et al.

U excludes the global mechanical energy,

U includes the energy of irregular motion, interacting energy between molecules, energy inside a molecule, and energy in a field.

The temperature measures how irregular the microscopic motion is. This will be understood in statistical physics.

1.2.3 Some applications

1) Exercises: (1.5) (1.6) (1.7) in the textbook

It can be deduced that

$$\begin{aligned}
C_V &\equiv \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \text{ (from(1.7))} \\
C_P &\equiv \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P \text{ (from(1.6))}
\end{aligned}$$

$H = U + PV$ called enthalpy

2) Free expansion of an ideal gas

Experimental finding: $T_1 = T_2$ in Fig. 1.3 in the textbook

Since $\Delta W = 0$, $\Delta T = 0$,

Therefore $\Delta Q = 0$ (since $\Delta T = 0$), $\Delta U = 0$ (from the 1st law)

We may take T and V as independent variables, $U = U(T, V)$. Therefore, $U = U(T)$ (since ΔV is non-zero).

3). 4). b). c). in the textbook, page 9.

1.3 The second law

1.3.1 Reversible and irreversible transformations

Observation:

All naturally occurring processes proceed in one direction only. They never, of their own accord, proceed in the opposite direction. E.g.,

- A stone resting on the ground never leaps up into the air.
- A cup of hot coffee never gets hotter
- The molecules of a drop of ink in a glass of water spread uniformly throughout the volume of the water. They never regroup into a drop-shaped clump.

The second law concerns the direction of the processes.

A *reversible* transformation is a transformation that the system retraces its history in time when the external condition retraces its history in time.

Important: If only the system retraces its history, the environment not, the transformation is not reversible.

Examples of irreversible transformations

- All naturally occurring processes are irreversible.

These are the processes that the systems relax from their non-equilibrium states to equilibrium states, they never go in the opposite direction.

- A process contains a relaxation from a non-equilibrium state to an equilibrium state. For example, as it is shown in Fig. 1.4

Examples of reversible transformations

- A and B systems are in thermal equilibrium.

As shown in Fig. 1.5. We increase the temperature of B by dT , then a certain amount of heat dQ will be transferred to A . Then we cool down B by dT , the same dQ will be transferred from A back to B .

Question: if dT is finite, is it still reversible?

- Fig. 1.8 in the textbook

A heat reservoir is a system so large that the gain or loss of any finite amount of heat does not change its temperature.

The system absorbs the heat from the reservoir and transfers the energy to the spring. This process can be reversed, different from free expansion.

- Reversible transformations have to be quasi-static, but reverse is not necessarily true.

But such examples are rare, we may usually think that quasi-static and reversible are equivalent.

Discussions: why irreversible?

E.g., as shown in Fig. 1.6, Newton's equations are reversible in time. Therefore, the mechanical motion of the

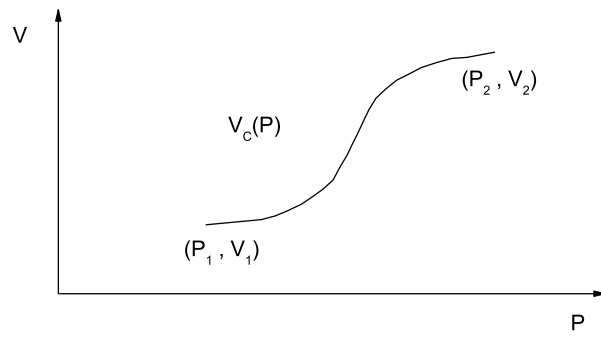


Figure 1.3:

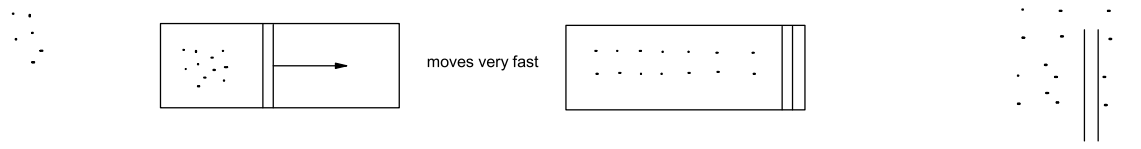


Figure 1.4:

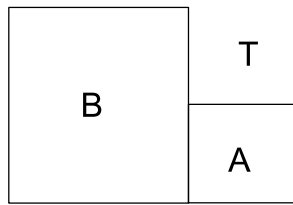


Figure 1.5:

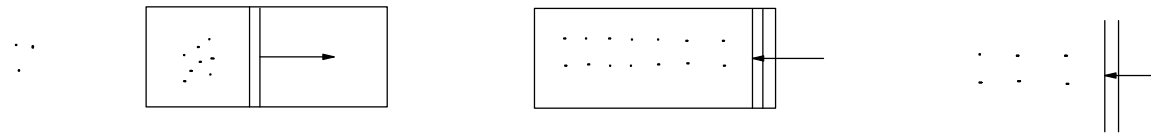


Figure 1.6:

microscopic particles is reversible. Why is the macroscopic process irreversible?

Indeed, microscopically, if we start from a microscopic configuration in the final macroscopic state with V_2 , and reverse the motion of all particles, the particles will come back to the microscopic state in the initial state with V_1 . But this probability is very small.

The probability for a particle to stay in V_1 is $(V_1/V_2)^N$. Since the number N of the particles is a big number $(V_1/V_2)^N$ is infinitesimal small. In simple words, the initial condition violates the reversibility of the Newton's law in time.

1.3.2 The second law

Kelvin statement: There exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work.

Otherwise, we would not have any energy crisis.

Clausius statement: There exists no thermodynamic transformation whose sole effect is to transfer a quantity of heat from a colder reservoir to a hotter reservoir.

That is why we need refrigerators.

E.g., when an ideal gas is expanded reversibly and isothermally, a quantity of heat absorbed from the reservoir is entirely converted to work. However, this process is allowed by the second law because the volume of the gas is changed, i.e., the word "sole" is violated.

Adiabatic expansions don't violate the second law, since the work is not converted from heat, rather from the change of state.

From the view of a relaxation from a non-equilibrium state to an equilibrium state. Clausius statement is obvious.

Kelvin and Clausius statements are equivalent.

Proof. standard way

$$K \text{ valid} \Rightarrow C \text{ valid}$$

$$C \text{ valid} \Rightarrow K \text{ valid}$$

alternative way

$$K \text{ false} \Rightarrow C \text{ false}$$

$$C \text{ false} \Rightarrow K \text{ false}$$

because it cannot happen

$$K \text{ valid} \quad C \text{ false}$$

$$\text{or} \quad K \text{ false} \quad C \text{ valid}$$

therefore it can only be

$$K \text{ valid} \quad C \text{ valid}$$

$$\text{or} \quad K \text{ false} \quad C \text{ false}$$

The key point: what are known, and what are unknown!

$$K \text{ false} \Rightarrow C \text{ false}$$

If K is false, we may extract heat from a reservoir at temperature T_1 , and convert it to work, with no other effect.

Experimentally, it is found that it is possible to convert work entirely into heat, e.g., simply press an ideal gas. (That is why we formulate K).

Therefore, we can convert this work into heat and deliver it to a reservoir at $T_2 > T_1$. Then, the net result of the two-step process is the transfer of an amount of heat from a colder reservoir to a hotter reservoir. C is false.

C false \Rightarrow K false.

Experimentally, it is found that it is possible to extract a quantity of heat from a reservoir at temperature T_2 , and convert a part of it to work, and deliver another part to a reservoir at $T_1 < T_2$.

Question: can it be $T_1 > T_2$?

(That is also why we formulate K)

Suppose C false, we may transfer heat Q_2 from a reservoir at temperature T_1 to a reservoir at $T_2 > T_1$. Then, we extract Q_2 from the reservoir at T_2 , and convert it partially to work, and reject certain heat to the reservoir at T_1 . The net result is that an amount of heat is extracted from the reservoir at T_1 and converted entirely into work, with no other effect. Hence, K is false.

1.4 Carnot's theorem

1.4.1 The Carnot engine

An engine is a machine which convert heat into work. An engine which does everything in a reversible way is called a Carnot engine.

e.g., as shown in Fig. 1.7

$a \rightarrow b$ is isothermal,

– heat Q_2 is absorbed by the system

$b \rightarrow c$ adiabatic

$c \rightarrow d$ isothermal

– heat Q_1 is rejected by the system

$d \rightarrow a$ adiabatic

Work is done by the system in every step, positively from $a \rightarrow b$ and $b \rightarrow c$, and negatively from $c \rightarrow d$ and $d \rightarrow a$.

In one cycle, $\Delta U = 0$, the work done by the system, according to the first law

$$W = Q_2 - Q_1$$

The efficiency of the engine is

$$\eta = \frac{W}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

We may prove that if $W > 0$, then $Q_1 > 0, Q_2 > 0$

Proof (reading materials): If $Q_1 = 0$, it violates the Kelvin statement .

Suppose $Q_1 < 0$, this means that the engine absorbs the amount of heat Q_2 from T_2 , and $-Q_1$ from T_1 , and convert the total amount $Q_2 - Q_1$ into work. (This sounds already impossible.) Then we convert the work $Q_2 - Q_1$ to heat, and deliver it to T_2 . Finally the net result is to transfer an amount of heat $-Q_1$ from T_1 to T_2 . By the Clausius statement ,this is impossible.

Therefore $Q_1 > 0$.

From $W = Q_2 - Q_1 > 0$, it follows $Q_2 > 0$

Exercise: If $W < 0$ and $Q_1 < 0$, then $Q_2 < 0$.

(This is a refrigerator, but it is trivial.)

better If $Q_1 < 0$, then $W < 0, Q_2 < 0$.

If the system is an ideal gas,

$$\eta = 1 - \frac{T_1}{T_2}$$

where T is an ideal-gas temperature scale.

Proof: Assuming $PV = NkT$, $U = C_V T + \text{constant}$, and C_V is a constant, for an adiabatic processd

$$dU = C_V dT = dQ - PdV = -PdV \quad (1.4.1)$$

Since $PV = NkT$

$$PdV + VdP = NkdT \quad (1.4.2)$$

Eliminate dT from (1.4.1), (1.4.2)

$$PdV + VdP = -\frac{Nk}{C_V} PdV$$

$$\left(1 + \frac{Nk}{C_V}\right)PdV + VdP = 0$$

therefore

$$\begin{aligned}V^\gamma P &= \text{constant} \\ \gamma &= 1 + \frac{Nk}{C_V}\end{aligned}$$

Then we have

$$V^{\gamma-1}T = \text{constant}$$

Therefore

$$\begin{aligned}V_b^{\gamma-1}T_2 &= V_c^{\gamma-1}T_1 \\ V_d^{\gamma-1}T_1 &= V_a^{\gamma-1}T_2 \\ \frac{V_b}{V_a} &= \frac{V_c}{V_d}\end{aligned}$$

$a \rightarrow b$ is isothermal

$$\Delta U = 0$$

$$Q_2 = \int_{V_a}^{V_b} PdV = NkT_2 \int_{V_a}^{V_b} \frac{dV}{V} = NkT_2 \ln \frac{V_b}{V_a}$$

$c \rightarrow d$

$$Q_1 = NkT_1 \ln \frac{V_c}{V_d}$$

Finally

$$\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

1.4.2 Carnot's theorem

No engine operating between two given temperature is more efficient than a Carnot engine.

Proof:

Construct a Carnot engine C and an arbitrary engine X as shown in Fig. 1.8

$$\begin{aligned}W &= Q_2 - Q_1 \\W' &= Q'_2 - Q'_1 \\Q_2 > Q_1 > 0 &\quad Q'_2 > Q'_1 > 0\end{aligned}$$

Let

$$\frac{Q_2}{Q'_2} = \frac{N'}{N} \quad (*)$$

where N, N' are integers. This equality will be valid by making N, N' sufficiently large.

It is important to keep in mind that the Carnot engine can be operated in reverse, i.e. change the sign of W, Q_1 and Q_2 .

Now operate the C engine N cycles in reverse, and the X engine N' cycles,

$$\begin{aligned}W_{\text{total}} &= N'W' - NW \\(Q_2)_{\text{total}} &= N'Q'_2 - NQ_2 = 0 \\(Q_1)_{\text{total}} &= N'Q'_1 - NQ_1\end{aligned}$$

On the other hand, from the first law and $(\Delta U)_{\text{total}} = 0$,

$$W_{\text{total}} = (Q_2)_{\text{total}} - (Q_1)_{\text{total}} = -(Q_1)_{\text{total}}$$

If $W_{\text{total}} > 0$, it violates the Kelvin statement.
Therefore

$$W_{\text{total}} \leq 0, \quad \text{i.e.} \quad (Q_1)_{\text{total}} \geq 0$$

In other words

$$N'Q'_1 - NQ_1 \geq 0$$

from (*)

$$\frac{Q_1}{Q_2} \leq \frac{Q'_1}{Q'_2}$$

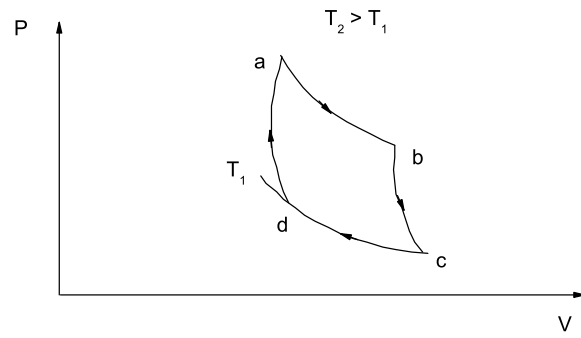


Figure 1.7:

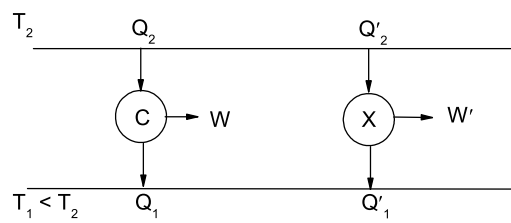


Figure 1.8:

i.e.

$$\left(1 - \frac{Q_1}{Q_2}\right) \geq \left(1 - \frac{Q'_1}{Q'_2}\right)$$

Since X can be a Carnot engine . Thus we have.

Corollary:

All Carnot engines have the same efficiency.

In the proof of the Carnot theorem, the key point is to choose one of the W_{total} , $(Q_2)_{total}$ and $(Q_1)_{total}$ to be zero, then apply the first and second laws to prove the theorem.

An alternative way to prove the Carnot theorem:

Operate the C engine N cycles in reverse and the X engine N' , and let

$$\begin{aligned} W_{total} &= N'W' - NW = 0 \\ (Q_2)_{total} &= N'Q'_2 - NQ_2 \\ (Q_1)_{total} &= N'Q'_1 - NQ_1 \end{aligned}$$

From the second laws,

$$(Q_2)_{total} \geq 0$$

Hence,

$$N'Q'_2 \geq NQ_2$$

therefore,

$$\frac{W}{Q_2} \geq \frac{W'}{Q'_2}$$

Note that assuming $W_{total} = W' - W = 0$, one may also prove the Carnot theorem. However, this is not general since the efficiency may depend on the work W .

1.4.3 Absolute scale of temperature

The Carnot's theorem tells something "absolute" it may be used for defining a better temperature scale.

If the efficiency of a Carnot engine is η , we define the absolute scale of temperature by

$$\frac{T_1}{T_2} = 1 - \eta$$

Since

$$0 \leq \eta < 1, \quad T_1 > 0, \quad T_2 > 0$$

(If $\eta = 1$, it violates the second law.) Note that η does not fix the unit, since $1 - \eta = T_1/T_2 = \alpha T_1/(\alpha T_2)$.

To define the unit, we note that

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

hence,

$$\frac{T_1}{Q_1} = \frac{T_2}{Q_2}$$

Similarly, we fix $W = Q_{n+1} - Q_n$ independent of n , and have

$$\frac{T_n}{Q_n} = \frac{T_{n+1}}{Q_{n+1}}$$

i.e., both W and the ratio T_n/Q_n are independent of n .

Choosing W such that

$$\begin{aligned} T_{n+1} - T_n &= \frac{T_n}{Q_n}(Q_{n+1} - Q_n) \\ &= \frac{T_n}{Q_n}W = 1K \end{aligned}$$

That is the unit of the absolute scale of temperature.

Here we assume that $1K$ is known empirically. If it is not, we may define the unit $T_{n+1} - T_n$ by fixing W to be a certain amount.

- The absolute scale of temperature is independent of the specific properties of any substance.

- $T = 0$ is the greatest low bound, and is called the absolute zero. No Carnot engine exists with a reservoir of $T = 0$. (But this has not yet meant that T can not be zero.)
- The absolute scale is identical with the ideal-gas scale $PV = NkT$

1.5 Entropy

The fact that some processes are irreversible already indicates that the initial and final states are characteristically different. There should be a state function which describes this property.

1.5.1 Clausius theorem

A cyclic transformation is a transformation whose final state is identical with the initial state. A reversible cyclic transformation is a cyclic transformation which is reversible. In any cyclic transformation through which the temperature is defined,

$$\oint \frac{dQ}{T} \leq 0$$

where the integral extends over one cycle of the transformation, dQ is the heat absorbed by the system. The equality holds if the cyclic transformation is reversible.

Proof. For an engine with two reservoirs it is already known that

$$1 - \frac{Q_1}{Q_2} \leq 1 - \frac{T_1}{T_2}$$

i.e.

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} \leq 0$$

“ $-$ ” means that the system rejects the heat, $-Q_1$ is the heat “absorbed” by the system.

For a general reversible cyclic transformation C as shown in Fig. 1.9, it can be divided by the isothermal lines (solid lines) and the adiabatic lines (dashed lines) into many infinitesimal Carnot transformations

or equivalently, it can be divided by the adiabatic lines into infinitesimal strips.

Exercise: prove it.

Since all transformation are reversible, if we add up all the infinitesimal cyclic transformations, the resulting transformation will be the original transformation C.

For each Carnot cyclic transformation

$$\frac{Q_j}{T_j} + \frac{Q_{j+1}}{T_{j+1}} = 0$$

therefore

$$\sum_j \frac{Q_j}{T_j} + \frac{Q_{j+1}}{T_{j+1}} = 0$$

$Q_j < 0$ means exothermic. Here j sums over all Carnot cyclic transformations. Since all processes inside C will not contribute.

$$\sum_{i \in C} \frac{Q_i}{T_i} = 0$$

If C is irreversible, it is easy to prove

$$\sum_i \frac{Q_i}{T_i} < 0$$

Corollary

For a reversible transformation

$$\int \frac{dQ}{T}$$

is independent of the path, and depends only on the initial and final states.

This allows us to define a state function such that

$$S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

or

$$dS = \frac{dQ}{T} \quad \text{is exact!}$$

S is called the entropy.

Properties of S

a) For an arbitrary transformation

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A)$$

The equality holds for a reversible transformation.

b) If

$$dQ = 0$$

$$S(B) - S(A) \geq 0$$

The equality holds for a reversible transformation. For a thermally isolated system, S always increases. Roughly speaking, this is the second law, e.g., taking an ideal gas as an example.

c) S is extensive.

It is clear from the definition since dQ is extensive.

1.5.2 Calculations of S

- By definition
- By constructing a reversible process
- With the help of $TdS = dU + dW$ in a reversible process.
- S is extensive

a) Reversible isothermal expansion of an ideal gas

Fig.1.8 in the book

Since the gas is ideal, $U = U(T)$, hence $\Delta U = 0$.

For the gas

$$\begin{aligned}(\Delta S)_{\text{gas}} &= \int \frac{dQ}{T} = \frac{\Delta Q}{T} \\ &= \frac{W}{T} \\ W = \int P \cdot dV &= NkT \int \frac{1}{V} dV \\ &= NkT \ln \frac{V_2}{V_1} \\ (\Delta S)_{\text{gas}} &= Nk \ln \frac{V_2}{V_1}\end{aligned}$$

The reservoir supplies the amount of heat $-\Delta Q$

$$(\Delta S)_{\text{reservoir}} = - Nk \ln \frac{V_2}{V_1}$$

The change in entropy of the whole system is zero. This is natural since the whole system is adiabatic, and the process is reversible.

The work is stored in the spring which can be used for reversing the process.

b) Free expansion of an ideal gas

Fig.1.3

This process is a little puzzling,

$$\Delta W = 0, \quad \Delta T = 0, \quad \Delta Q = 0, \quad \Delta U = 0$$

Why or how is S changed?

Because it is not a reversible process. But S is a state function, therefor

$$(\Delta S)_{\text{gas}} = Nk \ln \frac{V_2}{V_1}$$

the same as in a)

But in this case

$$(\Delta S)_{\text{reservoir}} = 0$$

since nothing is changed in the reservoir.

In comparison with a), an amount of useful energy $W = T(\Delta S)$ gas is just "lost". An irreversible process is "wasteful".

Therefore, the entropy may be viewed as a measure of the unavailability of useful energy in that state.

c) For a general reversible process, from (1.5) in the text book

$$dS = \frac{dQ}{T} = \frac{1}{T} \left[\left(\frac{\partial U}{\partial T} \right)_V dT + \left(\left(\frac{\partial U}{\partial V} \right)_T + P \right) dV \right]$$

since dS is exact

$$\left(\frac{\partial}{\partial V} \right)_T \left(\frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V \right) = \left(\frac{\partial}{\partial T} \right)_V \left(\left(\frac{\partial U}{\partial V} \right)_T + P \right) \frac{1}{T}$$

Hence

$$\frac{1}{T} \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V \right)_T = \frac{1}{T} \left(\left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right)_V + \left(\frac{\partial P}{\partial T} \right)_V \right) - \left(\left(\frac{\partial U}{\partial V} \right)_T + P \right) \frac{1}{T^2}$$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

therefore

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

This is the equation of entropy. If C_V and the equation of state are known, one can derive the entropy.

For an ideal gas,

$$PV = NkT, \quad \left(\frac{\partial P}{\partial T} \right)_V = \frac{Nk}{V}$$

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{NkT}{V} - P = 0$$

i.e. $U = U(T)$ consistent with the experiment Fig. 1.3

Exercises: Derive the entropy of an ideal gas.

Exercises: Prove

$$a) \quad TdS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$b) \quad \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

$$c) \quad \left(\frac{\partial x}{\partial y} \right)_w \left(\frac{\partial y}{\partial z} \right)_w = \left(\frac{\partial x}{\partial z} \right)_w$$

hint:

$\left(\frac{\partial x}{\partial y} \right)_w$ implies that there are only two independent variables

1.5.3 (Partially reading materials)

For reversible processes, the second law is equivalent to that the entropy is a state function

a) Adiabatic lines never intersect each other.

Since

$$dS = \frac{dQ}{T}$$

if two adiabatic lines intersect as shown in Fig. 1.10, S is not a state function.

Note that in Fig. 1.10, it is not possible $S_1 = S_2$. From the conclusion in b) below, this is clear.

b) An isothermal line and an adiabatic line intersect at most only once.

Since

$$TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

hence

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V > 0$$

therefore S is a monotonously increasing function of V .

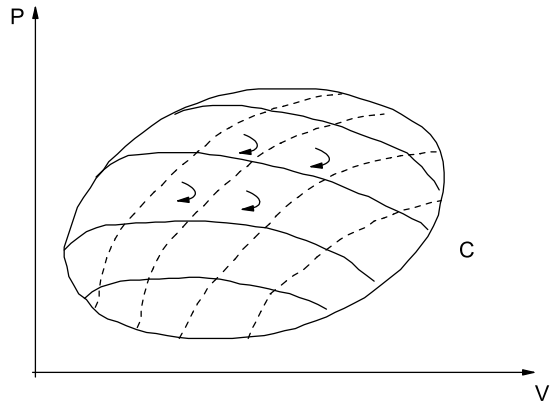


Figure 1.9:

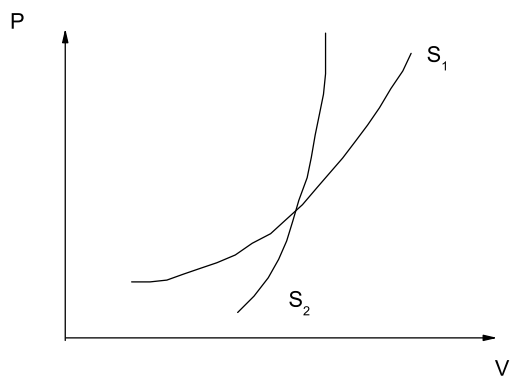


Figure 1.10:

The T line and the S line can not intersect two time as shown in Fig. 1.11.

c) One can deduce from the Kelvin statement that S is a state function.

If S is not a state function, we can construct a cyclic transformation as shown in Fig. 1.12. It means we may extract heat from a single reservoir and convert it entirely to work.

Similarly, we may prove the opposite statement of c).

1.6 Thermodynamic potentials

In dealing with different kinds of processes, it is convenient to introduce some more thermodynamic potentials.

Internal energy U

Free energy $A = U - TS$

A is the "useful" energy, TS is the unavailable energy. If S increases, the "useful" energy (or available energy) decreases. This has been demonstrated in the free expansion of an ideal gas.

Enthalpy $H = U + PV$

Gibbs potential $G = H - TS$

(Free enthalpy)

all are extensive

$$\begin{aligned} dU &= TdS - PdV \\ dA &= -SdT - PdV \\ dH &= TdS + VdP \\ dG &= -SdT + VdP \end{aligned} \quad (*)$$

All are exact.

From (*) above, we may derive the four Maxwell relations.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

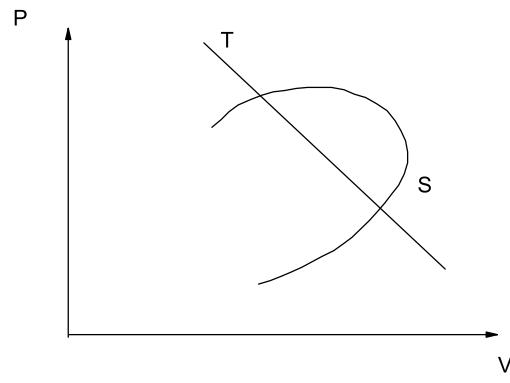


Figure 1.11:

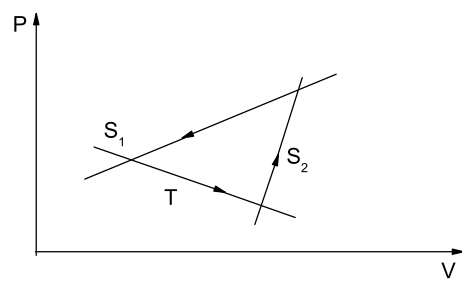


Figure 1.12:

$$\begin{aligned}
+\left(\frac{\partial S}{\partial V}\right)_T &= +\left(\frac{\partial P}{\partial T}\right)_V \\
\left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\
-\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P
\end{aligned}$$

Depending on the process, e.g. $dS = 0$, or $dV = 0$, or $dT = 0$, or $dP = 0$, it is convenient to choose different thermodynamic potential to characterize the system.

Theorem: For a mechanically isolated system ($dW = 0$) kept at constant temperature, the free energy never increases.

Proof: For a reversible transformation

$$dA = 0$$

For an irreversible transformation

$$\Delta Q < T\Delta S$$

$$\Delta U = +\Delta Q$$

hence

$$\Delta A = \Delta U - T\Delta S = \Delta Q - T\Delta S < 0$$

Corollary: For a mechanically isolated system kept in constant temperature, the equilibrium state minimizes the free energy.

Theorem : For a system kept at constant temperature and pressure, the Gibbs potential never increases.

Corollary: For a system kept at constant temperature and pressure, the equilibrium state minimizes the Gibbs potential.

Masius theorem.

Given one thermodynamic potential with proper independent variables, such as $A = A(T, V)$, $U = U(S, V)$, $G = G(T, P)$, $H = H(S, P)$, it is possible to derive all thermodynamic properties just by differentiation e.g.

$$\begin{aligned}A &= A(T, V) \\dA &= -SdT - PdV \\S &= -\left(\frac{\partial A}{\partial T}\right)_V & P &= -\left(\frac{\partial A}{\partial V}\right)_T \\U &= A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_V \\C_V &= \left(\frac{\partial U}{\partial T}\right)_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_V\end{aligned}$$

Exercise: Derive C_P

1.7 Phase transitions

A state of a system is described by some parameters, e.g., (P, T) or (P, V) . States in a certain region of the parameter space may share some common features, and states in another region may show different features. Then we observe gases, liquids and solids etc, called phases.

Between two phases there may occur a phase transition. A phase transition is a 'sudden' change from one phase to another.

For example, the transition between the gas phase and the liquid phase.

In the (P, T) plan, the transition takes place at a curve $P(T)$ as in Fig. 2.2 in the text book. $P(T)$ is called the vapor pressure at T . Practically, if the pressure is kept at

constant, the transition takes place at a constant temperature, and vice versa.

In Fig. 2.3 in the text book, the phase transition is shown in the (P, V) plan with a fixed temperature. From (a) to (d), there is a sudden jump in V .

at state 1. the system is all liquid

at state 2. the system is all gas

in between, some part is gas, and some other part is liquid.

Maybe it is better to look at the (T, V) plan. As T rises up, V increases.

It is important

(a) during the transition both P and T remain constant.

(b) in the state of the gas-liquid mixture, the liquid is the state 1, while the gas in the state 2. If heat is supplied, the liquid will be converted to the gas. V' and V'' are effective volumes.

Now, we investigate what the second law tells in this transition.

Let the mass of the liquid be m_1 and the mass of the gas be m_2 . If the system is in equilibrium

$$G = m_1 g_1 + m_2 g_2$$

here g is the Gibbs potential per unit mass, and called the chemical potential, g may depend on the density but not the total mass.

In an equilibrium state, according to the second law, G must be at minimum. That is, if any parameters other than P and T are varied slightly

$$\delta G = 0$$

Since (assume)

$$-\delta m_1 = \delta m_2 = \delta m$$

hence

$$\delta G = -(g_1 - g_2)\delta m = 0$$

The condition for equilibrium is then

$$g_1(P, T) = g_2(P, T)$$

This equation just determines the phase transition line. But g_1 and g_2 are not directly measurable.

Recall that in each phase, $dg = -sdT + vdP$, therefore

$$\left(\frac{\partial g}{\partial T}\right)_P = -s \quad (\text{entropy per unit mass})$$

$$\left(\frac{\partial g}{\partial P}\right)_T = v \quad (\text{volume per unit mass})$$

we see at the transition

$$\left(\frac{\partial(g_2 - g_1)}{\partial P}\right)_T = v_2 - v_1 > 0$$

The first derivative of g is discontinuous. That is why the transition is called "first-order", and v is the so-called order parameter.

Question: why at transition

$$\left(\frac{\partial(g_2 - g_1)}{\partial T}\right)_P = -(s_2 - s_1) < 0$$

Around the transition T and vapor P , let

$$\Delta g = g_2 - g_1$$

$$\Delta s = s_2 - s_1$$

$$\Delta v = v_2 - v_1$$

we have

$$\left(\frac{\partial \Delta g}{\partial T}\right)_P / \left(\frac{\partial \Delta g}{\partial P}\right)_T = -\frac{\Delta s}{\Delta v}$$

By the chain relation

$$\left(\frac{\partial \Delta g}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_{\Delta g} \left(\frac{\partial P}{\partial \Delta g}\right)_T = -1$$

we obtain

$$\left(\frac{\partial P}{\partial T}\right)_{\Delta g} = \frac{\Delta s}{\Delta v}$$

To prove the chain rule, we should keep in mind that Δg is a state function, i.e. there exists

$$f(T, P, \Delta g) = 0$$

Under equilibrium conditions, $\Delta g = 0$, the derivative of the vapor pressure should be

$$\frac{dP(T)}{dT} = \left(\frac{\partial P}{\partial T}\right)_{\Delta g=0}$$

Therefore

$$\frac{dP(T)}{dT} = \frac{\Delta s}{\Delta v} = \frac{l}{T\Delta v}$$

hence $l = T\Delta s$ called the latent heat. This is known as the Clapeyron equation. It governs the vapor pressure in any first-order transition.

If $\Delta s = 0, \Delta v = 0$, the transition becomes higher-order. The Clapeyron equation is not valid.

1.8 The third law

The entropy of a system at the absolute zero temperature is a universal constant, which may be taken to be zero.

It is equivalent to

A system cannot be cooled to the absolute zero temperature by a finite change of the thermodynamic parameters.

1.9 Summary

1.9.1 What is thermodynamics?

For macroscopic systems, one observes that some phenomena could not be explained by mechanics, electrodynamics,

et al. at least in the past times. These phenomena are related to "hot" or "cold".

Through the zeroth law, and the transformation between heat and work, one defines the temperature T and heat capacity C_V and C_P etc.

For describing the systems, there are two kinds of parameters

- Thermal parameters T, C_V, C_P
- "Traditional" parameters P, V, n

Thermodynamics investigates what laws govern these parameters, which may be or may not be measured in experiments.

- Only a certain number of parameters are independent, and this leads to the equation of state

$$f(P, V, T) = 0$$

it states that T is a state function.

- The first law, i.e. the energy conservation, leads to the state function, internal energy

$$U = U(P, V)$$

- The second law, it tells the direction of a thermodynamic process, and it leads to the entropy, which is also a state function

$$S = S(P, V)$$

All physical processes should obey the first and the second laws. Therefore, it is important to calculate U and S , i.e. to express them as functions of the parameters which may be measured from experiments.

For reversible processes, the equation

$$dU = TdS - dW$$

combines both the first and second laws.

1.9.2 What are the “difficulties”

From personal experience,

- How to calculate the partial derivative, e.g. from the equation of state

$$f(P, V, T) = 0$$

or

$$f(P, V, S) = 0.$$

The key point is to remember that such an equation (whether or not it is given explicitly) indicates that only two parameters are independent.

- How to construct a process, and to prove certain statements.

The key point here is to make clear what are possible and impossible.

e.g., the Kelvin statement states that it is impossible to extract a quantity of heat from a single heat reservoir, and to convert it entirely into work without any other effect.

This means that it is possible to convert an amount of work entirely to heat and deliver it to a single reservoir.

This also means that it is possible to extract an amount of heat from one reservoir, and convert a part of it to work, and deliver the other part to another reservoir; or convert it entirely to work, but with other effect, e.g., change of the volume.

If $\Delta Q, \Delta W$ take negative values, it means the quantities go in the opposite direction as they are assumed.

1.9.3 An ideal gas

- Experimentally, it is observed that for a given temperature

$$PV = \text{constant}$$

This indicates that there are only two independent parameters. We may also write $PV = f(\theta)$, and θ is a certain scale of the temperature. If we fix the function $f(\theta)$, the scale of the temperature is defined.

Since the scale of temperature needs to be defined, we can simply define

$$PV = NkT$$

This is just the equation of state.

It happens that T defined in this way is the same as the absolute scale (At least, if C_V is constant, — theoretically, it is valid but maybe not easy to show it by experiments.)

- From the free expansion

$$U = U(T)$$

(also possible from the second law)

Since

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT}$$

assuming (or approximately) C_V is independent of T ,

$$U = C_V T + \text{const.}$$

and

$$H = (C_V + Nk)T + \text{const.}$$

$$C_P - C_V = Nk$$

$$\begin{aligned} TdS &= dU + PdV \\ dS &= C_V \frac{dT}{T} + \frac{Nk}{V} dV \end{aligned}$$

hence

$$S = C_V \ln T + Nk \ln V$$

Exercise

Prove that for an idea gas, $T_V = T_P$.

Prove (1.5) (1.6) (1.7) in the textbook.

Prove that for an engine, if $W < 0$ and $Q_1 < 0$, then $Q_2 < 0$.

(This is a refrigerator, but it is trivial.)

Better, if $Q_1 < 0$, then $W < 0, Q_2 < 0$.

Prove that for a general reversible cyclic transformation C as shown in Fig. 1.9, it can be divided by the isothermal lines (solid lines) and the adiabatic lines (dashed lines) into many infinitesimal Carnot transformations.

or equivalently, it can be divided by the adiabatic lines into infinitesimal strips.

Derive the entropy of an ideal gas.

Prove

$$a) \quad TdS = C_P dT - T \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$b) \quad \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1$$

$$c) \quad \left(\frac{\partial x}{\partial y} \right)_w \left(\frac{\partial y}{\partial z} \right)_w = \left(\frac{\partial x}{\partial z} \right)_w$$

Derive C_P from $A(T, V)$.

Exercises 1, 2, 3 and 5 in the textbook.