Thermal Physics Notes

Compiled by Nhat Pham
based on lectures from PHYS20027
and Blundells' *Concepts in Thermal Physics*

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Contents

1 Lecture 1 (Week 13)

1.1 Definitions

1.1.1 Thermodynamic limit

Thermodynamics apply to system that is *in equilibrium* and also within the thermodynamic limit

Definition 1.1.1. The thermodynamic limit is when we study a large number of particles or a small number of particles for a long time. When we take this limit, we can describe the system without knowing all individual, *microscopic* properties of all the particles. Instead, we can completely describe the system using *macroscopic* properties.

Macroscopic properties can be variables such as pressure, time, volume, etc.

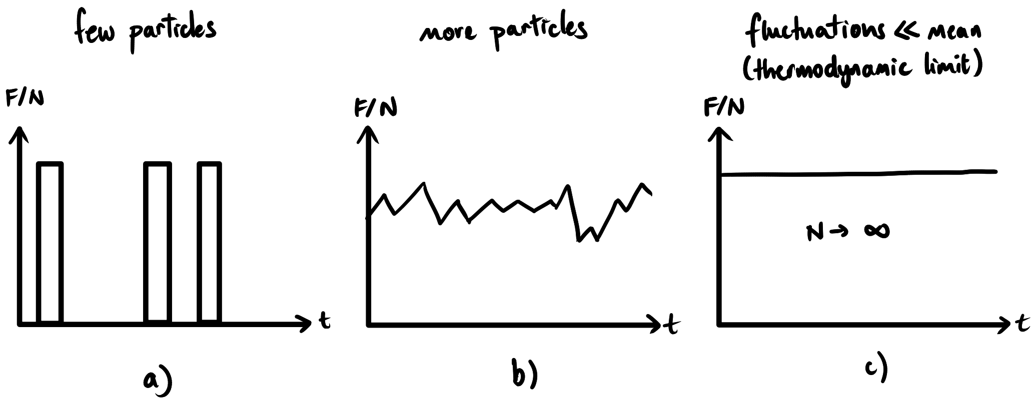

Figure 1.1: Force per particle versus time as we reach the thermodynamic limit.

1.1.2 Thermodynamic system

Definition 1.1.2. A thermodynamic system is a body which has well defined interactions with its surrounds and can be considered separately from them.

Example of a thermodynamic system: gas in an enclosure, where interactions with surrounding might be through heat or transfer through walls.

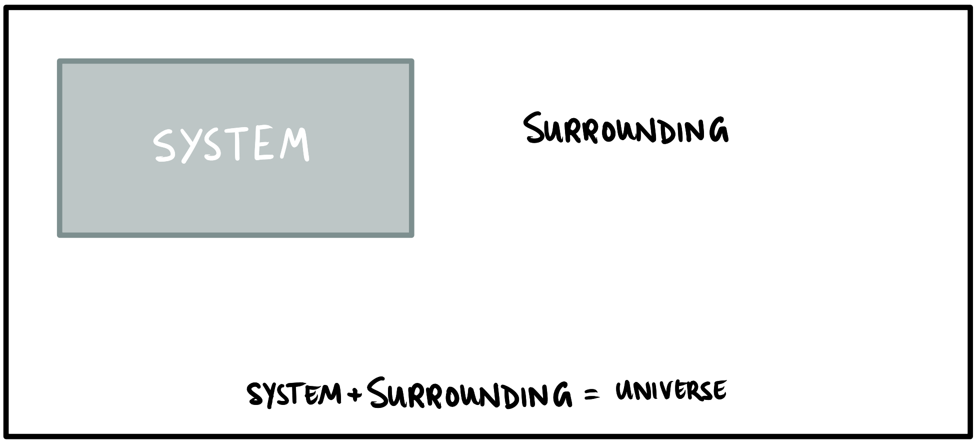

Figure 1.2: A thermodynamic system

1.1.3 Thermal equilibrium

Definition 1.1.3. A system is in thermal equilibrium when its macroscopic observables have ceased to change with time. Two systems are in thermal equilibrium if no heat flows between them when they are connected by a path permeable to heat.

There are also metastable states, where variables my change slowly with time, so the system is *not* in thermal equilibrium.

1.1.4 Extensive and intensive variables

- **Extensive** variables scales with the size of the system. Examples are the number of particles, volume, entropy, magnetic moment. They are mostly upper case.
- **Intensive** variables are independent of the size of the system. Examples are number density, temperature, magnetisation, pressure, entropy density. They are mostly lower case.

1.2 Functions and equations of state

Definition 1.2.1. A state function assumes a unique value for each equilibrium state of the system. The value does not depend on how they system got to the state—it is path independent.

Mathematically, functions of state have the following properties.

- Depend on (x, y) but not the path taken to (x, y).
- Have exact differentials, the number of variables does not matter. See 1.2.1.

Derivation 1.2.1. Recall the Taylor expansion of a function $f(x)$:

$$f(x + \delta x) = f(x) + f'\delta x + \frac{1}{2!}f''(\delta x)^2 + \ldots \tag{1.1}$$

In the limit $\delta x \longrightarrow \mathrm{d}x$ we can ignore higher order terms because they are sufficiently small. We are left with the first derivative, and rewrite it so that:

$$f(x + \mathrm{d}x) - f(x) = \frac{\mathrm{d}f}{\mathrm{d}x}\,\mathrm{d}x = \mathrm{d}f \tag{1.2}$$

We can use this result and expand it to 2 dimensions. We then arrive at the *exact differential* of $f(x, y)$:

$$\mathrm{d}f = f(x + \mathrm{d}x\,, y + \mathrm{d}y) - f(x, y) = \frac{\partial f}{\partial x}\,\mathrm{d}x + \frac{\partial f}{\partial y}\,\mathrm{d}y \tag{1.3}$$

The condition for a function to have an exact differential is that its mixed partial derivatives are equal. In other words:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \tag{1.4}$$

On the other hand, functions that are path-dependent are *non-state functions*. In thermodynamics, heat and work are non-state functions. Their derivatives are inexact. The notation for this is:

$$đW, đQ$$

In the thermodynamic limit and thermodynamic equilibrium, the variables are dependent on each other and are constrained by an equation of state. For example $f(x, y, z) = 0$. The ideal gas equation is an equation of state.

$$pV - nRT = 0 \tag{1.5}$$

This allows us to relate thermodynamic variables to each other. For example:

$$\frac{\partial^2 m}{\partial T^2} = \frac{1}{T}\frac{\partial C}{\partial B}$$

We can find out the value of one side by knowing the other one.

2 Lecture 2 (Week 13)

A TL;DR overview of the laws of thermodynamics:

- **Zeroth Law:** If two systems are separately in equilibrium with a third system, then they are in equilibrium with each other.
- **First Law:** Energy is conserved. Heat and work are both forms of energy.
- **Second Law:** Heat cannot be converted to work with 100% efficiency. Entropy of the universe cannot decrease (this gives a definite direction of time).
- **Third Law:** You cannot cool anything to absolute zero (0 Kelvins)

These are statements of empirical facts, not deeper theory that sits below these laws.

2.1 The First Law

Heat is the energy in transfer between one system and another or one system and the surroundings.

- $đQ$ is the heat supplied **to** the system.

Work is the change in energy of a system affected by changing its parameters.

- $đW$ is the work done **on** the system.

Internal energy is the sum of all the components of energy in a system.

Definition 2.1.1. The conservation of energy of both heat (Q) and work (H):

$$\Delta U = \Delta Q + \Delta W \tag{2.1}$$

In differential form:

$$\mathrm{d}U = đW + đQ \tag{2.2}$$

2.1.1 Work done compressing a gas

Suppose a piston can be moved into a chamber with a gas. If it moves fast, we generate sound waves, if there is friction, then energy will be dissipated as heat. These losses will not end up in the gas so the change is **irreversible**.

To have **reversible** changes, we must have a frictionless piston and we must move it slowly.

Definition 2.1.2. The reversible work done to compress a gas is expressed by

$$đW = -pA \times \frac{dV}{A} = -p\,dV \tag{2.3}$$

The sign is negative because if we are doing work **on** the gas, then dV is negative because the volume is decreasing. For irreversible changes,

$$đW \geq -p\,dV \tag{2.4}$$

2.1.2 Work done in other systems

- Stretching a string: $đW = \vec{F} \cdot d\vec{l}$
- Expanding a surface: $đW = \gamma\,dA$
- Magnetic material: $đW = \vec{B} \cdot d\vec{m}$ or $\vec{m} \cdot d\vec{B}$

2.2 Constraints

- **Adiabatic** Thermally isolated system—there is no heat flow in or out. $đQ = 0$ or $dS = 0$
- **Isothermal:** Temperature is fixed by an external reservoir. $dT = 0$
- **Isobaric:** Pressure is fixed. $dp = 0$
- **Isochoric:** Volume is fixed. $dV = 0$

Paths are correspondingly called *adiabat, isotherm, isobar,* and *isochar.*

2.3 Heat capacities

A way to quantify the response of the system to external changes. Two heat capacities we study are

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, C_p = \left(\frac{\partial Q}{\partial T}\right)_p,$$

The equation of state for a general gas (not necessarily ideal) is $f(p,T,V) = 0$. We only have 2 independent variables that we can write our internal energy as a function of any two of those. For example, $U(p,V)$ or $U(V,T)$.

Let's qualitatively arrive at the expressions of C_V and C_p.

For C_V, suppose a box with fixed walls. Heat supplied into the system will increase the temperature of the gas inside.

For C_p, suppose a box with a piston. The gas is allowed to expand and move the piston to keep the pressure constant. If we put heat into the system, the gas expands, doing work on the system. Thus, not all of the heat supplied increased the temperature of the system. We expect then that $C_p \geq C_V$.

Derivation 2.3.1. Assume $U = U(V, T)$ and $f(p, V, T) = 0$. The exact differential of U is

$$\mathrm{d}U = \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T \tag{2.5}$$

From the equation of the first law, 2.1, substitute $đW$ with 2.3, set $dV = 0$ for constant volume, and divide by $\mathrm{d}T$,

$$\left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_V \tag{2.6}$$

Then for C_p, equate 2.5 with 2.1 then divide by $\mathrm{d}T$ and set $\mathrm{d}p = 0$:

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p \left(p + \left(\frac{\partial U}{\partial V}\right)_T\right) + C_V \tag{2.7}$$

For a general gas, we can normally stop here.

With the general expression, we can evaluate this for different gasses. The most simple is monotonic ideal gas.

Example 2.3.1. For an ideal gas that is monotonic, $U = \frac{3}{2}nRT$ and thus is only a function of temperature. We can cancel any partial derivatives of U where T is kept constant.

$$C_V = \frac{3}{2}nRT \tag{2.8}$$

$$C_p = \left(\frac{\partial V}{\partial T}\right)_p p + \frac{3}{2}nR \tag{2.9}$$

Using the ideal gas relation 1.5, we have:

$$C_p = \frac{3}{2}nR + nR = \frac{5}{2}nR \tag{2.10}$$

We can also consider **Virial Expansion** and the **Van de Waals** equation, which models real gas.

2.4 Non-ideal gases

2.4.1 Virial Expansion

This is a general form for an equation of state of gas or fluid. For an ideal gas, $A = 1$ and all other coefficients are zero. Gases become ideal when $\rho \to 0$.

$$\frac{p}{RT\rho} = A + B\rho + C\rho^2 + D\rho^3 + \dots \tag{2.11}$$

2.4.2 Van de Waals equation

This is a special case of the virial expansion, for $\rho \ll 1$, the we can ignore second order terms and above.

$$\left(p + \frac{a}{V^2}\right)(V - b) = nRT \tag{2.12}$$

3 Lecture 3 (Week 13)

3.1 The Second Law

Definition 3.1.1. There are several equivalent statements of the second law:

- **Lord Kelvin 1851:** Work can be converted to heat with 100% efficiency but not the reverse.
- **Clausius 1854:** Heat flows from hot to cold, and not spontaneously the other way around.

Both of these statements are **equivalent**—to understand this we need to look at thermodynamic cycles, specifically the *Carnot cycle*. This concept is used in engines. Since internal combustion engines are difficult to understand, we look at the *external* combustion engines. One type is the *Stirling* engine.

Qualitatively, the source of heat is at the bottom (which can come from a hot plate). The difference between the hot plate and the cold plate runs the engine (cool video embedded in the lecture). Here's a link to diagrams & animations: Low Differential Stirling.

3.2 The Carnot Cycle

There are four stages in the cycle. This is a *closed cycle*. Thus, the work done can be described by integrating both sides of 2.3 to get

$$W = \int p \, \mathrm{d}V \tag{3.1}$$

On the other hand, the total change $\Delta U = 0$ after one complete cycle.

Here are the steps in the Carnot cycle:

1. **A to B:** Isothermal expansion at T_H. Volume increases as pressure decreases due to supplied heat Q_H.
2. **B to C:** Adiabatic expansion (gas cools to T_L) as pressure keeps decreasing and volume keeps increasing.

3. **C to D:** Isothermal compression at T_L. Heat leaves the system and the volume decreases while pressure increases.
4. **D to A:** Adiabatic compression (gas heats to T_H). Pressure increase as a result as temperature increases.

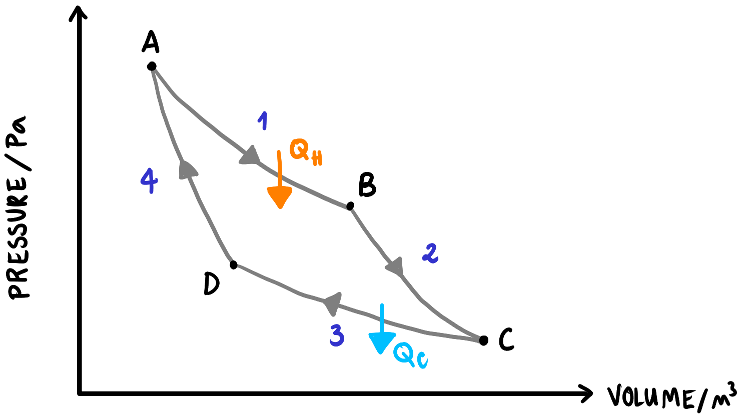

Figure 3.1: Carnot cycle P-V plot

Physically, there must be a hot reservoir and a cold reservoir connected to our system, which is an enclosed piston connected to a flywheel. These two are connected to a switch each (3.2).

Here's the physical interpretation:

1. The cold switch is open, and heat is supplied to the system. The gas must expand along the isotherm, pushes the piston and drives the flywheel.
2. In stage 2, both switches are open, the system is thermally isolated. The flywheel continues to spin while the gas continues to expand.
3. In stage 3, the cold switch is now closed. Heat leaves the system and the gas gets compressed.
4. In stage 4, both switches are open, the system is thermally isolated. The piston is back to its original position after the flywheel compresses the gas.

3.2.1 The Carnot relation

We can also analyse the Carnot cycle mathematically.

Let's consider an isothermal expansion. An isothermal expansion (see 2.2) demands $\mathrm{d}T = 0$, but $U = U(T)$ thus $\Delta U = 0$. Therefore, $\Delta Q = -\Delta W$ from 2.1. From 3.1, we evaluate the integral using 1.5.

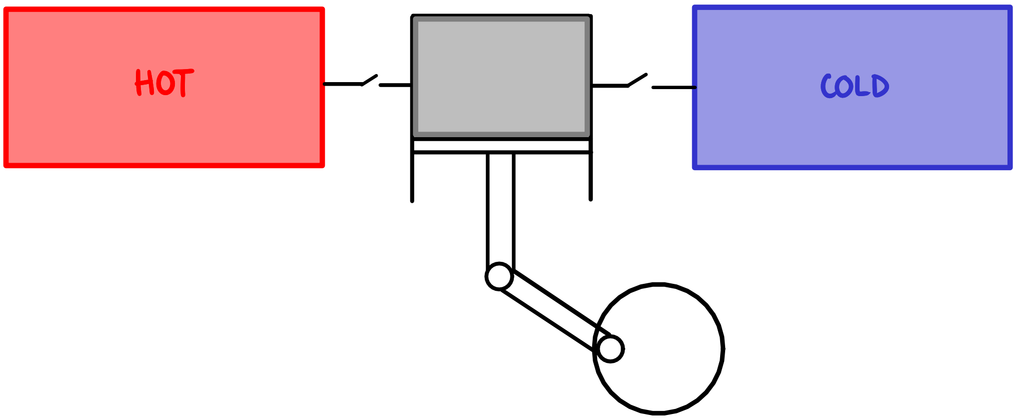

Figure 3.2: An example of what how the Carnot cycle might be implemented

Now let's consider an adiabatic expansion. Recall from first year that we can write $PV^{\gamma} = \text{const}$ and thus $TV^{\gamma-1} = \text{const}$. Since it is equal to a constant, the product TV at each stages are equal. Remember that $\gamma = \frac{C_p}{C_V}$.

Definition 3.2.1. We have the following mathematical relations for each stages of the Carnot cycle, with $\gamma = \frac{C_p}{C_V}$.

1. $Q_H = nRT_H \ln \frac{V_B}{V_A}$
2. $T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1}$
3. $-Q_L = nrT_L \ln \frac{V_D}{V_C}$
4. $T_L V_D^{\gamma-1} = T_H V_A^{\gamma-1}$

Use stages 2 and 4 from 3.2.1 to eliminate $\frac{T_H}{T_L}$. We arrive at:

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \tag{3.2}$$

Finally, using stages 1 and 3 and 3.2 which we just found, we arrive at the *Carnot relation*:

$$\frac{Q_H}{Q_L} = \frac{T_H \ln\left(\frac{V_B}{V_A}\right)}{T_L \ln\left(\frac{V_C}{V_A}\right)} = \frac{T_H}{T_L} \tag{3.3}$$

Finally, we can derive the efficiency of the cycle, which is the ratio between work done and heat available. The work done is the difference between heat flowing in and heat flowing out.

The heat available is what is supplied.

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \tag{3.4}$$

It could also be useful to consult simplified diagrams of Carnot engines and a reversed Carnot engine (a refrigerator).

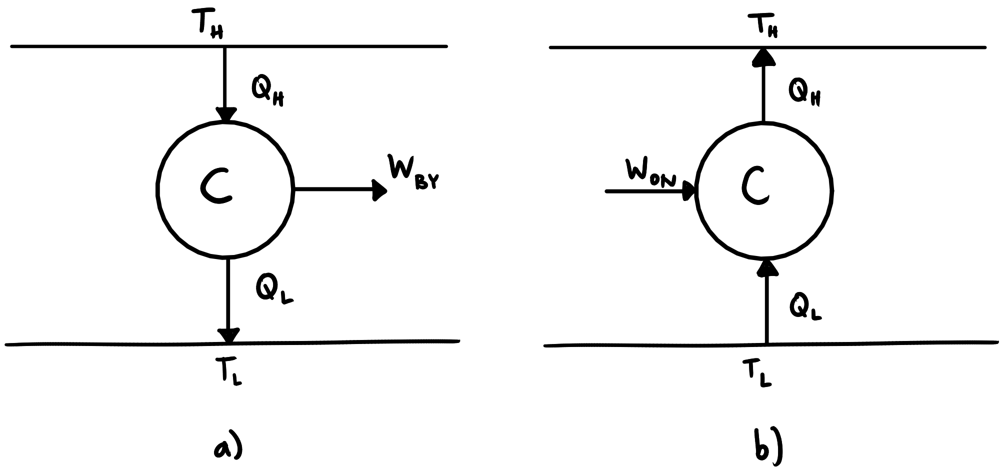

Figure 3.3: (a) shows the Carnot engine where the engine performs work and (b) shows the reversed Carnot engine where we perform work on the engine.

3.2.2 The Carnot theorem

The consequences of the Carnot engine are:

Theorem 3.2.1 *No engine operating between two reservoirs can be more efficient than the Carnot engine.*

Proof by contradiction will lead to this theorem. In essence:

Proof. Suppose there is an engine **X** such that its efficiency exceeds that of the Carnot engine, so that $\eta_x > \eta_c$. Connect engine **X** to the Carnot engine in reverse, and expand out the inequality to get

$$\frac{W}{Q_H^x} - \frac{W}{Q_H^C} > 0$$

From the first law, we find

$$W \equiv Q_H^C - Q_L^C = Q_H^x - Q_L^x$$

We rearrange this into

$$Q_H^C - Q_H^x = Q_L^C - Q_L^x$$

The LHS is > 0 as part of our assumption, this means the RHS is also > 0. However, the LHS is heat *dumped* from the hot reservoir, while the RHS is heat *removed* into the cold reservoir. If cold reservoir is losing heat and hot reservoir is gaining heat. Then energy is being transferred from cold to hot. This is a direct contradiction with the Second Law (Clausius' statement). Thus, we must abandon our initial assumption—there cannot be such an engine **X**. □

This leads to the second theorem.

Theorem 3.2.2 *All reversible engines have exactly the Carnot efficiency.*

It doesn't matter if we use an ideal gas or a non-ideal gas, if an engine is reversible, then the theorem holds.

Proof by contradiction will show this holds.

Proof. Suppose we now have an engine R which is less efficient than the Carnot engine. Connect the Carnot engine in forward direction to engine R in reverse. Like the previous proof, we have

$$Q_H^C - Q_H^R = Q_L^C - Q_L^R$$

Due to our assumption, both sides are negative. Once again, we have heat which is extracted from the hot reservoir and dumping it into the cold reservoir. This violates the second law, so we must abandon our assumption. □

The Carnot efficiency is exactly 1 if and only if $T_L = 0$.

$$\eta_c = 1 - \frac{T_L}{T_H} < 1 \tag{3.5}$$

3.3 Thermodynamic absolute temperature

Kelvin used the Carnot relation in 3.5 to define absolute temperature. This sets the **zero** of the temperature scale.

Prior to 2019, the size of Kelvin was set by the triple point of water. This all changed to the new S.I. system which is based on universal constants.

We use an ideal gas and ideal gas laws as a primary thermometer.

4 Lecture 4 (Week 14)

4.1 Clausius' Theorem

Results from a general analysis of the Carnot cycle. For each part of the cycle by index i, calculate

$$\sum_i \frac{\Delta Q_i}{T_i} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \tag{4.1}$$

For a Carnot cycle, the first term is equal to the second term, thus the whole sum is 0. If we look at the small addition of Q then $\Delta Q \to đQ$ then the sum becomes an integral. We have.

$$\oint \frac{đQ_{rev}}{T} = 0 \tag{4.2}$$

Definition 4.1.1. For a general cycle (either reversible or irreversible), Clausius' theorem states

$$\oint \frac{đQ}{T} \leq 0 \tag{4.3}$$

We can prove this theorem through a set up of a generalised cycle (multiple parts that are either reversible or irreversible), as shown in Figure 4.1.

Consider the following *general* cycle:

Derivation 4.1.1. Because this is a closed cycle, it follow the first law, where $\Delta U = 0$, or $W_s = \sum_i \delta Q_i$ where W_s is the total work done by the system.

Assuming each reservoir is connected to the master reservoir at the temperature T_0 via an individual Carnot engine, we can form a schematic as shown in Figure **??**

For each of the engine, there is a bit of work done, and the rest is heat that goes into our system. This shows that

$$\delta Q_i^0 = \delta W_i + \delta Q_i \tag{4.4}$$

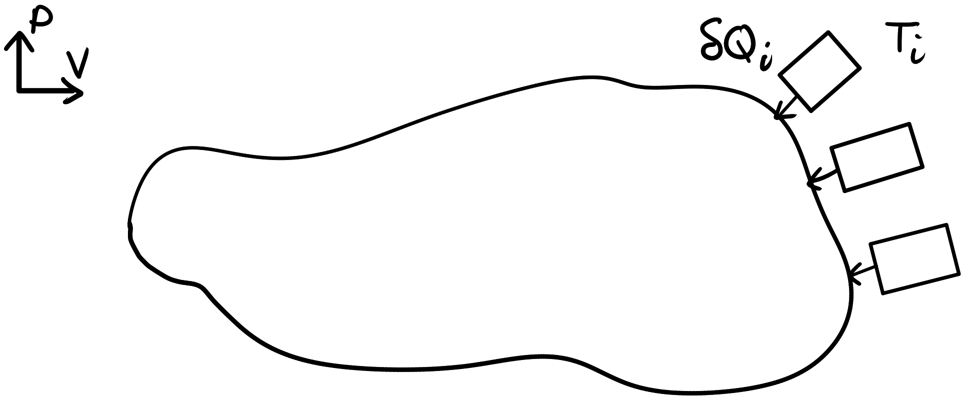

Figure 4.1: An engine with multiple sources of heat δQ_i.

If we sum over all the heat engines, we get

$$Q_0 = \sum_i \delta Q_i^0 = \sum_i \delta W_i + \sum_i \delta Q_i \tag{4.5}$$

We can group the first sum in W_C for the work done by the Carnot engines, and the second sum as W_S for the work done by the system, as established at the start.

$$Q_0 = W_C + W_S \tag{4.6}$$

Thus, the total heat that flows out from the master reservoir is the sum of the work done by the Carnot engine and the work done by the system.

Effectively, this is the perfect conversion of heat into work. From the second law, we insist that

$$W_C + W_S \leq 0 \tag{4.7}$$

otherwise there would be a violation. This inequality comes from the fact that the work that is coming out of the Carnot engine must actually be negative, so that we are doing work *on* these engines to convert heat from the master reservoir to work done by the system. If this quantity is negative, we expect that $W_S \leq W_C$ where both sides are positive, if this shows the magnitude of both terms, then it makes sense that the work we are doing on the system must either result in the same amount of work done by the system (perfect efficiency), or less than that. If $W_S > W_C$, this shows that the work we are doing on the system is resulting in more work than what we are putting in, which is forbidden.

Therefore, $Q_0 = \sum_i \delta Q_i^0 \leq 0$. Using the Carnot relation, which is that the ratio of the heat is equal to the ratio of the temperature, we get

$$T_0 \sum_i \frac{\delta Q_i}{T_C} = \sum_i \frac{\delta Q_i}{T_C} \leq 0 \tag{4.8}$$

If we take the limit as each δQ_i gets incredibly small or $i \to \infty$, the temperature of the reservoir becomes the temperature of the system. We arrive at

$$\oint \frac{dQ}{T} \leq 0 \tag{4.9}$$

We have proved that any valid system, reversible or irreversible, must obey this inequality.

4.2 Entropy

Definition 4.2.1. For a reversible closed cycle, the LHS expression in 4.3 is exactly equal to 0, which indicates that it is a state function. We write this state function as entropy S

$$\begin{aligned} \mathrm{d}S &= \frac{\text{đ}Q_{\text{rev}}}{T} \\ T\,\mathrm{d}S &= \text{đ}Q_{\text{rev}} \end{aligned} \tag{4.10}$$

Like any state function, the difference of entry at two points is just the integral evaluated at those two points.

This is the thermodynamic definition of entropy. Later, we will look at the statistical interpretation in terms of disorder.

We can directly measure S as a function of temperature if we keep V the same. Taking the partial derivative of T on each side, we arrive at

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{4.11}$$

Definition 4.2.2. Entropy is expressed as a function of temperature as

$$S(T) = \int_0^T \frac{C(T)}{T}\,\mathrm{d}T \tag{4.12}$$

In other words, entropy is the area under a (C/T)-T curve.

Substitute the differential of entropy into the first law, expressed by equation 2.1, we can also write the first law for as

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{4.13}$$

This applies for irreversible changes as well as reversible processes. How can we justify this?

For reversible changes, $\text{đ}W = -p\,\mathrm{d}V$ and $\text{đ}Q = T\,\mathrm{d}S$, while for irreversible changes $\text{đ}W \geq -p\,\mathrm{d}V$ and $\text{đ}Q \leq T\,\mathrm{d}S$. If we add the irreversible terms together it all balances out and we still get $\mathrm{d}U$. Another way of looking at it is that 4.13 is composed of only state function,s thus it must be valid for all changes, independent of path.

4.3 Irreversibility—entropy cannot decrease

We can prove that entropy cannot decrease. Consider a cyclic process which has irreversible and reversible parts, as shown in Figure 4.3.

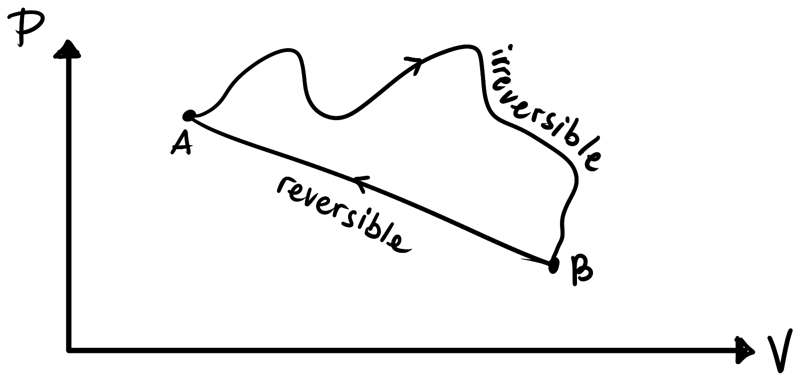

Figure 4.3: A cyclic process that has irreversible process from A to B and reversible process from B to A.

Derivation 4.3.1. From Clausius' theorem in Equation 4.3,

$$\begin{aligned} \int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ_{\text{rev}}}{T} &\le 0 \\ \int_A^B \frac{đQ_{\text{rev}}}{T} &\ge \int_A^B \frac{đQ}{T} \end{aligned} \tag{4.14}$$

If we let A tend to B so the points become infinitesimally close together, we have the differential form instead, substitute in dS, we get that for an *isolated system*, where $đQ = 0$

$$\mathrm{d}S \ge \frac{đQ}{T} \equiv \mathrm{d}S \ge 0 \tag{4.15}$$

This means for an isolated system, entropy **cannot** decrease.

4.4 The thermodynamic arrow of time

Hence, the entropy of the universe must increase with time, since the universe is an isolated system. Increasing entropy is synonymous with increasing "time". We can consider this to be the thermodynamic arrow of time.

Later, we will consider the statistical interpretation of entropy.

4.5 Joule expansion

Suppose we have two chambers that are thermally isolated. They are connected by a tube with a valve. Initially, all the gas is in the left chamber. When we suddenly open the valve, the change is *irreversible*, so the pressure and volume are not well-defined during the expansion. This is called a *free expansion* so the gas **does not do work on the surroundings.**

We now ask: What is the change in entropy when the system reaches its final state (it is in internal equilibrium)?

We don't know specifically the path, it is not well-defined. What we know, however, is the start and end points. Since entropy is a state function, we fortunately only need the start and end points. Effectively, we can use a well-defined path which would give us the same answer since we are dealing with path-independent functions.

We choose a reversible isothermal path. The path are different but if pressure and volume are the same at the start and end points, it will be equivalent to the irreversible path.

Since the path is isothermal, $U = U(T) = 0$ so from the first law and the ideal gas relations, we have

$$\mathrm{d}S = nR\frac{\mathrm{d}V}{V} \tag{4.16}$$

We can further integrate this to give us a simple result.

Definition 4.5.1. In the **isothermal** case, the change in entropy is given as

$$\Delta S = nR\ln\frac{V_1}{V_0} \tag{4.17}$$

We only calculated this for a system—the change in the entropy of the universe is not necessarily the same for the reversible and irreversible expansion.

5 Lecture 5 (Week 14)

5.1 Thermodynamic Potentials

We can combine state functions to make another state function. There are infinitely many possible combinations but only a few are useful. Here are several examples:

U	Internal energy
$F = U - TS$	Helmholtz free energy
$G = U - TS + pV$	Gibbs free energy
$H = U + pV$	Enthalpy

These definitions are only correct where the work term $đW = -p\,\mathrm{d}V$. Also, we assume that it is a closed system with a fixed number of particles (gas cannot leave the system). We will now look at each of the following examples in turn.

5.2 Internal energy

Looking at 4.13, we see that $U = U(S, V)$. We call S and V as the natural variables of U. Recall from Definition 1.2.1, we can find this for U since it is a state function.

Comparing the exact differential and the equation expressing the first law, we find that

$$T = \left(\frac{\partial U}{\partial S}\right)_V \text{ and } p = -\left(\frac{\partial U}{\partial V}\right)_S \tag{5.1}$$

5.3 Helmholtz Free energy

Using the first law, we can expand the equation for the Helmholtz free energy. We find that

$$F = F(V, T) \text{ and } \mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}T \tag{5.2}$$

where its natural variables are V and T.

Its exact differential leads to the results that

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \text{ and } S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{5.3}$$

This is particular useful because V and T are often common experiment conditions. The system will evolve to minimise F at constant V and T. This means as the system evolves, it will do work on the environment in order to minimise F, so that F is the maximum work you can get out of a system (hence “free” energy).

5.4 Gibbs Free energy

Doing similar steps as before, we find that

$$G = G(p, T) \text{ and } \mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p \tag{5.4}$$

Its exact differentials show that

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \text{ and } V = \left(\frac{\partial G}{\partial p}\right)_T \tag{5.5}$$

Same with F, the system will evolve to minimise G. So G is the maximum work you can get out of the system with constant p, and T

5.5 Enthalpy

Doing similar steps as before, we find that

$$H = H(S, p) \text{ and } \mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p \tag{5.6}$$

Its exact differentials show that

$$T = \left(\frac{\partial H}{\partial S}\right)_p \text{ and } V = \left(\frac{\partial H}{\partial p}\right)_S \tag{5.7}$$

Note that constant S is the same as constant Q, the cycle is adiabatic. Enthalpy as a quantity is useful because if you have an adiabatic change at constant pressure, ΔH is the heat absorbed by the system at constant p (e.g., a chemical reaction). At constant pressure, $\mathrm{d}H = \mathrm{d}Q$.

5.6 Maths of partial derivatives

Proofs aren’t necessarily, but these following identities are extremely useful.

Definition 5.6.1. Below are some partial derivative identities:

1. Chain rule (all terms must have the same constraints)

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial y}\right)_y \left(\frac{\partial y}{\partial x}\right)_y \tag{5.8}$$

2. Reciprocal theorem

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y} \tag{5.9}$$

3. Reciprocity theorem or triple product rule

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{5.10}$$

4. Convert an exact differential into a partial derivative into a partial one

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V \Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{5.11}$$

5. Maxwell relations (exchange derivatives w.r.t. natural variables). See 5.6.2.

5.6.1 Pseudo-proofs

These proofs are not presented explicitly. They are meant to help understand the identities in 5.6.

To prove the **reciprocal** and **reciprocity** theorems, take a function $f(x, y, z) = 0$, with $x = x(y, z)$, $y = y(x, z)$, and $z = (x, y)$. If we write x and z in differential forms, and substitute $\mathrm{d}x$ into the expression for $\mathrm{d}z$, we notice that we can equate the coefficients of $\mathrm{d}z$, which shows the **reciprocal** theorem holds.

Then if we look at the coefficients of $\mathrm{d}y$, we can rearrange and use **reciprocal** theorem to show the **reciprocity** theorem.

5.6.2 Maxwell relations

To demonstrate the Maxwell relations, let's use the Helmholtz relation, see Section 5.3 for the differential forms.

If we take the derivatives again with respect to other natural variables,

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial^2 F}{\partial V \partial T}\right)_{V,T} \text{ and } \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial^2 F}{\partial T \partial V}\right)_{V,T} \tag{5.12}$$

we can see that

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{5.13}$$

This is a Maxwell relation. We don't have to memorise all the Maxwell equations, but we can easily derive them when needed.

6 Lecture 6 (Week 14)

6.1 Cooling gases and Joule-Thomson expansion

There are several ways to cool gases. One way is to expand gas *adiabatically* and make it do work on the environment. This is different from a Joule expansion, where the gas expands freely. A Joule expansion does not do work on the environment. We can either do this using a piston and a flywheel (Figure 6.1) or by using a turbine (turbo expander) (Figure 6.2).

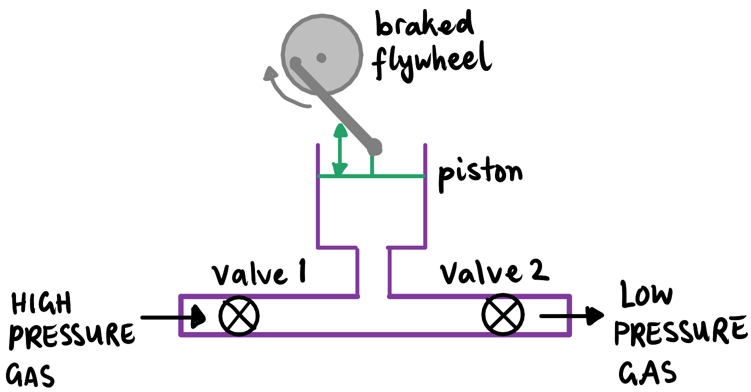

Figure 6.1: We open the high pressure valve, gas comes in the chamber and moves the piston up (doing work on the piston), the flywheel spins with friction to remove energy and once the piston reaches the highest position, it moves down. The low pressure valve is opened and low pressure gas is forced out by the lowering piston.

Adiabatic expansion is quite inefficient at low temperature. A better alternative is the *Joule-Thomson* or *Joule-Kelvin* expansion (JT or JK process). See Figure 6.3.

We assume the JT process is adiabatic—high pressure gas comes through and expands to the other side without any heat exchange.

6.1.1 Conservation of enthalpy

We might want to find the work done as gas moves through the plug in the centre.

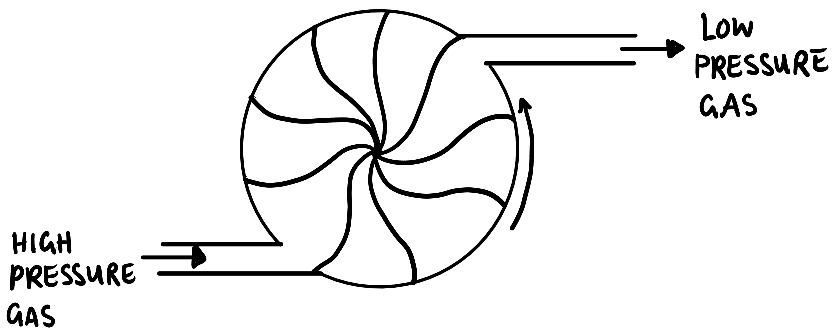

Figure 6.2: High pressure gas comes in, drives the turbine by doing work on it, heat is dissipated through friction, and then low pressure gas comes out.

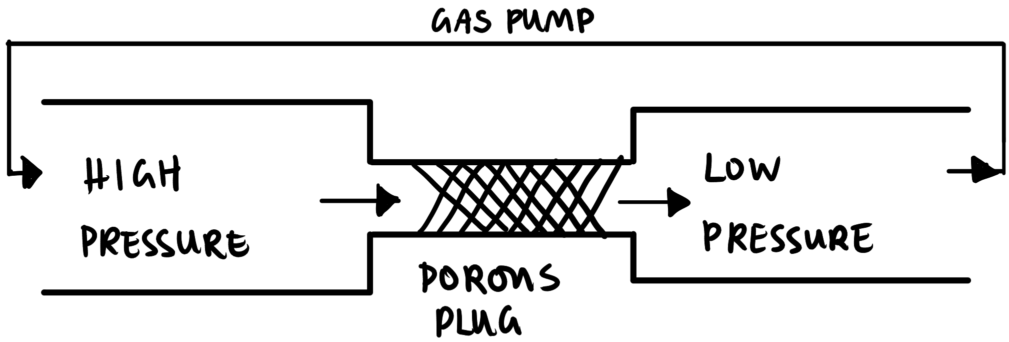

Figure 6.3: High pressure gas comes in and goes the rough a porous plug which removes a lot of energy through friction, low pressure gas comes out of the other end and is pumped back into the engine. The pressure difference is maintained with a compressor. This principle of cooling is used in many devices like refigerators, or helium liquefiers.

Imagine, for the sake of representation, there are piston on both sides of the engine. The left piston maintains pressure p_1 as it forces gas through the plug, while the right piston moves to the right at p_1 as gas moves through plug. Force is $F = pA$, therefore:

The work done on gas to move distance L_1 in the left chamber	$W = p_1AL_1 = p_1V_1$
The work done on gas to move distance L_2 in the right chamber	$W = P_2AL_2 = p_2V_2$

Definition 6.1.1. The net work done on the gas in a Joule-Thomson expansion is

$$\Delta W = p_1V_1 - p_2V_2 \tag{6.1}$$

As the gas moves through the plug, there is a change in internal energy, $\Delta U = U_2 - U_1$. From the first law, for an adiabatic process (no heat transfer), $\Delta U = \Delta W$. We know ΔW from 6.1, so

$$p_1V_1 + U_1 = p_2V_2 + U_2 \tag{6.2}$$

This is the definition of *enthalpy* which we mentioned in Section 5.5, which means $H_1 = H_2$. In other words, enthalpy is conserved in a JT expansion.

6.1.2 The Joule-Thomson coefficient

We can quantify how much cooling takes place by defining a coefficient, called the Joule-Thomson coefficient as

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_H \tag{6.3}$$

Since the constant H is difficult to use so we can derive an expression at constant pressure instead. We can use what we know from previous lectures and 5.6 to get to this.

Derivation 6.1.1. From the reciprocity theorem, we can write

$$\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_P = -1 \tag{6.4}$$

Substitute this into our definition for the JT coefficient so far to get

$$\mu_{\mathrm{JT}} = -\frac{1}{\left(\frac{\partial p}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_p} \tag{6.5}$$

We then borrow our results from Section 5.5 the differential form of enthalpy, divide by dT at constant p to get

$$\left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_p \tag{6.6}$$

We also divide by dp at constant T

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V \tag{6.7}$$

Substitute back into what we got from reciprocity to get

$$\mu_{\mathrm{JT}} = -\frac{1}{C_p}\left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right] \tag{6.8}$$

We use a Maxwell relation to make this nicer

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \tag{6.9}$$

We can then use this for our final expression:

Definition 6.1.2. The JT coefficient at constant pressure is

$$\mu_{\mathrm{JT}} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] \tag{6.10}$$

To get cooling we need $\mu_{\mathrm{JT}} > 0$. For an ideal gas, $\mu_{\mathrm{JT}} = 0$, so there's never any cooling. But for a real gas, this varies with temperature. We call the temperature below which you will get cooling via the JT process the **inversion temperature**.

Definition 6.1.3. The inversion temperature T_i for a JT process is

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T_i} \tag{6.11}$$

Below this temperature, we can cool gas using the JT process, beyond this temperature, we can use any adiabatic expansion to get to T_i.

There are JT coefficient curves at various temperatures for different gases.

6.1.3 Helium liquefier (not examined)

From a gas storage, the gas travels through a compressor. Next, it goes through a heat exchanger, then through the Turbine 1, then through another heat exchanger and finally through Turbine 2. It is then pushed back around the circuit once again, in order to cool down other incoming gases (thus it functions as the heat reservoir in the heat exchangers). It goes through this step until the final low-pressure gas that leaves Turbine 2 cools from 300K to 10K.

At the same time, the compressor also has another stream coming into the liquefier, but only going through the heat exchanger and not through the turbines (the first stream is used to maintain heat exchange for this stream), after it leaves this, it has the same temperature as the other stream, but maintains a high-pressure.

After that this high-pressure gas enters the JT process to become liquefied.