Thermodynamics

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Physics and Astrophysics BSc

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NOTES ON THERMODYNAMICS

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VERSION

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§§ 1.1.1 Macroscopic and Microscopic Systems

The study of any branch of natural science *must* begin with the definition of *system*

Definition 1.1.1 (System). A *system* is a finite region of space containing matter inside a closed surface, known as the *wall*.
Everything outside of the system, even other systems, that are in interaction with the system are known as the *surroundings* of the system.
A system is said to be *closed* if there's no matter flux between itself and its surroundings.
The set of the system, surroundings and all the rest is known as *universe*, and it's usually indicated with Ω.

All systems can be studied with two points of view

1. A microscopic point of view (molecular or less)
2. A macroscopic point of view (human scale or more)

Taking as our example system the cylinder chamber of a car, we can define the following *macroscopic coordinates*, i.e. descriptors of the system in a macroscopic point of view

1. Mass of gas contained
2. Volume of the chamber
3. Pressure of the gas
4. Temperature of the gas

These coordinates are *macroscopic* also because

- Do not involve assumptions about the structure of matter, fields or radiation
- Are low in number
- Are fundamental

- Can be, generally, directly measured

If we instead consider a system from the microscopic point of view, we can define the system as

1. N particles with energy states E_i
2. Particle interactions with fields and through collisions

And more.
Microscopic systems that can be considered isolated or embedded in other systems are known as *ensemble systems*. In microscopic systems, the equilibrium state is defined as the state with the highest probability, i.e. the state which will have a higher occupation number or *population*.
In general, microscopic coordinates

1. Consider the structure of matter, fields and radiation
2. Are many in number
3. Are described by mathematical models and usually not directly measurable
4. Must be calculated using the previous models

In the study of thermodynamics, in the next chapter or two, we will use the macroscopic description. The major difference with the other branches of science lays in the fact that in thermodynamics, a macroscopic quantity is always present and defined, known as *temperature*.
Generally, in thermodynamics the quantities chosen are known as *thermodynamic coordinates*, which are macroscopic coordinates that determine the internal state of the system. Systems for which thermodynamic coordinates can be defined are known as *thermodynamic systems*

§§ 1.1.2 Zeroth Law of Thermodynamics

Consider a thermodynamic system A, for which we can define two independent coordinates, (X, Y), the first being a generalized force and the other being a generalized displacement. We define:

Definition 1.1.2 (Equilibrium State). A state for which the coordinates (X, Y) are constant as long as the external conditions don't change, is known as an *equilibrium state*

Equilibrium states *depend on proximity of other systems and nature of the boundary*, if we put A in contact with another system B with coordinates (X', Y') we then can define two types of walls:

Definition 1.1.3 (Adiabatic Walls). If the walls between the system A and B are *adiabatic*, then the equilibrium states are *independent* and possible for each value of (X, Y) and (X', Y')

Definition 1.1.4 (Diathermal Walls). If the walls between the system A and B are *diathermal*, the equilibrium states of the two systems aren't independent anymore, and thus are defined only for a set of coordinates (X, Y, X', Y')

We subsequently define

Definition 1.1.5 (Thermal Equilibrium). Thermal equilibrium is defined as the state achieved by two or more systems, characterized by a restricted amount of values of system coordinates, after being put in contact through a diathermal wall.

From the definition of thermal equilibrium, an important law follows

Law 1 (0th Law of Thermodynamics). Suppose that two thermodynamic systems A and B are separated by an adiabatic wall and simultaneously in contact with a third system C through a diathermal wall. It follows that if:

- A is in thermal equilibrium with C
- B is in thermal equilibrium with C

Then, A must be in thermal equilibrium with B

Suppose that now that the system A and B are at equilibrium with each other at some coordinates (X_A, Y_A) and (X_B, Y_B). If we remove the system A, the system B will undergo a change of state to coordinates (X_2, Y_2) which must be in thermal equilibrium with the state (X_B, Y_B). It must follow then that there's a quantity, known as *temperature*, which remains constant during this transformation, thus:

Definition 1.1.6 (Temperature). We define the *temperature* as the property in common between states in thermal equilibrium. A change of state with constant temperature (i.e. in *thermal equilibrium*) is known as an *isothermal transformation* or an *isothermal process*.
Temperature *must* be a scalar quantity, and it's usually indicated with T. For each possible value of T there exists a defined family of isothermal processes.

§§ 1.1.3 Temperature Measurements

In order to define a *temperature scale*, we choose a thermodynamic system for which are known its properties, known as the *thermometer*, and define a set of empirical rules for assigning a value of T for each isotherm.
Suppose that the system is well described by the generalized force X and the generalized displacement Y. Then, for defining a temperature scale we will

- Choose a convenient path in the (X, Y) plane, like $Y = const$. Then, since one of the two quantities is fixed, we must have that if the system undergoes an isothermal process, we must have that
$$\theta = \theta(X)$$
Where θ is our temperature scale
- We suppose, arbitrarily, that $\theta(X) \propto X$, thus
$$\theta_A(X) = aX$$

The scale that we defined previously has, in particular, that

$$\lim_{X \to 0} \theta_A(X) = 0$$

I.e. it's an *absolute* temperature scale. Examples of absolute scales are the *Kelvin* and *Rankine* temperature scales.
Experimentally, the standard gas for thermometric evaluations is molecular hydrogen H_2.

For most thermodynamic scales, being $Y = const$ completely arbitrary, it's convenient to define $Y = Y_1 = const$ as the *triple point* of water, it being the point in which liquid water, ice and vapor exist in the same place and time. This point is measured to be at a temperature of

$$T_{TP} = 0.01^\circ\mathrm{C} = 273.16\mathrm{K}$$

From the absolute arbitrary temperature scale we have defined before, defined X_{TP} the coordinate at which we have the triple point, we have

$$\theta_A(X_{TP}) = aX_{TP} = 273.16\mathrm{K} \Longrightarrow a = \frac{273.16\mathrm{K}}{X_{TP}}$$

Thus, in general, an absolute thermometric scale can be defined as follows

$$\theta_A(X) = 273.16\frac{X}{X_{TP}}\mathrm{K} \tag{1.1}$$

Thus, it's possible to define this scale in terms of pressures (generalized forces) or volumes (generalized displacements), using the triple point coordinates as reference point.

§§§ 1.1.3.1 Temperature Scales

The most common temperature scales are two in the metric system of units and two in the imperial system. If we use the definition (1.1) for the Kelvin scale, we have

Definition 1.1.7 (Celsius Temperature Scale). Defined by Anders Celsius (SWE), used in the metric system of units

$$T\left(^\circ C\right) = T\left(K\right) - 273.15$$

Definition 1.1.8 (Rankine Temperature Scale). Absolute temperature scale defined by William Rankine (UK), used in the imperial system of units

$$T\left(R\right) = \frac{9}{5}T\left(K\right)$$

Definition 1.1.9 (Fahrenheit Temperature Scale). Temperature scale define by Daniel G. Fahrenheit (GER), used in the imperial system of units

$$T\left(^\circ F\right) = \frac{9}{5}T\left(R\right) - 459.67$$

With these definitions we can find conversions between these scales, and for commonly used scales like Fahrenheit and Celsius we get the following conversion formula

$$T\left(^\circ F\right) = \frac{9}{5}R\left(^\circ C\right) + 32 \tag{1.2}$$

Note that the Celsius temperature scale has the same dimensions of intervals of the Kelvin scale, thus, a temperature difference in Celsius degrees is the same in Kelvins. Thanks to future concepts, the Kelvin scale will be defined as the absolute scale of temperature, since it's tied to energetic properties of the system itself.

§ 1.2 Thermodynamic Equilibrium

§§ 1.2.1 Definition of Equilibrium

Given a thermodynamic system A, *any* change of coordinates defines a *change of state* for the system.
A non-influenced system is known as an *isolated system*, but these kinds of systems aren't important in the study of classical thermodynamics, since these systems can't be studied macroscopically.
There are various kinds of equilibrium, namely

- Mechanical equilibrium: equilibrium of forces in the system
- Chemical equilibrium: the system is in mechanical equilibrium and it doesn't undergo in spontaneous chemical reactions
- Thermal equilibrium: the system is in mechanical and chemical equilibrium, and there is no change of coordinates when the system is separated from its surroundings via a diathermal wall
- Thermodynamic equilibrium: the system is in mechanical, chemical, thermal equilibrium contemporaneously

Note that for having thermodynamic equilibrium, all the previously stated equilibriums must be satisfied, and the system doesn't undergo in changes of state.
In fact, if a system is not in mechanical equilibrium then the system is in a *non equilibrium state* and therefore thermodynamic coordinates cannot be defined, and so goes for the other equilibriums.
Specifically, when the system is in *thermodynamic* equilibrium, it *does not* change state, note instead how instead *thermal* equilibrium is defined via changes of state, since in order for a system to be defined in thermal equilibrium undergoes an *isothermal* change of state, but still a change of state.

§§ 1.2.2 Thermodynamic Relationships at Equilibrium

Given any mole of gas, it's experimentally verifiable that if:

- Fixed volumes and temperature imply that the pressure can't be chosen
- Fixed pressure and temperature imply that the volume can't be chosen
- Fixed pressure and volume imply that the temperature can't be chosen

Clearly, if we use these three coordinates to describe a thermodynamic system, only one of the two can be chosen.
These relations were found empirically by Gay-Lussac and Boyle.
The first experiment, done by Gay-Lussac deals with the relationship between V and T. It has been found that, heating a solid with linear length l_0 at rest, that

$$l(T) = l_0 + \sum_{i=1}^{\infty} a_i l_0 \Delta T^i \tag{1.3}$$

With a_i being numerical coefficients depending on the material composition of the system. For small temperature variations ΔT, it can be said that

$$l(T) \simeq l_0 + a l_0 \Delta T \tag{1.4}$$

Here a, is known as the *linear thermal dilatation coefficient*. In general $a > 0$, but in nature materials with $a < 0$ are found, one of these is water, and all oxides.
Keeping the first order approximation, and using $V_0 = l_0^3$, we can say

$$V(T) \simeq l_0^3 (1 + 3a\Delta T) = V_0 (1 + \beta \Delta T) \tag{1.5}$$

The coefficient $\beta = 3a$ is the *volumetric thermal dilatation coefficient*. This experiment, when repeated with fluids, thanks to their incompressibility, gives

THEOREM 1.1 (First Law of Gay-Lussac). *Given a fluid with volumetric compressibility β, contained in a volume V_0, when undergoing a change of temperature ΔT expands or contracts following this equation*

$$V(T) = V_0 (1 + \beta \Delta T) \tag{1.6}$$

If we define the absolute zero of the kelvin scale as the temperature such that $V(T_0) = 0$, we get

$$V(T) = V_0 \frac{T}{T_0} \tag{1.7}$$

If the volume is kept constant and instead the variation of pressure is measured, we have

THEOREM 1.2 (Second Law of Gay-Lussac). *Given a fluid with compressibility β, if it undergoes a change of temperature at constant volume, the pressure will follow this equation*

$$p(T) = p_0 (1 + \beta \Delta T) \tag{1.8}$$

If we use the kelvin scale as defined before, we get

$$p(T) = p_0 \frac{T}{T_0} \tag{1.9}$$

Both these laws were derived empirically through experimentation, and give the behavior of volume and pressure with respect to changes of temperature. One might ask what happens when temperature is constant, and that's what has been found by Boyle

THEOREM 1.3 (Boyle's Law). *Given a fluid undergoing pressure and volume changes in thermal equilibrium, then*

$$pV = p_0 V_0 \tag{1.10}$$

Note that if a gas verifies all the previous laws, we have

$$pV = \frac{p_0 V_0}{T_0} T \tag{1.11}$$

This equation gives the empirical dependencies of the three thermodynamic coordinates, (p, V, T) and is for this known as the *equation of state*.
If we also consider that the volume of the gas is $V \propto n$, where n are the *moles* of gas, one has

$$pV = nRT \tag{1.12}$$

Where $R = 8.31 \mathrm{J/Kmol}$ is a conversion constant known as the *gas constant*.
All previous experiments considered that we specifically had what's called a *hydrostatic system*, i.e. a system which has

- Uniform pressure
- Constant mass
- Surface, gravitational and electromagnetic effects can be considered negligible

§§ 1.2.3 Thermodynamic Diagrams

The previous relations can be used to determine what are known as *thermodynamic diagrams*, which permit the graphical description of changes of state in a thermodynamic system.
As we saw, of the three coordinates (p, V, T) only two are independent. Thanks to this, we can define 2D Cartesian planes which have as coordinates either pV, pT, VT. We could also define a surface, known as the pVT surface, which describes *all* the possible configurations of the system, "extruding" the pV, pT and VT

§§§ 1.2.3.1 pV Diagrams

Consider now an empirical case of water in thermal equilibrium at $94°\mathrm{C}$ in a vessel of $2\mathrm{m}^3$. If the vessel is sealed and there's *no air*, it's seen that water is in equilibrium with its vapor. It's notable how, if we map all the possible pV transformations of water, the diagram will be divided in three zones by what are known as *critical isotherms*.
These isotherms all coincide in a special point, known as the *critical point*. An image of such diagram follows

§§§ 1.2.3.2 pT Diagrams

Pressure-temperature diagrams, are instead useful for defining phase transition isotherms of the system. Considering water again, three main curves can be defined between the states of matter. These curves are known as

- Fusion curve
- Sublimation curve
- Vaporization curve

In the first one, along the curve, the set of states described are states of solid-liquid equilibrium, in the second curve solid-vapor equilibrium and liquid-vapor equilibrium.
At the intersection of these three lines we find the *triple point*. It's important to remember that this point is represented only in this diagram as a point, while in others is instead a curve.

§§ 1.2.4 Differential Changes of State

In order to properly define a mathematical framework for describing the thermodynamic of substances, we have to rewrite differential calculus in a way which is physically significant.
Suppose that in a pV diagram, a substance undergoes a really small transition to another equilibrium state. If the volume changes by a differential $\mathrm{d}V$ and the pressure by a differential $\mathrm{d}p$, we *must* have

- For any volume V, we have $\mathrm{d}V << V$, but $\mathrm{d}V$ is big enough to be considered macroscopic

- For any pressure p, and consequent molecular perturbations to pressure δp_{mol}, we must have

$$\delta p_{mol} << \mathrm{d}p << p$$

With these considerations, both volume and pressure can be considered as mathematically continuous functions between the two equilibrium states.
Remembering that of (p, V, T) only two of the three are independent, we can define the differentials of these quantities, since

$$\begin{cases} p = p\left(V, T\right) \\ V = V\left(p, T\right) \\ T = T\left(p, V\right) \end{cases}$$

Thus

$$\begin{cases} \mathrm{d}p = \left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T \\ \mathrm{d}V = \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T \\ \mathrm{d}T = \left(\frac{\partial T}{\partial p}\right)_V \mathrm{d}p + \left(\frac{\partial T}{\partial V}\right)_p \mathrm{d}V \end{cases} \tag{1.13}$$

Where, as a subscript of the parentheses, we indicated which of the coordinates is kept constant.
For volume specifically, we can define two things in particular

1. Volumetric expansivity β as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{1.14}$$

2. Isothermal compressibility κ

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{1.15}$$

Therefore, the differential changes of volume can be described as follows

$$\mathrm{d}\log\left(V\right) = \beta \mathrm{d}T - \kappa \mathrm{d}p \tag{1.16}$$

§ 1.3 Work

In general, we can define two kinds of work that can be made by a system, or that the system can be subjected to:

- External work, which is the one exerted from the system to the surroundings
- Internal work, which is the one exerted from one part of the system to another

In general, we are only interested in *external work* in our macroscopic treatment.
Consider now a hydrostatic system contained in a piston chamber with adiabatic walls. By definition, if the piston has surface S, we define the pressure as

$$p = \frac{F}{S} \tag{1.17}$$

We now consider an *infinitesimal* displacement of the piston, with force $\underline{F}$. The amount of work is then, as usual

$$đW = \underline{F} \cdot \mathrm{d}\underline{r} \tag{1.18}$$

Thus, if the piston moves along the x axis

$$đW = pS\mathrm{d}x = p\mathrm{d}V \tag{1.19}$$

This work is commonly known as *thermodynamic work* and shouldn't be confused with *other* kinds of work that might be done from external forces, aka *mechanical work*.
The main question that pops to mind is how is actually infinitesimal work defined in a thermodynamic system. The action of the piston itself creates instability, and thus even in an infinitesimal displacement the gas isn't anymore in mechanical equilibrium, even for a small amount of time. An approximation is made in order to make calculations possible, i.e. the *quasi-static approximation*, defined as follows

Definition 1.3.1 (Quasi Static Process). A quasi static process is an infinitesimal thermodynamic transformation. Specifically, a quasi static process is one such that the system is always in a neighborhood of an equilibrium configuration, thus it can be thought as always being in an equilibrium state. This approximation thus renders our previous calculations valid.

The "*d slashed*" differential operator is there to indicate one thing and one thing only: work is *path dependent*, as already seen in any course in classical mechanics.
Note that in literature, the previous definition of work tends to differ by a minus sign. It's just a convention which simply indicates the sign of work depending whether it's made *on* or *by* the system. In our case, if the system is making work *on* the surroundings, like when it expands, we have $W > 0$ and vice versa.
The path dependence of work makes its calculation not always immediate. Thanks to the existence of the state equation, we can tho define a relationship $p(V)$ which basically makes the pressure an integrating factor for work.

§§ 1.3.1 Quasi-static Processes

Let's start to consider now quasi static processes in ideal gases. We already know that for an ideal gas the equation of state holds, which is

$$pV = nRT$$

We can then define the implicit dependence $p(V, T)$ as

$$p(V, T) = \frac{nRT}{V}$$

In the special case of *isothermal* processes (constant T), we can then integrate the work differential and obtain

$$W_T = nR \int_{V_A}^{V_B} \frac{1}{V} \mathrm{d}V = nR \log\left(\frac{V_B}{V_A}\right) \tag{1.20}$$

For an *isobaric* process (p is constant), the integration is trivial and gives

$$W_p = p\,(V_B - V_A) \tag{1.21}$$

Another special case to consider is when the case study is composed by multiple hydrostatic systems in thermal equilibrium, separated by a diathermal wall. In this general case, work is additive thanks to its definition, and the total work of the composite system is none other than the sum of the work of the single component systems

2 Heat

As we might have understood, the main study of thermodynamics is *changes of state* (duh). There are various ways to induce a change of state in a system:

1. External forces, thus when $W \neq 0$
2. Changes in temperature $W = 0$, *something*$\neq 0$
3. Both at once

That *something* must be something special, since it's not mechanical nor an expansion of the system. This "something" is known as *heat*.

Definition 2.0.1 (Calorimetric Heat). «*Heat*» is that quantity that gets transferred between a system and its surroundings by virtue of *temperature only*. An adiabatic wall is thus a heat insulator, while a diathermal wall is a heat conductor.

§ 2.1 First Law of Thermodynamics

§§ 2.1.1 Internal Energy Function

Consider now the last example system that we treated, a simple ideal gas inside an adiabatic cylinder chamber with a piston. As we saw before, in this special case work is *path independent*. The mathematical result that we obtain is that a *potential must exist and is unique*. This potential is known as the *internal energy* of the gas, and for an adiabatic process gives

$$W_{AB} = U(p_A, V_A, T_A) - U(p_B, V_B, T_B) \tag{2.1}$$

In classical thermodynamics, thanks to this result, it's *not needed* to know the exact functional shape of the internal energy, but only its difference between the equilibrium points.
Now a little consideration on notation must be given. Thanks to the ideal gas equation of state, we can always write the internal energy differential with two of the three thermodynamic coordinates, thus, taking two of the three possible combinations

$$\begin{aligned} \mathrm{d}U_1 &= \frac{\partial U}{\partial p}\mathrm{d}p + \frac{\partial U}{\partial V}\mathrm{d}V \\ \mathrm{d}U_2 &= \frac{\partial U}{\partial V}\mathrm{d}V + \frac{\partial U}{\partial T}\mathrm{d}T \end{aligned}$$

One might mistakenly say that the derivatives with respect to the volume are equal in both cases, but this is *absolutely* not true in general.

For avoiding confusion, from now on, the following notation will be used

$$\mathrm{d}U = \left(\frac{\partial U}{\partial p}\right)_T \mathrm{d}p + \left(\frac{\partial U}{\partial T}\right)_p \mathrm{d}T \tag{2.2}$$

Where the subscript specifies *which* of the remaining coordinates is being kept constant.

We can now continue with trying to understand how heat fits in our thermodynamic calculations. Consider a generic system which undergoes two transformations, one adiabatic and one non-adiabatic. In the first transformation we already calculated that

$$W = \Delta U$$

In the second transformation this is not true. Since we're still working in the realm of physics, if there are no dissipative processes, as in our case, *must* be conserved.

As we defined before, there is a heat flow between the system and its surroundings, and we can write then the *first law of thermodynamics*

$$\boxed{\Delta U = Q - W} \tag{2.3}$$

This extremely important equation implies three fundamental things:

1. An internal energy function exists
2. Energy is conserved
3. Heat is energy in transit by means of temperature differences.

Note that with this definition, we *do not* and *cannot* know heat during processes, but only its flow, specifically

$$Q = \int_{t_2}^{t_1} \frac{\mathrm{d}Q}{\mathrm{d}\tau} \mathrm{d}\tau$$

I.e. internal energy is *not* separable in mechanical (work) and thermal (heat). As with work, saying that there's an amount of heat in a body doesn't make any sense.

As with work, heat is path dependent, and its differential inexact.

With what we have said before, the first law can be rewritten in differential form as

$$\boxed{\mathrm{d}U = \text{đ}Q - \text{đ}W} \tag{2.4}$$

Via integration of this equation, it's possible to easily determine how the coordinates of the system change.

Note that for a hydrostatic system we have

$$\mathrm{d}U = \text{đ}Q - p\mathrm{d}V$$

§ 2.2 Calorimetry

§§ 2.2.1 Heat Capacity

Consider a system which undergoes a change of state for which there's a variation of temperature, we can define a new quantity, the *heat capacity*, as

$$C = \frac{đQ}{\mathrm{d}T} \tag{2.5}$$

Since both heat capacity and internal energy are extensive, it's useful to define the specific versions of these quantities by dividing them by the number of moles of matter n. Specifically, said N_A Avogadro's number, we have that

$$n = \frac{N}{N_A} = \frac{m}{\mathcal{M}} \tag{2.6}$$

Where $\mathcal{M}$ is the *molecular weight* and $N_A = 6.022 \times 10^{23}\ \mathrm{mol}^{-1}$. Thus

$$c = \frac{1}{n}\frac{đQ}{\mathrm{d}T} \tag{2.7}$$

Note that heat capacity can assume different values depending on the process!
It's important to define then the specific heat capacity at constant pressure and constant volume for hydrostatic processes

$$\begin{cases} c_p = \dfrac{1}{n}\left(\dfrac{đQ}{\mathrm{d}T}\right)_p \\ c_V = \dfrac{1}{n}\left(\dfrac{đQ}{\mathrm{d}T}\right)_V \end{cases} \tag{2.8}$$

Heat capacity has units of E/nT and it's usually measured in non-standard units, like the *calorie*

Definition 2.2.1 (Calorie). A «*calorie*» indicates the amount of heat necessary to raise the temperature of water by one degree Celsius. By definition

$$1\ \mathrm{cal} = 4.186\ \mathrm{J} \tag{2.9}$$

§§ 2.2.2 Calorimeters

A *calorimeter* is an instrument used to measure heat variations and specific heats of substances. The simplest calorimeter is the *mixture calorimeter*, basically an adiabatic container filled with a defined amount of water.
Consider now the measuring phase. Suppose that we want to find the specific heat of some external body with mass m_x and initial temperature T_x.
If the water in the calorimeter is at a temperature T_{H_2O} with m_{H_2O} mass of water. After the immersion of the external body we will have a heat flow between the two, until the calorimeter and the body will be in thermal equilibrium at a temperature T_{eq}.
For what we have written before, by definition of specific heat we can write

$$\begin{aligned} Q_{H_2O} &= m_{H_2O}C_{H_2O}\left(T_{eq} - T_{H_2O}\right) \\ Q_x &= m_x C_x \left(T_{eq} - T_x\right) \end{aligned} \tag{2.10}$$

By virtue of the first law, being the calorimeter adiabatic we must have that the increase in temperature of the water is only due to the heat flux from the external body, and thus

$$Q_{H_2O} = -Q_x$$

Note the minus sign, we must have $Q = Q_{H_2O} + Q_x = 0$, if this wasn't satisfied we would have an adiabatic calorimeter that by calculation is not adiabatic!
Equating and solving for C_x, which is the specific heat that we want to find, we have

$$C_x = \frac{m_{H_2O} C_{H_2O} \left(T_{eq} - T_{H_2O}\right)}{m_x C_x \left(T_x - T_{eq}\right)} \tag{2.11}$$

The passages are omitted, it's really easy to rederive it, just watch out for the minus sign.
One now might (rightfully) say: «*doesn't the calorimeter have mass, and therefore interfere with the previous calculation somehow?*»
The answer is *yes*. We therefore must account for this problem by defining an «*equivalent mass*» of the calorimeter, i.e. the equivalent mass in water of the calorimeter itself.
For this problem we have that both the water and the calorimeter are always in thermal equilibrium, thus if we have m_1 masses of water with C_{H_2O} specific heat, and our calorimeter with C_c as specific heat with $m^\star$ as equivalent mass of it, we have

$$C = C_c + C_1 = \left(m_1 + m^\star\right) C_{H_2O}$$

Consider now adding m_2 mass of water to the calorimeter, at some temperature T_2, if the calorimeter is at temperature T_1 we have that there will be an exchange of heat between the new mass of water and itself, thus $Q_1 = -Q_2$, which implies

$$\left(m_1 + m^\star\right) C_{H_2O} \left(T_{eq} . T_1\right) = -m_2 C_{H_2O} \left(T_{eq} - T_2\right)$$

With some easy algebra, solving for $m^\star$, our equivalent mass, we have

$$m^\star = \frac{m_1 \left(T_1 - T_{eq}\right) + m_2 \left(T_2 - T_{eq}\right)}{T_1 - T_{eq}} = m_2 \frac{T_2 - T_{eq}}{T_{eq} - T_1} + m_1 \tag{2.12}$$

§ 2.3 Heat Flow

§§ 2.3.1 Conduction and Convection

In order to treat heat flow between two bodies, we have to see (empirically) that if we take a square rod with cross-sectional surface S and temperatures T_1 and T_2 at its two faces, that the heat flow between the two parts depends on

- Surface area
- Time
- Temperature differences
- The inverse of the distance between the two parts

If the two faces are distant x, then we can write that

$$Q = \kappa\left(\frac{ST}{x}\right)\Delta T \tag{2.13}$$

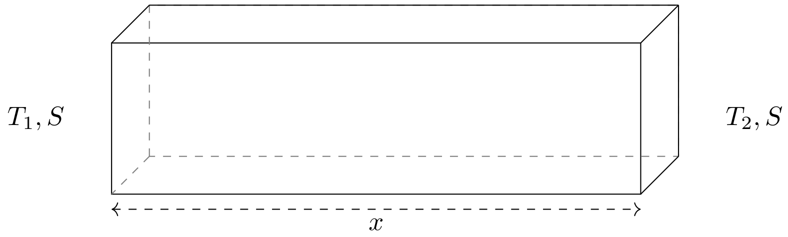

Figure 2.1: The experimental rod we use to derive the empirical heat flow equation

Where κ is a proportionality constant known as the «*thermal conductivity*». If we make this rod infinitesimal (and why not, consider that not all things can be approximated with rods), we have, after defining a heat flow vector $\underline{q}$ as

$$\underline{q} = \frac{1}{S}\frac{\text{đ}Q}{\mathrm{d}T} \tag{2.14}$$

That, being $x \to \mathrm{d}^3 r$ in the general case,

$$\underline{q} = \frac{1}{S}\frac{\text{đ}Q}{\mathrm{d}t} = -\kappa\nabla T \tag{2.15}$$

This is what's known as *Fourier's heat equation*, which tells us that the heat flux depends directly on the properties of the medium, contained in κ, and its cross sectional surface.
Note the specific case where the medium is isotropic. We will have that the heat will be proportional to the temperature at the point, and thus our heat conduction equation becomes

$$\frac{\partial T}{\partial t} = -\kappa\nabla T \tag{2.16}$$

Another special case is that of convection. Consider two bodies with conductivity κ_1 and κ_2, each thick d_i. Defined the *heat transfer coefficient* of the 2 bodies as

$$h_i = \frac{\kappa_i}{d_i} \tag{2.17}$$

Which fits to the empirical *heat convection equation* or *Newton's law on convection*

$$\frac{1}{S}\frac{\text{đ}Q}{\mathrm{d}t} = h\Delta T \tag{2.18}$$

The coefficient h in this case is the total heat transfer coefficient of the system, and can be intended as an *electrical conductance*, calculated as follows

$$\frac{1}{h} = \frac{1}{h_1} + \frac{1}{h_2} \tag{2.19}$$

This is clearly generalizable to the general case with N bodies using a simple sum.

§ 2.4 Ideal Gases

§§ 2.4.1 Hydrostatic Systems

As we know from what we wrote before, for a hydrostatic system we have

$$\text{đ}Q = \mathrm{d}U + p\mathrm{d}V \tag{2.20}$$

Chosen two thermodynamic coordinates, specifically T, V for ease, we have

$$\text{đ}Q = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \tag{2.21}$$

This is the differential first law for hydrostatic systems.
From this equation we have a new definition for the specific heat C of a system.
Considering an isochoric process ($V = const$) we have, after deriving with respect to T

$$\left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \tag{2.22}$$

I.e., the derivative of the internal energy function at constant volume is the heat capacity at constant volume.
It's then possible to write, at constant pressure

$$\left(\frac{\text{đ}Q}{\mathrm{d}T}\right)_p = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p = C_p \tag{2.23}$$

Remembering that $\partial_T V = \beta V$ we have, solving for the derivative of the internal energy

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{\beta V} - p \tag{2.24}$$

§§ 2.4.2 Joule Expansions

Consider a thermally insulated vessel divided in two compartments with an ideal gas inside in one and the vacuum on the other compartment. If we remove the wall separating the gas from the vacuum the gas will rush to fill the vacuum. This kind of expansion is known as a *Joule expansion* or a *free expansion* of the gas.
Since the vessel doesn't change volume during the expansion of the gas and cannot exchange heat with its surroundings, the complete process must have $W = Q = 0$. If we insert this into the differential form of the 1st law of thermodynamics we have

$$\mathrm{d}U = \text{đ}Q - \text{đ}W = 0 \Longrightarrow U = U_0 \tag{2.25}$$

In general tho, the internal energy is a function of two variables, thus

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V = 0$$

Since for having $đQ = 0$ we must also have $\mathrm{d}T = 0$, we must have that $\partial_V U = 0$ and thus the internal energy must be dependent only on temperature. For a *free expansion* we must then have

$$\mathrm{d}U = \frac{\mathrm{d}U}{\mathrm{d}T}\mathrm{d}T \tag{2.26}$$

it has been studied by Rossini and Frandsen, that for real gases the internal energy depends also on the pressure, and therefore we now have an idea on how to define *ideal* gases

§§ 2.4.3 Thermodynamics of Ideal Gases

The previous experiment gives a framework to better define an ideal gas. In general an ideal gas is defined as a gas which, *at the low pressure limit*, follows these two equations

$$\begin{cases} pV = nRT \\ \left(\frac{\partial U}{\partial p}\right)_T = 0 \end{cases} \tag{2.27}$$

The second equation, together with the ideal gas equation of state, creates this ideal gas that when it expands, the internal energy behaves exactly like if it was a free expansion.
In fact, it's easy to prove that since

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = 0 \tag{2.28}$$

Then, by definition

$$\mathrm{d}U = \frac{\mathrm{d}U}{\mathrm{d}T}\mathrm{d}T \tag{2.29}$$

I.e. It depends only on temperature. Now from the first law we have

$$\begin{cases} đQ = \mathrm{d}U + đW \\ đW = p\mathrm{d}V \\ \mathrm{d}U = \frac{\mathrm{d}U}{\mathrm{d}T}\mathrm{d}T \end{cases} \tag{2.30}$$

Noting that in an isochoric process $\mathrm{d}U = C_V\mathrm{d}T$, then we have the first law for ideal gases

$$\boxed{đQ = C_V\mathrm{d}T + p\mathrm{d}V} \tag{2.31}$$

Remembering that for every equilibrium state we have

$$pV = nRT$$

We can write

$$p\mathrm{d}V = \mathrm{d}\left(pV\right) - V\mathrm{d}p = nR\mathrm{d}T - V\mathrm{d}p$$

Hence

$$\boxed{đQ = \left(C_V + nR\right)\mathrm{d}T - V\mathrm{d}p} \tag{2.32}$$

Deriving with respect to T again, we have a mathematical relationship between C_V and C_p, known as «*Mayer's relation*»

$$C_p = C_V + nR \tag{2.33}$$

Thus, we get two ways of writing the first law for ideal gases

$$\boxed{\begin{aligned} đQ &= C_V \mathrm{d}T + p\mathrm{d}V \\ đQ &= C_p \mathrm{d}T - V\mathrm{d}p \end{aligned}} \tag{2.34}$$

Note that *in general*, the heat capacity depends strongly on the temperature T. This relationship will be better studied with statistical mechanics later.

§§§ 2.4.3.1 Quasi-static Adiabatic and Polytropic Processes

Let's consider now quasi-static adiabatic processes, in the specific case of ideal gases. From the first law, we have that for an adiabatic process

$$\begin{cases} p\mathrm{d}V = -C_V \mathrm{d}T \\ V\mathrm{d}p = C_p \mathrm{d}T \end{cases} \tag{2.35}$$

we can solve the system quite easily by dividing the two equations, and after defining the «*adiabatic index*» of a gas γ as

$$\gamma = \frac{C_p}{C_V} = \frac{c_p}{c_V} \tag{2.36}$$

we have

$$\frac{V}{p}\frac{\mathrm{d}p}{\mathrm{d}V} = -\gamma \tag{2.37}$$

Solving this simple differential equation we get

$$pV^\gamma = \kappa \tag{2.38}$$

Where $\kappa \in \mathbb{R}$ is a constant. Note that this relationship holds if and only if the process is quasi-static.
We might want to see the functional definition of work in this process.
We have, for a quasi-static adiabatic transformation between two equilibrium points A and B

$$W_{AB} = \int_A^B \kappa V^{-\gamma} \mathrm{d}V = \frac{\kappa}{1-\gamma}\left(V_B^{1-\gamma} - V_A^{1-\gamma}\right) \tag{2.39}$$

Since $\kappa = p_A V_A^\gamma = p_B V_B^\gamma$, we have

$$W_{AB} = \frac{1}{1-\gamma}\left(p_B V_B - p_A V_A\right) = \frac{nR}{1-\gamma}\left(T_B - T_A\right) \tag{2.40}$$

Recognizing from the first law that since $đQ = 0$, then

$$đW = -\mathrm{d}U = -C_V \mathrm{d}T$$

Which gives back a new form of Mayer's relation

$$C_V = \frac{nR}{1-\gamma} \tag{2.41}$$

Let's consider now the most generic quasi-static transformation that we might have with an ideal gas. The transformation equation must be a tweak of the one we found before, specifically, instead of having pV^γ with γ being the adiabatic index, we might use a parameter α which can take different values.
Thus

$$pV^\alpha = \kappa \qquad \begin{cases} \alpha = 1 & pV = \kappa, \quad \kappa = nRT \\ \alpha = 0 & p = \kappa \\ \alpha \to \infty & V = \kappa \\ \alpha = \gamma & pV^\gamma = \kappa \\ \alpha \in \mathbb{R} & \text{general case} \end{cases} \tag{2.42}$$

Note that we have managed to define the most generic transformation possible. Note that since it's always true that, for an ideal gas

$$\mathrm{d}U = C_V \mathrm{d}T$$

And that in general $\oint Q \neq 0$, we have, noting that we simply substituted γ with the parameter α, that

$$\oint Q = \left(C_V + \frac{nR}{1-\alpha} \right) \mathrm{d}T \tag{2.43}$$

Defined the polytropic specific heat C_α, we have by definition

$$C_\alpha = C_V + \frac{nR}{1-\alpha} \tag{2.44}$$

Giving us this simple equation for polytropic processes

$$\oint Q = C_\alpha \mathrm{d}T \tag{2.45}$$

3 Thermal Engines and Entropy

§ 3.1 Engines

§§ 3.1.1 Heat-Work Conversion

From the first principle of thermodynamics it's easy to understand how work of *any* kind can be converted to heat and vice-versa.
Suppose that we have two heat reservoirs at temperatures $T_1 < T_2$. We might construct a cyclical process between these two sources, which we will call a «*thermodynamic cycle*». For any cycle we can define the following quantities

- The total amount of heat absorbed by the system $|Q_{abs}|$
- The total amount of heat rejected by the system $|Q_{rej}|$
- The total work done by the system $|W|$

From these quantities we can define the *thermal efficiency* of the cycle as

$$\eta = \left|\frac{W}{Q_{abs}}\right| \tag{3.1}$$

From the first law we have

$$\begin{aligned} \Delta U &= Q_T + W_T \\ Q_T &= |Q_{abs}| - |Q_{rej}| \\ W_T &= |W| \\ \eta &= \left|\frac{W}{Q_{abs}}\right| \end{aligned}$$

We immediately notice that the first equation must be equal to zero. In fact, $\mathrm{d}U$ is an exact differential, and therefore in *any* cyclic transformation it's equal to zero. Mathematically, we have

$$\oint_\gamma \mathrm{d}U = U\left(\gamma(A)\right) - U\left(\gamma(A)\right) = 0$$

Plugging in the second and the third equations into the first one, we must have

$$\begin{aligned} |W| &= |Q_{abs}| - |Q_{rej}| \\ \eta &= 1 - \left|\frac{Q_{rej}}{Q_{abs}}\right| \end{aligned} \tag{3.2}$$

It's clear now how a 100% conversion of heat into work makes little sense. In order to have $\eta = 1$ we must have $Q_{rej} = 0$, and we'll prove later that this *is not* possible.

§§ 3.1.2 Stirling Engine

We begin to try to harness, physically, the power of the first (and what will become the second) principle of thermodynamics by building *thermal engines*. There are two main kinds of engines:

- External combustion engines, when the heat sources are outside the system
- Internal combustion engines, when the system itself performs the combustion

The simplest engine, in terms of ease of construction, is the «*Stirling engine*». This engine is an external combustion engine which converts heat from fuel to mechanical work, through the usage of hot air. In a pV diagram, the cycle that the hot air makes is described by two isotherms, one at the combustion temperature T_H and one at a lower temperature T_L. The cycle is completed by two isochoric processes. The processes between the equilibrium points of the system are

- $A \to B$ Isothermal compression of the gas in contact with the low temperature reservoir at T_L, here the system rejects heat Q_{AB}
- $B \to C$ Isochoric heating of the gas. Here the gas heats up while in contact with the hot reservoir, absorbing heat Q_{BC}
- $C \to D$ Isothermal expansion of the gas in contact with the hot reservoir at T_H. The gas absorbs heat Q_{CD}
- $D \to A$ Isochoric cooling of the gas. Here the gas is in contact with the cold reservoir and rejects heat Q_{DA}

We have, by definition

$$\begin{aligned} |Q_H| &= |Q_{H1}| + |Q_{H2}| \\ |Q_L| &= |Q_{L1}| + |Q_{L2}| \end{aligned} \tag{3.3}$$

Quick spoiler: thanks to the first law of thermodynamics these heats are *explicitly calculable*. From the first principle we have that in the isochoric heating and cooling we must have $đW = 0$, $đQ = \mathrm{d}U$

$$đQ_{BC} = đQ_{DA} = C_V \mathrm{d}T$$

Thus, integrating on these two transformations we get

$$\begin{cases} Q_{BC} = C_V \left(T_H - T_L\right) \\ Q_{DA} = -C_V \left(T_H - T_L\right) \end{cases}$$

On the isothermal compression and expansion instead we have, from the first principle $\mathrm{d}U = 0$, and thus $đQ = p\mathrm{d}V$. Using the equation of state of ideal gases for writing the explicit functional relationship between p and V, we have

$$\begin{cases} Q_{CD} = nRT_H \displaystyle\int_C^D \frac{1}{V}\mathrm{d}V = nRT_H \log\left(\frac{V_D}{V_C}\right) \\ Q_{AB} = nRT_L \displaystyle\int_A^B \frac{1}{V}\mathrm{d}V = nRT_L \log\left(\frac{V_B}{V_A}\right) = -nRT_L \log\left(\frac{V_D}{V_C}\right) \end{cases} \tag{3.4}$$

After indicating the *volumetric compression ratio* r as

$$r=\frac{V_{max}}{V_{min}}=\frac{V_C}{V_B}=\frac{V_D}{V_A} \tag{3.5}$$

We have

$$\begin{cases} Q_{abs}=Q_{BC}+Q_{CD}=nc_V\left(T_H-T_L\right)+nRT_H\log\left(r\right) \\ Q_{rej}=Q_{DA}+Q_{AB}=-\left[nc_V\left(T_H-T_L\right)+nRT_L\log\left(r\right)\right] \end{cases} \tag{3.6}$$

Thus

$$\eta=1-\left|\frac{Q_{rej}}{Q_{abs}}\right|=1+\frac{Q_{rej}}{Q_{abs}}=1-\frac{nc_V\left(T_L-T_H\right)-nRT_L\log\left(r\right)}{nc_V\left(T_H-T_L\right)+nRT_H\log\left(r\right)} \tag{3.7}$$

Which, rearranging, becomes

$$\boxed{\eta_S=\frac{R\left(T_H-T_L\right)\log\left(r\right)}{c_V\left(T_H-T_L\right)+RT_H\log\left(r\right)}} \tag{3.8}$$

§§ 3.1.3 Internal Combustion Engines

§§§ 3.1.3.1 Otto Engine

The first internal combustion engine that we will treat is the *Otto engine*, commonly known as the *four-stroke* engine. The gas makes a cycle which might seem similar to the Stirling cycle, but this is quickly disproved by noting that the two isothermal processes are substituted by two adiabatic processes. Since during an adiabatic process $Q=0$, we must have that the heat absorbed and rejected by the system must come from the isochoric processes.
The heats in these two transformations are

$$\begin{cases} Q_{BC}=nc_V\left(T_C-T_B\right) \\ Q_{DA}=nc_V\left(T_A-T_D\right) \end{cases}$$

Using the equation of state and the adiabatic process equation, we have

$$\begin{cases} pV=nRT \\ pV^{\gamma}=\kappa \end{cases} \Longrightarrow TV^{\gamma-1}=\kappa \tag{3.9}$$

Thus

$$\begin{cases} T_CV_C^{\gamma-1}=T_DV_D^{\gamma-1} \\ T_AV_A^{\gamma-1}=T_BV_B^{\gamma-1} \end{cases} \Longrightarrow \begin{cases} \dfrac{T_C}{T_D}=\left(\dfrac{V_D}{V_C}\right)^{\gamma-1} \\ \dfrac{T_A}{T_B}=\left(\dfrac{V_B}{V_A}\right)^{\gamma-1}=\left(\dfrac{V_C}{V_D}\right)^{\gamma-1} \end{cases} \tag{3.10}$$

Indicated again the compression ratio

$$r=\frac{V_D}{V_C}$$

We get

$$\begin{cases} \dfrac{T_C}{T_D} = r^{\gamma - 1} \\ \dfrac{T_A}{T_B} = r^{1-\gamma} = \dfrac{T_D}{T_C} \end{cases} \tag{3.11}$$

Thus

$$\eta_O = 1 + \frac{Q_{DA}}{Q_{BC}} = 1 + \frac{T_A - T_D}{T_C - T_B} = 1 + \frac{T_B \frac{T_D}{T_C} - T_D}{T_C - \frac{T_C}{T_B} T_A}$$

After some algebra for rearranging the terms, we get

$$\eta_O = 1 + \frac{T_B}{T_A} \frac{\frac{T_D}{T_C} \left(1 - T_C\right)}{\frac{T_C}{T_D} \left(T_D - 1\right)} = 1 + \frac{T_D}{T_C} \frac{1 - T_C}{T_D - 1}$$

After again some algebra, we get for the Otto engine the following efficiency

$$\eta_O = 1 - \frac{1}{r^{\gamma - 1}} \tag{3.12}$$

§§§ 3.1.3.2 Diesel Engine

The Diesel engine is another example of internal combustion engine. It's also a four-stroke engine, but the cycle is different from the previous. We have

1. $A \to B$ The gas undergoes an adiabatic compression until combustion starts
2. $B \to C$ Isobaric expansion of the gas after combustion, the gas absorbs Q_{BC} from the hot reservoir
3. $C \to D$ Adiabatic expansion of the gas
4. $D \to A$ Isochoric cooling of the gas, the gas rejects Q_{DA} to the cold reservoir

The heats can be calculated immediately, and we have

$$\begin{cases} Q_{abs} = Q_{BC} = nc_p \left(T_C - T_B\right) \\ Q_{rej} = Q_{DA} = nc_V \left(T_A - T_D\right) \end{cases} \tag{3.13}$$

From the adiabatic compression and expansion we get similarly to the Otto engine

$$\begin{cases} T_A V_A^{\gamma - 1} = T_B V_B^{\gamma - 1} \\ T_C V_C^{\gamma - 1} = T_D V_D^{\gamma - 1} \end{cases} \Longrightarrow \begin{cases} \dfrac{T_A}{T_B} = \left(\dfrac{V_B}{V_A}\right)^{\gamma - 1} \\ \dfrac{T_C}{T_D} = \left(\dfrac{V_D}{V_C}\right)^{\gamma - 1} \end{cases}$$

For the efficiency we have, since the parts of the cycle where the gas absorbs and rejects heat are two and two only, we can write immediately

$$\eta_D = 1 + \frac{Q_{DA}}{Q_{BC}} = 1 - \frac{c_p \left(T_D - T_A\right)}{c_V \left(T_C - T_B\right)} \tag{3.14}$$

After defining the «*combustion ratio*» r_c and the compression ratio r defined as follows

$$\begin{cases} r_c = \dfrac{V_C}{V_B} \\ r = \dfrac{V_A}{V_B} \end{cases} \tag{3.15}$$

We have, after some tedious algebra

$$\eta_D = 1 - \frac{1}{r^{\gamma-1}}\left(\frac{r_c^{\gamma-1} - 1}{r_c - 1}\right) \tag{3.16}$$

§§§ 3.1.3.3 Brayton Engine

Another particular type of engine is the «*Brayton engine*», this engine cycle is used in turbojet engines and in turbines in general. This cycle is also particular and works with adiabatic and isobaric transformations as follows

1. $A \to B$ Adiabatic compression of the gas until the combustion point
2. $B \to C$ Isobaric expansion of the ignited gas, Q_{BC} gets absorbed from the hot reservoir
3. $C \to D$ Adiabatic expansion of the gas
4. $D \to A$ Isobaric compression of the gas, Q_{DA} gets rejected to the cold reservoir

As before, it's straightforward to calculate the rejected and absorbed heat, and we have

$$\begin{cases} Q_{abs} = Q_{BC} = nc_p\left(T_C - T_B\right) \\ Q_{rej} = Q_{DA} = -nc_p\left(T_D - T_A\right) \end{cases} \tag{3.17}$$

Without calculating for the temperature coordinates, since the calculation is similar to the previous one, after defining the «*pressure compression ratio*» r_p as

$$r_p = \frac{p_C}{p_B} \tag{3.18}$$

We get for the efficiency of the Brayton cycle

$$\eta_B = 1 - \frac{1}{r_p^{\frac{\gamma-1}{\gamma}}} \tag{3.19}$$

§§ 3.1.4 Carnot Engine

The most important, and the simplest engine is the one created by *Sadi Carnot*. This cycle is composed by four transformations between two heat reservoirs at temperatures $T_H > T_L$. The cycle goes as follows

1. $A \to B$ The gas undergoes an isothermal expansion in contact with the hot reservoir at T_H, absorbs Q_{AB}
2. $B \to C$ Adiabatic expansion of the gas
3. $C \to D$ Isothermal compression of the gas in contact with the cold reservoir at T_L, rejects Q_{CD}
4. $D \to A$ Adiabatic expansion of the gas

We have, by definition, that the rejected and absorbed heats are

$$\begin{cases} Q_{abs} = Q_{AB} = nRT_H \int_A^B \frac{1}{V}\mathrm{d}V = nRT_H \log\left(\frac{V_B}{V_A}\right) \\ Q_{rej} = Q_{CD} = nRT_L \int_C^D \frac{1}{V}\mathrm{d}V = -nRT_L \log\left(\frac{V_D}{V_C}\right) \end{cases} \tag{3.20}$$

From the two adiabatic processes we get

$$\begin{cases} T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1} \\ T_L V_D^{\gamma-1} = T_H V_A^{\gamma-1} \end{cases} \Longrightarrow \frac{T_L}{T_H} = \left(\frac{V_A}{V_D}\right)^{\gamma-1} = \left(\frac{V_B}{V_C}\right)^{\gamma-1} \tag{3.21}$$

Defined the compression ratio

$$r = \frac{V_A}{V_B} = \frac{V_D}{V_C}$$

We have, for the efficiency of the Carnot cycle

$$\eta_C = 1 + \frac{T_L \log\left(\frac{V_D}{V_C}\right)}{T_H \log\left(\frac{V_B}{V_A}\right)} = 1 + \frac{T_L}{T_H}\frac{\log(r)}{\log\left(\frac{1}{r}\right)} = 1 - \frac{T_L}{T_H} \tag{3.22}$$

The fact that the efficiency of an ideal Carnot cycle depends *only* on the temperature of the two reservoirs is an extremely important condition that we will derive after defining irreversibility and the second law of thermodynamics.

§ 3.2 Second Law of Thermodynamics

The second law of thermodynamics can now be derived from empirical facts. The experience of scientists with engines and work-heat conversion made sure that some fundamental conditions could be written down.
The first one is the so called *Clausius statement of the second law of thermodynamics*

THEOREM 3.1 (Clausius Statement). *It's not possible to transfer heat from a cold reservoir to a hot reservoir without introducing work in the system, i.e. it's not possible to build a refrigerator which transfers heat without work*

Another statement, which was a more *operative* statement, was written down by Kelvin and Planck

THEOREM 3.2 (Kelvin-Planck Statement). *It's not possible to build a thermal engine for which* $W = Q$*, i.e. it's not possible to build a machine which converts heat from a hot source to work without rejecting heat to a cold source*

These statements are equivalent, and it's demonstrable as follows

Proof. Suppose that the Clausius refrigerator exists, then we will have that if there's a cold source at T_1 and a hot source at T_2, this engine will extract Q_2 from the cold source and reject Q_2 to the hot source. Suppose that now we connect in parallel another machine which extracts Q_1 from the hot source at T_1 and rejects Q_2 to the cold source at T_2. Calculating the total heat transfer from the two heat reservoirs we will have

$$\begin{cases} Q_H = Q_2 - Q_1 \\ Q_L = Q_2 - Q_2 = 0 \end{cases} \tag{3.23}$$

These two connected machines complete a thermodynamic cycle, thus we will have

$$W = Q_2 - Q_1, \qquad Q_L = 0$$

But, this machine is exactly a Kelvin-Planck machine, since it's converting 100% of the heat taken form the hot source into work, without rejecting heat to the cold source.
Let's work the other way around and suppose that a Kelvin-Planck machine exists. This machine will take Q_1 from a hot source at T_1 and converts it all into work. Suppose that we connect in parallel a refrigerator, which takes Q_2 from the cold source at T_2 and with the work of the KP machine rejects $Q_1 + Q_2$ to the hot source.
If we again check the total heat transfer between the reservoirs we have that

$$\begin{cases} Q_H = (Q_1 + Q_2) - Q_1 = Q_2 \\ Q_L = -Q_2 \end{cases} \tag{3.24}$$

Thus, the two connected machines behave like a Clausius refrigerator, taking Q_2 from a hot source and rejecting Q_2 to the hot source, without any work.

□

It's clear that these two statements are therefore equal, even if they look different. These statements are what's called the «*second law of thermodynamics*», which can be summarized in

- Heat flow from a cold to a hot source is possible *if and only if* work is done on the system
- Spontaneous heat flow can happen only from a hot source to a cold one
- It's impossible to have a machine with 100% efficiency

§§ 3.2.1 Reversibility and Irreversibility

From the second law of thermodynamics it's clear that *not all processes are equal*, and especially *not all processes are reversible*. Irreversibility is a fundamental part of nature, and it can be divided into two main kinds of irreversibility:

- External irreversibility

- Internal irreversibility

In order to understand what irreversibility really is, we need to define *reversibility*

Definition 3.2.1 (Reversible Process). Consider a process from a state A to a state B. If during this process Q heat is transferred and W heat is transferred, it's said to be «*reversible*» if and only if going back from B to A $-Q$ heat gets transferred and $-W$ work is done

Consider now some isothermal mechanical transformations, like the irregular stirring of a viscous fluid or the inelastic deformation of a solid in contact with a heat reservoir. For a complete restoration to the initial state we must have that Q heat must be extracted from the reservoir and completely transformed into work, which is a violation of the Kelvin-Planck statement.
If the same process is made in a thermally insulated container, there must be a rise in temperature T, thus $\Delta U \neq 0$. In the backwards process we will have $Q = \Delta U$ which is completely converted into work, again violating Kelvin-Planck, therefore, all processes exhibiting dissipative effects are *irreversible* and work gets dissipated into internal energy. These are examples of «*external mechanical irreversibility*».
If we have a process that transforms internal energy into mechanical energy and then again into internal energy, like a free expansion or the snapping of a stretched wire, we're looking at a case of «*internal irreversibility*». Take the free or Joule expansion. There will be a change of state from $A = (V_i, T)$ to $B = (V_f, T)$. For a complete restoration of the system till the first state we must have an isothermal compression till the volume V_i, where there is no friction, hence the transformation is quasi-static and work is made from an external machine.
Since $W < 0$, we have $Q < 0$ and therefore $Q = -W$, which is again a violation of Kelvin-Planck, making this process irreversible.
Consider now instead a finite transfer of heat between a system and a reservoir, with temperature difference ΔT. Suppose that we have conduction from the system to the reservoir if $T_r < T_s$. In order to have a reversible process, for transferring heat back to the system from the reservoir we must have a self-acting device between the two temperatures, i.e. a Clausius refrigerator, violating the second law. This is known as a process exhibiting *external thermal irreversibility*.
The same can be said with chemical process. We have that all chemical reactions which involve a change of structure *must* be irreversible. More generally, all spontaneous natural processes are irreversible.
In general we can define again reversibility as

Definition 3.2.2 (Reversible Process). A process is said to be «*reversible*» if and only if thermodynamic equilibrium conditions are satisfied and there are no dissipative phenomena, i.e.

1. It's a quasi static process
2. There is no energy dissipation

Therefore, it's an *ideal* process.

§§ 3.2.2 Carnot Theorem and Absolute Temperature

One of the main consequences of the second law of thermodynamics is what's known as the «*Carnot theorem*»

THEOREM 3.3 (Carnot). *No heat engine can have an efficiency higher than its Carnot equivalent*

Proof. Given an engine working between two reservoirs at temperatures $T_H > T_L$, we define the *Carnot equivalent engine* as the engine with the same efficiency as the Carnot machine

$$\eta_C = 1 - \frac{T_L}{T_H} = \left|\frac{W}{Q_H}\right|$$

The Carnot engine will hence absorb Q_H from the hot reservoir, perform work $|W|$ and reject $|Q_C| = |Q_H| - |W|$ to the cold reservoir.
Consider now a second engine which performs the same amount of work, but absorbs $|Q'_H|$ from the hot reservoir and rejects $|Q_C| = |W| - |Q'_H|$ heat to the cold reservoir

$$\eta = \left|\frac{W}{Q'_H}\right|$$

I.e. it will absorb Q'_H from the same hot reservoir.
Let's assume that $\eta > \eta_C$, thus

$$\left|\frac{W}{Q'_H}\right| > \left|\frac{W}{Q_H}\right| \Longrightarrow |Q_H| > |Q'_H|$$

Now suppose that we reverse the Carnot engine and take in the work $|W|$ produced by the second machine. We will have that the total rejected heat to the cold source will be

$$Q_{rej} = (|Q_H| - |W|) - (|Q'_H| - |W|) = |Q_H| - |Q'_H|$$

Since in order to have $\eta > \eta_C$ we must have $|Q_H| > |Q'_H|$ we have that $Q_{rej} > 0$, and the complete machine is a Clausius refrigerator which transfers $|Q_H| - |Q'_H|$ from a cold to a hot reservoir without performing work, therefore in order to have the second law of thermodynamics hold we also must have, for *any* machine

$$\eta \leq \eta_C \tag{3.25}$$

□

Corollary 3.2.1 (Equality of Carnot Efficiencies). All Carnot engines, working between two reservoirs, have the same efficiency η.

Proof. Suppose that we have two Carnot engines with η_1 being the efficiency of the first and η_2 being the efficiency of the second.
Suppose that the engine 1 is driving the engine 2 backwards. Thus

$$\eta_1 \leq \eta_2$$

If we reverse both engines, we will then have engine 2 driving engine 1 backwards, i.e.

$$\eta_2 \leq \eta_1$$

Therefore, since the reservoirs are the same, the only way to support both statements is that

$$\eta_1 = \eta_2 \tag{3.26}$$

□

This theorem and its corollary are *fundamental* for defining an *absolute temperature scale*, also known as the *thermodynamic temperature*. We have proven that due to the second law of thermodynamics

1. All (reversible) Carnot engines working between two reservoirs are *equal*
2. The efficiency of any Carnot machine working between $T_2 < T_1$ is *always*

$$\eta_{12} = 1 - \frac{T_2}{T_1}$$

From the definition of efficiency itself, we also have

$$\eta = 1 - \left|\frac{Q_2}{Q_1}\right| \propto \varphi\left(T_1, T_2\right)$$

With $\varphi(T_1, T_2)$ being a random, smooth enough function of the temperatures of the two reservoirs. Solving for the heats we have

$$\left|\frac{Q_1}{Q_2}\right| = \frac{1}{1 - \varphi\left(T_1, T_2\right)} = f\left(T_1, T_2\right)$$

Where f is another smooth enough, random, function of the temperatures only. We have therefore found that heat (as we thought before) depends only on temperature.
In order to better determine the functional shape of f, we take three temperatures $T_1 > T_2 > T_3$ and plug three Carnot machines working between them, then

$$\left|\frac{Q_1}{Q_2}\right| = f\left(T_1, T_2\right)$$
$$\left|\frac{Q_1}{Q_3}\right| = f\left(T_1, T_3\right)$$
$$\left|\frac{Q_3}{Q_2}\right| = f\left(T_3, T_2\right)$$

From the second and the third equation it's then possible to see that

$$\left|\frac{Q_1}{Q_2}\right| = f\left(T_1, T_2\right) = \frac{f\left(T_1, T_3\right)}{f\left(T_2, T_3\right)} = \frac{\psi\left(T_1\right)}{\psi\left(T_2\right)} = \frac{T_1}{T_2} \tag{3.27}$$

Note how the constraint on f imposes that it must be a different function of a single variable, which, for the pleasure of everyone can just be taken to be the *absolute* temperature of the reservoir.
This temperature can be calculate to give, at the triple point of water, the already well known value of

$$T_{TP} = 273.16 \text{ K} \tag{3.28}$$

The units there are the usual Kelvins of thermodynamics.

§§ 3.2.3 Entropy

All the previous statements, albeit bulky in words, can be "shortened" mathematically with the introduction of a new quantity, known as the (thermodynamic) «*entropy function*». Suppose again that we have a generic engine with efficiency η_G working between two reservoirs at *absolute* temperatures $T_C < T_H$.
Due to Clausius' theorem we will have

$$\eta_G = 1 + \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H} = \eta_C$$

With η_C being the efficiency of a Clausius engine working between the same two reservoirs.
Rearranging, we will get

$$\frac{Q_L}{T_L} + \frac{Q_H}{T_H} \leq 0 \tag{3.29}$$

And, imagining the presence of infinite reservoirs between the two temperatures, we can generalize everything to an integral

$$\int_C^H \frac{\text{đ}Q}{T} = S_H - S_C \leq 0 \tag{3.30}$$

Thanks to the fundamental theorem of calculus we have defined a primitive function S, known as *entropy*.
By definition, then, the absolute temperature becomes an «*integrating factor*» for the inexact differential $\text{đ}Q$, as was the pressure the integrating factor for work.
We thus have

$$\text{đ}Q = T\mathrm{d}S \tag{3.31}$$

Suppose now that we have two generic equilibrium states A and B. If we perform a reversible transformation from A to B and vice versa we will have

$$\oint \mathrm{d}S = \int_A^B \frac{\text{đ}Q}{T} - \int_A^B \frac{\text{đ}Q}{T} = 0 \tag{3.32}$$

I.e., in a *reversible* cycle the total entropy will always be equal to zero. The equality is clear, since we have *defined* the cycle reversible, i.e., from (3.29) considering the two points we have chosen and the reversibility of the transformation, we must choose the equality instead of them being less than 0.
It's important to note that the equality holds *if and only if* the process in study is *reversible*. It does not hold for irreversible processes, albeit it's still possible to define an entropy function even in that case.
Consider now this special case, where the process A to B is irreversible, while the process B to A is reversible.
We will have in the full cycle

$$\oint \frac{\text{đ}Q}{T} = \int_A^B \frac{\text{đ}Q}{T} - \int_A^B \mathrm{d}S < 0$$

Where we used the equality (3.2.3) in the reversible part. Indicating the result of that integral simply as ΔS, we will have that, thanks to the generality of the irreversible path chosen between A and B, that *entropy increases in irreversible paths*

$$\Delta S > \int \frac{\text{đ}Q}{T} > 0 \tag{3.33}$$

All statements can be simply written in a single equation as

$$\Delta S \geq \int \frac{đQ}{T} \tag{3.34}$$

Consider now the two separate processes that the system performs and the surrounding environment performs. Said ΔS_{surr} as the entropy variation of the surroundings and ΔS_{sys} the one of the system, thanks to the definition of system and surroundings we can define the entropy variation of the universe, ΔS_{Ω}, and therefore

$$\boxed{\Delta S_{\Omega} = \Delta S_{surr} + \Delta S_{sys} \geq 0} \tag{3.35}$$

For irreversible transformations, this reduces to the *principle of increase of the entropy of the universe*. This is the mathematical formulation of the second law of thermodynamics.

With these definitions we can rewrite the first law of thermodynamics in a way that includes the second law. Imposing (3.2.3) we get

$$\boxed{\mathrm{d}U = T\mathrm{d}S - đW} \tag{3.36}$$

Which, considering only ideal gases and thermodynamic work, becomes

$$\boxed{\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V} \tag{3.37}$$

It's clear that then, the "natural" variables of internal energy are entropy and volume

$$U_{nat} = U(S, V)$$

§§§ 3.2.3.1 TS Diagrams

The definition of entropy as a state variable lets us design a new kind of thermodynamic diagram, known as the «*T-S diagram*».

For the definition of the functional relations that get drawn on this diagram, for an ideal gas, we can calculate the generic functional dependency of entropy with respect to pressure, volume and temperature.

Rewriting the relationship (3.37) in terms of entropy, we have

$$T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V$$

Which can directly be integrated after taking into account the equation of state $pV = nRT$ and $\mathrm{d}U = nc_V\mathrm{d}T$.

$$\Delta S(T, V) = nc_V \int_A^B \frac{1}{T}\mathrm{d}T + nR\int_A^B \frac{1}{V}\mathrm{d}V = nc_V \log\left(\frac{T_B}{T_A}\right) + nR\log\left(\frac{V_B}{V_A}\right)$$

In terms of the other two combinations of state variables, we have after algebraic manipulation of the differentials, remembering that:

$$\begin{cases} p\mathrm{d}V = \mathrm{d}\left(pV\right) - V\mathrm{d}p \\ \mathrm{d}\left(pV\right) = nR\mathrm{d}T \end{cases}$$

We have that entropy can be rewritten as follows

$$T\mathrm{d}S = n\left(c_V + R\right)\mathrm{d}T - V\mathrm{d}p = nc_p\mathrm{d}T - V\mathrm{d}p$$

Or, also, noting that

$$T = \frac{pV}{nR} \Longrightarrow \mathrm{d}T = \frac{1}{nR}\left(p\mathrm{d}V + V\mathrm{d}p\right)$$

Entropy can be rewritten again as

$$\mathrm{d}S = \frac{nc_V}{p}\mathrm{d}p + \frac{nc_p}{V}\mathrm{d}V$$

The integration of the previous differential forms are trivial. One thing to note is that in the case of an adiabatic and reversible transformation (isoentropic), we will have *by definition*

$$\mathrm{d}S = 0$$

for the second law of thermodynamics, is important to remember that when the process is *irreversible* the previous equation does not hold anymore, since $\mathrm{d}S \neq đQ$ at that point, and we will have

$$\mathrm{d}S > 0$$

4 Thermodynamic Potentials

§ 4.1 Maxwell Relations

By looking at the differential relationship that includes the second and the first law of thermodynamics, if we count that the thermodynamic variables (p, V, T) are deeply tied by the equation of state, we might imagine to construct new exact differentials using *Legendre transforms*.

Definition 4.1.1 (Legendre Transform). Given a smooth enough scalar field $f : \mathbb{R}^n \to \mathbb{R}$, which satisfies the equation (without loss of generality $n = 2$)

$$\mathrm{d}f = u\mathrm{d}x + v\mathrm{d}y$$

Can be «*Legendre-transformed*» into a new function $g(u, y)$, called the «*characteristic function*», which satisfies

$$\mathrm{d}g = -x\mathrm{d}u + v\mathrm{d}y$$

The transformation can be obtained from the differentials themselves noting that:

$$u\mathrm{d}x = \mathrm{d}\left(ux\right) - x\mathrm{d}u$$

We have then

$$\mathrm{d}g = u\mathrm{d}x + v\mathrm{d}y - \mathrm{d}\left(ux\right)$$

I.e.

$$\mathrm{d}g = \mathrm{d}f - \mathrm{d}\left(ux\right) \Longrightarrow g = f - ux \tag{4.1}$$

An example of Legendre transforms in physics is given by the derivation of the Hamiltonian function from the Lagrangian of a system

The reduction to two variables immediately jumps to eye as something already seen before in thermodynamics. We can therefore think to define *multiple* characteristic functions for describing thermodynamic systems.
We begin from the internal energy. We know that U has natural variables (S, V), thus its use is convenient only when dealing with changes in volume and entropy.
We might want to define a new characteristic function in terms of pressure and entropy via a Legendre transform. This function is known as «*enthalpy*».

Definition 4.1.2 (Enthalpy). Given the internal energy of a system as

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

We can define the *enthalpy* H as the Legendre transform of U with respect to p, thus

$$\mathrm{d}H = \mathrm{d}U + \mathrm{d}\left(pV\right) = T\mathrm{d}S + V\mathrm{d}p \tag{4.2}$$

Another convenient characteristic function is given by the Legendre transform of U with respect to T, known as the *free energy*, or the *Helmholtz free energy*

Definition 4.1.3 (Helmholtz Free Energy). Given the internal energy of a system, we define the *Helmholtz free energy* F as the Legendre transform of the internal energy with respect to temperature

$$\mathrm{d}F = \mathrm{d}U - \mathrm{d}\left(TS\right) = -S\mathrm{d}T - p\mathrm{d}V \tag{4.3}$$

The same approach can be repeated with enthalpy, obtaining the *Gibbs free energy*

Definition 4.1.4 (Gibbs Free Energy). Given the enthalpy function, if we apply a Legendre transform with respect to the temperature T, we get the *Gibbs Free Energy* G as

$$\mathrm{d}G = \mathrm{d}H - \mathrm{d}\left(TS\right) = -S\mathrm{d}T + V\mathrm{d}p \tag{4.4}$$

All these potentials are deeply tied, and one can be recovered from another one through sequences of Legendre transforms, with respect to temperature, pressure, entropy and volume.
In general, explicitly writing the natural variables of each potential, we can put them all together in a system

$$\begin{cases} \mathrm{d}U\left(S,V\right) = T\mathrm{d}S - p\mathrm{d}V \\ \mathrm{d}H\left(S,p\right) = T\mathrm{d}S + V\mathrm{d}p \\ \mathrm{d}F\left(T,p\right) = -S\mathrm{d}T - p\mathrm{d}V \\ \mathrm{d}G\left(T,V\right) = -S\mathrm{d}T + V\mathrm{d}p \end{cases} \tag{4.5}$$

Being potentials also includes the fact that these are all *exact differentials*, which we remember in the following definition.

Definition 4.1.5 (Exact Differential). Given a differential form ω, defined as

$$\omega = A(x,y)\mathrm{d}x + B\left(x,y\right)\mathrm{d}y$$

It's said to be «*closed*» if and only if $\mathrm{d}\omega = 0$, where

$$\mathrm{d}\omega = \left(\frac{\partial A}{\partial y} - \frac{\partial B}{\partial y}\right)\mathrm{d}x\mathrm{d}y = 0$$

It's «*exact*» if and only if exists a potential function $f \in C^2$ such that

$$\mathrm{d}f = \omega \Longrightarrow \begin{cases} \dfrac{\partial f}{\partial x} = A(x,y) \\ \dfrac{\partial f}{\partial y} = B(x,y) \end{cases}$$

An exact differential form is necessarily closed, since $\mathrm{d}\omega = \mathrm{d}^2 f = 0$ by definition of the differential operator.
Note that then, also

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial A}{\partial y} = \frac{\partial B}{\partial x} = \frac{\partial^2 f}{\partial y \partial x}$$

Thanks to Schwartz's theorem for C^2 functions, we know already that the two mixed derivatives are necessarily equal.

The previous statements lets us find what are known as the *Maxwell relations* between the thermodynamic variables. We have

$$\begin{cases} \mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \Longrightarrow \left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial p}{\partial S}\right)_V \\ \mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p \Longrightarrow \left(\dfrac{\partial T}{\partial p}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_p \\ \mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V \Longrightarrow \left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_V \\ \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p \Longrightarrow \left(\dfrac{\partial S}{\partial p}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_p \end{cases} \tag{4.6}$$

Also:

$$\begin{cases} p = -\left(\dfrac{\partial U}{\partial V}\right)_S = \left(\dfrac{\partial F}{\partial V}\right)_T \\ V = \left(\dfrac{\partial H}{\partial p}\right)_S = \left(\dfrac{\partial G}{\partial p}\right)_T \\ T = \left(\dfrac{\partial U}{\partial S}\right)_V = \left(\dfrac{\partial H}{\partial S}\right)_p \\ S = -\left(\dfrac{\partial F}{\partial T}\right)_V = \left(\dfrac{\partial G}{\partial T}\right)_p \end{cases} \tag{4.7}$$

§§ 4.1.1 $T\mathrm{d}S$ Equations

The previous findings help us find new constitutive equations for entropy, called the $T\mathrm{d}S$ equations. From the internal energy we have that

$$\mathrm{d}S = \frac{1}{T}\left(\mathrm{d}U + p\mathrm{d}V\right) \tag{4.8}$$

Which implies that the natural variables of entropy are volume and temperature. Thus

$$T\mathrm{d}S = T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + T\left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V = đQ$$

By definition and the application of the third Maxwell relation, we get

$$\begin{cases} T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{đQ}{\mathrm{d}T}\right) = C_V \\ \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \end{cases}$$

All combined into the previous equation, we get the *first $T\mathrm{d}S$ equation.*

$$\boxed{T\mathrm{d}S = C_V \mathrm{d}T + T\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V} \tag{4.9}$$

If we repeat the same process that we had done in (4.8), but instead we use the enthalpy, we have

$$\mathrm{d}S = \frac{1}{T}\left(\mathrm{d}H - V\mathrm{d}p\right) \tag{4.10}$$

Thus the natural variables become T, p and we have

$$T\mathrm{d}S = T\left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + T\left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p = đQ$$

And therefore, by definition of specific heat and using the fourth Maxwell relation, we have

$$\begin{cases} T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{đQ}{\mathrm{d}T}\right)_p = C_p \\ \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \end{cases}$$

Which, combined give the *second $T\mathrm{d}S$ equation*

$$\boxed{T\mathrm{d}S = C_p \mathrm{d}T - T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p} \tag{4.11}$$

A third can be obtained by writing S as a function of (p, V), giving us

$$T\mathrm{d}S = T\left(\frac{\partial S}{\partial p}\right)_V \mathrm{d}p + T\left(\frac{\partial S}{\partial V}\right) \mathrm{d}V = đQ$$

Considering (reversible) isobaric and isochoric processes we have

$$\begin{cases} T\left(\frac{\partial S}{\partial V}\right)_p \left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{đQ}{\mathrm{d}T}\right)_p = C_p \\ T\left(\frac{\partial S}{\partial p}\right)_V \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{đQ}{\mathrm{d}T}\right)_V = C_V \end{cases}$$

Resulting in the *third $T\mathrm{d}S$ equation*

$$\boxed{T\mathrm{d}S = C_V\left(\frac{\partial T}{\partial p}\right)_V \mathrm{d}p + C_p\left(\frac{\partial T}{\partial V}\right)_p \mathrm{d}V} \tag{4.12}$$

§§ 4.1.2 Internal Energy Equations

Following the same idea we had previously, we can write a set of equations for the internal energy. We have in general that for a hydrostatic system

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

If we derive with respect to the volume V we have

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

Using the third Maxwell relation we have the *first internal energy equation*

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p} \tag{4.13}$$

Deriving with respect to pressure we get instead

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

Using the fourth Maxwell relation we immediately get the *second internal energy equation*

$$\boxed{\left(\frac{\partial U}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T} \tag{4.14}$$

§§ 4.1.3 Heat Capacity Equations

From the $T\mathrm{d}S$ equations it's possible to find two new equations with respect to the heat capacities of the gas. Equating the first two $T\mathrm{d}S$ equations we have

$$C_p\mathrm{d}T - T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p = C_V\mathrm{d}T + T\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V$$

This implies that

$$\left(C_p - C_V\right)\mathrm{d}T = T\left[\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}p + \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}V\right]$$

Thanks to the equation of state we can see T as a function of (p, V), and by solving the previous equatoin with respect to $\mathrm{d}T$ and expressing explicitly the differential we have

$$\begin{cases} \left(\frac{\partial T}{\partial p}\right)_V = \frac{T}{C_p - C_V}\left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial T}{\partial V}\right)_p = \frac{T}{C_p - C_V}\left(\frac{\partial V}{\partial T}\right)_p \end{cases}$$

Solving and noting that, thanks to the implicit variable theorem we have

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

We get the first of the two *heat capacity equations*

$$\boxed{C_p - C_V} = T\left(\frac{\partial V}{\partial T}\right)_p^2\left(\frac{\partial p}{\partial V}\right) \tag{4.15}$$

From the $T\mathrm{d}S$ equation we also get that in an isoentropic process, (i.e. they're both zero) we must have

$$\begin{cases} C_p\mathrm{d}T = T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p \\ C_V\mathrm{d}T = -T\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V \end{cases}$$

Solving for $\gamma = C_p/C_V$ we have

$$\gamma = -\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_S$$

Which, rearranged gives the *second heat capacity equation*

$$\boxed{\gamma = -\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial V}\right)_S} \tag{4.16}$$

§ 4.2 Real Gases

§§ 4.2.1 Van der Waals Equation

So far we have treated only *ideal* gases, in the low pressure limit and without interaction between the particles, which are considered point-like.

This clearly isn't enough to describe real gases, which have interactions between themselves and are not point-like. A solution was devised by *Johannes Diderik van der Waals*, which in his studies he started from the Lennard-Jones potential to describe molecular interactions and build from there an

equation of state for real gases.
The Lennard Jones potential is found empirically as

$$U_{LJ}(r) = U_0 \left[\alpha_1 \left(\frac{1}{r} \right)^{12} - \alpha_2 \left(\frac{1}{r} \right)^{6} \right] \tag{4.17}$$

With α_1 and α_2 as parameters which depend on the gas. It's possible to build from it two parameters, a, b known as the *Van der Waals parameters* in order to apply corrections to pressure and volume.
We begin by considering molecules as hard spherical shells, which occupy some volume V_0, thus, for n moles of this gas, we can apply a correction to the volume of the gas as

$$V_R = (V - nb) \tag{4.18}$$

And, considering the attractive forces between molecules, we can also find a correction for pressure, which will be higher at the center of the gas

$$p_R = p + a \left(\frac{n}{V} \right)^2 \tag{4.19}$$

Inserting it into the equation of state, we have

$$p_R V_R = \left[p + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT \tag{4.20}$$

Which is the *Van der Waals equation of state*, useful for describing the thermodynamic behavior of real gases. This equation has also critical points (saddles) for pressure and volume. After doing some optimization calculus on $p(V)$ we find

$$\begin{cases} p_C = \dfrac{a}{27b^2} \\ V_C = 3nb \\ T_C = \dfrac{8a}{27Rb} \end{cases} \tag{4.21}$$

At these critical points the gas undergoes a *phase transition* and changes state of matter. In phase transitions more than one state exists in the system, and the Van der Waals equation is ill-equipped for treating systems with more than one coexisting phase

§§ 4.2.2 Phase Transitions

Phase transitions are one of the most commonly known thermodynamic behaviors, just imagine the freezing ice outside in the winter or boiling water in order to cook some pasta or brew a nice hot tea.
Phase transitions of any kind show experimentally a really particular behavior: during a phase transition the temperature is constant.
The most known types of phase transition are:

1. Fusion, as in ice melting inside a drink
2. Solidification, as when water becomes ice
3. Sublimation, as when dry ice evaporates at room temperature

4. Deposition, as when a gas leaves a solid trace in a container
5. Vaporization, as when water reaches the boiling point and becomes a vapor

Since temperature is constant in each of these transitions, the heat produced must also be constant and proportional to the amount of mass undergoing the transition. This heat is known as *latent heat*, and it's describable simply as

$$Q_l = m\lambda \tag{4.22}$$

Where λ is a constant which depends on the type of transition and the substance.
Consider now a system undergoing a transition from one state to another, thus at a fixed temperature T_{pt}. If we have a fraction of substance x in the final phase we might say that, if we denote the phases as i, f, then being entropy and volume extensive coordinates, we have

$$\begin{cases} \Delta S = n\left(1-x\right)S_i + nxS_f \\ \Delta V = n\left(1-x\right)V_i + nxV_f \end{cases}$$

The latent heat entropy is defined as

$$\lambda = T\Delta S = T\left(S_f - S_i\right) \tag{4.23}$$

The best suited thermodynamic potential for the description is the Gibbs free energy, for which must hold $G_i = G_f$. Therefore

$$-S_i \mathrm{d}T + V_i \mathrm{d}p = -S_f \mathrm{d}T + V_f \mathrm{d}p \Longrightarrow \left(V_i - V_f\right)\mathrm{d}p = \left(S_i - S_f\right)\mathrm{d}T$$

We immediately recognize the latent heat divided by the transition temperature on the right, and thus, writing everything in terms of the derivative of pressure with respect to temperature, we get the so called «*Clausius Clapeyron equation*»

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{m\lambda}{T\Delta V} \tag{4.24}$$

This equation is integrable after imposing some approximations.
Firstly consider vaporization of a liquid or the sublimation of a solid. Clearly $V_f >> V_i$, thus $\Delta V \approx V_f$, and said

$$V_f = \frac{nRT}{p}$$

We have

$$\frac{\mathrm{d}\log(p)}{\mathrm{d}T} = \frac{m\lambda_v}{RT^2} \tag{4.25}$$

Which, integrated and solved for $p(T)$ gives

$$p(T) = p_0 e^{-\frac{m\lambda_v}{R}\left(\frac{1}{T} - \frac{1}{T_v}\right)} \tag{4.26}$$

In case of solidification of a liquid this approximation doesn't hold anymore, but being ΔV approximately fixed and constant we can directly integrate and obtain again from (4.24)

$$p(T) = p_0 + \frac{m\lambda_s}{\Delta V}\log\left(\frac{T}{T_s}\right) \tag{4.27}$$

From these equations is possible to draw the critical isotherms in a $p - T$ plane and describe multiple phases of a substance. It's also possible to define a surface, which comprises all the relations between the thermodynamic variables, known as the pVT surface. Slices of this surface will then give the $p - V$, $p - T$ and $V - T$ planes which can be used to schematize different phenomena.