Physics S2 (2025-2026)

Part 1: Thermodynamics

I. Thermodynamic systems

Born in the 19th century, **thermodynamics** is a branch of physics that studies the properties of matter on a macroscopic scale. Its creation led to numerous applications: engines, thermal power stations, air conditioning, refrigeration machines, etc.

1. States of matter

Matter exists on Earth mainly in three well-known states: solid, liquid and gas. These states, or phases, have specific properties:

- A **solid** has its own shape and volume.
- A **liquid** does not have its own shape, but it has its own volume.
- A **gas** has neither shape nor volume of its own.

The solid and liquid phases are called **condensed phases** because their densities are of the same order of magnitude and are approximately 1000 times greater than those of gases. For example, water has density 1.0 kg/L while air only 1.3 g/L. The liquid and gas phases are called **fluid phases** because they can flow.

2. From microscopic to macroscopic

Describing a mole of matter means describing 10^{23} interacting particles! In classical physics, we cannot even solve the so-called three-body problem (the Sun and two planets) analytically. Thus, an exact resolution of a problem with one mole of matter is unthinkable. The most efficient numerical simulations can treat 10^{12} molecules. Storing the position and speed of a molecule in single precision (32 bits) requires 6x32/8 = 24 bytes. To store the position of 10^{10} particles, or 2.10^{-14} moles or 5.10^{-11} L of gas, you need 1TB!

Particles are in constant motion, even if they appear non-moving on a macroscopic scale. We call this constant motion "**thermal agitation**" to point out its disordered nature. The higher the temperature, the greater the thermal agitation. Only at **absolute zero**, which is the temperature corresponding at 0 K (-273.15°C), there is no thermal agitation. (Note, however, that absolute zero can never be reached; it can only be approached asymptotically.)

Let's imagine a simple system, a cylinder loosely filled with balls and closed by a movable piston. Let's study the motion of the piston. If there are just a few balls, the motion will take

place in spurts, but if the number of balls is very large, the number of shocks occurring each moment is, on average the same. We will no longer be able to measure the force from each ball, but an average force, induced by the **pressure** exerted by the balls on the piston. In thermodynamics, we study phenomena arising from the motion of a macroscopic number of particles; thus, it is more appropriate to use the notion of pressure rather than measuring the force exerted by each particle.

Definition 1: Pressure

When a fluid is in contact with a wall, it exerts a force on it. The larger the wall, the greater the force, and the coefficient of proportionality between force and surface is called pressure. The mathematical relationship is:

$$d\vec{F} = P\, d\vec{s}$$

The surface unit $d\vec{s}$ is orthogonal to the wall and points outwards.

Pressure is measured in Pascal (Pa): $1\ \mathrm{Pa} = 1\ \mathrm{N/m^2}$.

We have just seen that the impacts of many particles against a wall can no longer be studied one-by-one, but on average, using the quantity called pressure. The same is true for their velocities, which, instead of being studied individually, can also be studied on average using the macroscopic concept of **temperature**.

Definition 2: Temperature

Temperature T is a quantity that measures the kinetic energy of microscopic particles arising from thermal agitation. In a monoatomic gas, the average kinetic energy is

$$\langle E \rangle = \frac{3}{2} k_B T$$

where T is the temperature in Kelvin and $k_B = 1.38 \cdot 10^{-23}\ \mathrm{J \cdot K^{-1}}$ Boltzmann's constant.

Caution: temperature and heat are different physical quantities (video).

3. State variables

As discussed above, using the notion of pressure rather than describing all the shocks against a wall could simplify our problem. There are other important quantities, called **state variables**, which allow us to describe the state of the system on a macroscopic scale. Within the scope of our class, the most important state variables are:

- Pressure
- Temperature
- Volume
- Quantity of matter (or mass)

There are two main categories of state variables:

- **Extensive** state variables depend on the size of the system. This is the case for volume or quantity of matter: if we double the size of the system, these variables will also double.
- **Intensive** state variables do not depend on the size of the system. This is the case for temperature or pressure: if we double the size of the system, these parameters remain unchanged.

In the following, we will study *thermodynamic systems*, i.e. systems made up of a very large number of particles. We distinguish the following types:

- **Open** systems exchange matter and energy with the external environment.
- **Closed** systems exchange energy but not matter with the external environment.
- **Isolated** systems exchange neither matter nor energy with the external environment.

4. Thermodynamic equilibrium

A thermodynamic system is said to be **in equilibrium** if its state variables are all defined and constant over time. This implies that it is in **mechanical equilibrium** (i.e. there is no macroscopic motion), as well as **thermal equilibrium** (i.e. there is no heat exchange).

In the following, we will study a simplified gas model: the **ideal gas**, for which it is assumed that its particles do not interact with each other. In this case, there exists an equation, called the **state equation**, which connects the different state variables of the system:

$$PV = nRT$$

where

1. P is the pressure of the gas (measured in Pa),
2. V is its volume (in m^3),
3. T is its temperature (measured in K),
4. n is the quantity of matter (measured in mol), and
5. R is the so-called ideal gas constant with a value $R = 8.314\ \mathrm{J{\cdot}K^{-1}mol^{-1}}$.

5. Internal energy

The **internal energy U** of a thermodynamic system is the average value of the total energy of the microscopic particles composing the system. It is expressed in Joule (J). It is a "**state function**", that is, a quantity that depends on the state variables of the system:

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

We will often write it U for simplicity, but we should always keep in mind that it is a state function.

We call **heat capacity at constant volume** the quantity C_v such that the variation dU of the internal energy of the system when the temperature varies by dT is given by:

$$dU = C_v(T)\, dT$$

It is measured in $\mathrm{J \cdot K^{-1}}$.

Within the context of our course, we will assume that $C_v(T)$ does not depend on temperature. Thus, when the temperature changes by ΔT, the change in internal energy is:

$$\Delta U = C_v\, \Delta T$$

For condensed phases, we often use similar quantities that are defined per unit mass: the **specific heat capacity at constant volume** c_v, which is measured in $\mathrm{J \cdot K^{-1} kg^{-1}}$, and the **specific internal energy** u, which is measured in $\mathrm{J \cdot kg^{-1}}$. In this case, for a quantity of mass m,

$$C_v = m\, c_v$$

Example 1: Heating up water

We want to heat up 150 kg water arriving in a water heater initially at 10°C up to 60°C. The specific heat capacity at constant volume of water is $c_v = 4.2\ k\mathrm{J \cdot K^{-1} kg^{-1}}$.

We use the formula:

$$dU = m\, c_v dT$$

$$\int_{Ui}^{Uf} dU = m\, c_v \int_{Ti}^{Tf} dT$$

$$\Delta U = m\, c_v \Delta T = 150 \times 4.2 \times 50 = 31\,500\ k\mathrm{J}$$

For comparison, this corresponds to 8.75 kWh (the unit of energy used for electricity). The current price per kWh is about 0.25€. The corresponding cost is thus 2.18€.

II. Thermodynamic processes

1. Definitions

A **thermodynamic process** is a process during which a system transitions from an initial state of equilibrium to a final state of equilibrium. This process can be reversible or irreversible. To illustrate this, let's consider an enclosure containing a gas separated from the outside environment by a piston that can move without friction. We'll discuss two different scenarios:

In the first case, we start to push the piston very slowly at time t_1 to compress the gas (see Figure 1). The gas remains at all times in equilibrium with the outside environment. We stop pushing at time t_2, and the gas reaches its final state of equilibrium. This process could be carried out in the opposite direction by releasing the piston very gently, and it is called **reversible**.

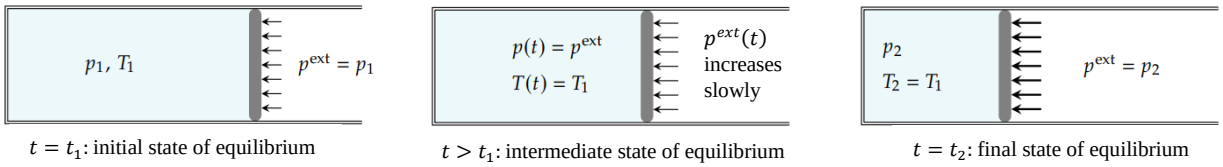


Figure 1 : A reversible thermodynamic process (source: femto-physique.fr)

In the second case, we drop a mass m on the piston, as shown in Figure 2: the system will be initially in a non-equilibrium state, where the pressure will have to readjust, until it reaches the final equilibrium state. If we remove the mass, the system will not return to the initial state, because part of the mechanical energy will have been converted into heat. This process is called **irreversible**.

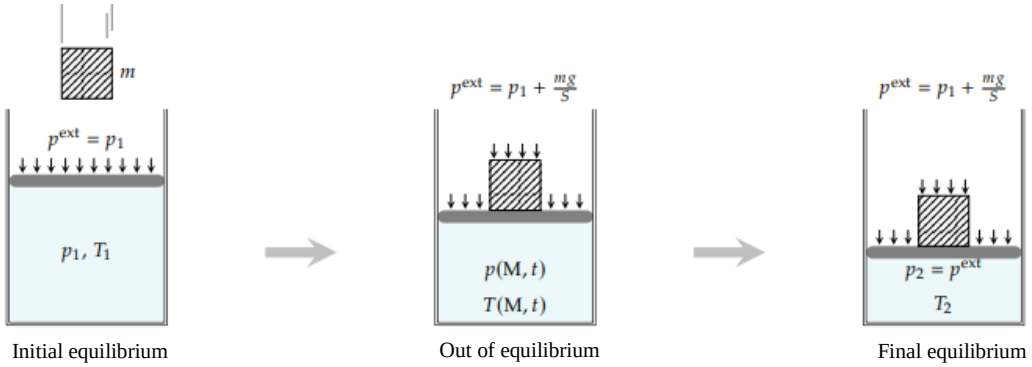


Figure 2 : An irreversible thermodynamic process (source: femto-physique.fr)

In addition to these two main categories of processes, the following processes are also used in thermodynamics:

- An **isobaric** process is a process occurring at constant pressure P.
- An **isochoric** process is a process occurring at constant volume V.
- An **isothermal** process is a process occurring at constant temperature T.
- A **monobaric** process is a process occurring at constant external pressure P_{ext}.
- A **monothermal** process is a process occurring at constant external temperature T_{ext}.

Note: The last two processes, monobaric and monothermal, corresponding to the French terms "monobare" and "monotherme" respectively, are not widely used in the English scientific literature.

2. Macroscopic work

Energy exchanges between a system and the external environment can be macroscopic in nature. This type of energy exchange is called work, is denoted by W, and is expressed in Joules (J). By convention, work is considered positive if the system receives energy and negative if it loses energy.

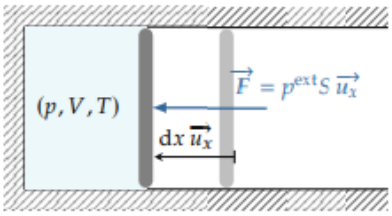


Figure 3 : Work of a force (source: femto-physique.fr)

Let's return to our previous example of a gas in a container. If we push the piston by exerting a force on it over a distance dx, then the volume varies by $dV = S\,dx$, where S is the surface of the piston. The work is defined as

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV$$

The negative sign in the formula reflects the fact that we are calculating the energy received by the system. When the volume of gas decreases ($dV < 0$), the work is positive.

3. Thermal transfer

Thermal transfers or heat exchanges take place at a microscopic level, in three different ways: (Video)

- **Convection**: heat transfer occurs with the movement of a fluid (e.g. fan heating).
- **Conduction**: this is heat transfer without any mass moving. It is due to a temperature difference between two areas of the same object. (e.g. a heated metal bar) (For a small detour on apparent/"feels like" temperature used in weather see this video.)
- **Radiation**: heat transfer induced by electromagnetic waves.

Heat transfer is denoted Q and is expressed in Joules (J). A thermodynamic process during which no heat exchange takes place is called **adiabatic** ($Q = 0$). A very fast process can be considered adiabatic, as mechanical equilibrium can be achieved much more quickly than thermal equilibrium. In reality, there is no perfectly adiabatic process. Eventually, thermal equilibrium is always achieved.

4. First Law of Thermodynamics

The first law of thermodynamics describes conservation of energy. Within the context of this course, we only consider problems for which the kinetic and potential energy of the system do not change. The internal energy of the system can therefore only change in two ways: by work or heat transfer. In mathematical terms, we write:

$$\Delta U = Q + W$$

In this expression:

- The term ΔU describes a difference in internal energy between two different times: the initial state and the final state, no matter how the system transitions from the initial to the final state.
- The terms W and Q are scalar quantities and are positive when they are received.
- The terms W and Q depend on the way in which the thermodynamic process takes place, as we will see in the following section: there is no «Δ» in front of W and Q!
- If the initial and final states are the same, then $\Delta U = 0$. We call this a "**cycle**".

5. Enthalpy

Enthalpy is a state function defined as:

$$H = U + PV$$

It is built from internal energy and is measured in Joules (J).

Similarly to the heat capacity at constant volume, which is defined from internal energy, we can use enthalpy to define a **heat capacity at constant pressure** C_p:

$$dH = C_p \, dT$$

It is measured in $J \cdot K^{-1}$.

For condensed phases, we often use a similar quantity defined per unit mass, the **specific heat capacity at constant pressure** c_p, measured in $J \cdot K^{-1} kg^{-1}$. Similarly, the **specific enthalpy** h is defined as enthalpy per unit mass and is measured in $J \cdot kg^{-1}$.

Example 2: Change of state (phase transition)

A quantity of $m = 1\,\mathrm{g}$ of ice at temperature $T_1 = 250\,\mathrm{K}$ and constant external pressure is heated to transform it into water at temperature $T_2 = 300\,\mathrm{K}$. We want to calculate the change in enthalpy ΔH. We are given the following:

- The specific heat capacity of ice is $c_{ice} = 2.1\ k\mathrm{J}\cdot\mathrm{K}^{-1}\mathrm{kg}^{-1}$
- The specific heat capacity of water is $c_{water} = 4.2\ k\mathrm{J}\cdot\mathrm{K}^{-1}\mathrm{kg}^{-1}$
- The specific enthalpy of fusion of ice at 273 K is $h_{fusion} = 335\ k\mathrm{J}\cdot\mathrm{kg}^{-1}$

We model the whole process as a series of the following stages:

- Transition of ice from $T_1 = 250\,\mathrm{K}$ to $T_{fusion} = 273\,\mathrm{K}$ (ΔH_1)
- Phase transition from ice to liquid water at constant temperature (ΔH_2)
- Transition of water from $T_{fusion} = 273\,\mathrm{K}$ to $T_2 = 300\,\mathrm{K}$ (ΔH_3)

Therefore, we have

$$\Delta H_1 = m\, c_{ice}(T_{fusion} - T_1)$$

$$\Delta H_2 = m\, h_{fusion}$$

$$\Delta H_3 = m\, c_{water}(T_2 - T_{fusion})$$

The total change in enthalpy is

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = 496.7\,\mathrm{J}$$

6. Special cases for work and heat transfer

a. Isochoric process

In the case of an isochoric process ($dV = 0$), the work is zero:

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV = 0$$

Thus the heat transfer is $Q = \Delta U$.

b. Monobaric process

In the case of constant external pressure $P_{ext} = P_0$ with P_0 constant, the work is written as:

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV = -P_0 \int_{V_i}^{V_f} dV = -P_0 \left(V_f - V_i\right)$$

If the process is isobaric and the volume can change, then it is necessarily monobaric.

In this case, heat transfer is $Q = \Delta H$.

c. Reversible isothermal process

In the case of a reversible isothermal process of an ideal gas at temperature T_0, the work is:

$$W = -\int_{V_i}^{V_f} P_{ext}\, dV = -\int_{V_i}^{V_f} \frac{nRT_0}{V}\, dV = -nRT_0 \int_{V_i}^{V_f} \frac{1}{V}\, dV = nRT_0 \ln\left(\frac{f}{i}\right)$$

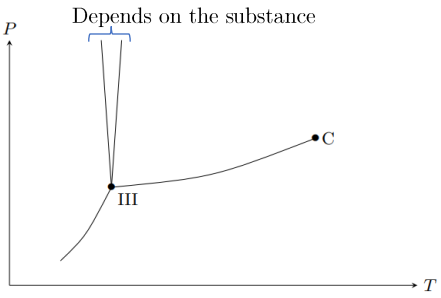
III. Diagrams

1. Introduction

A **phase diagram** is a chart that maps the stable phase(s) of a sample of pure substance as a function of two, usually intensive, state variables. A priori, the stable phase of a pure substance depends on three state variables T, P and V_m (molar volume) or v (specific volume).

2. (P,T) diagram

The figure on the right shows the generic form of a **(P,T) phase diagram** in the vicinity of the so-called triple point (defined below).



The slope of the almost vertical line is positive for most chemical substances, but there are exceptions for which the slope is negative, foremost among which is water.

There are two special points on this diagram:

- The **triple point** (denoted III) where the three phases coexist in a stable way (video).
- The **critical point** C beyond which the liquid and gas phases are indistinguishable and only form a single phase called supercritical fluid (video).

Below are two examples of (P,T) diagrams:

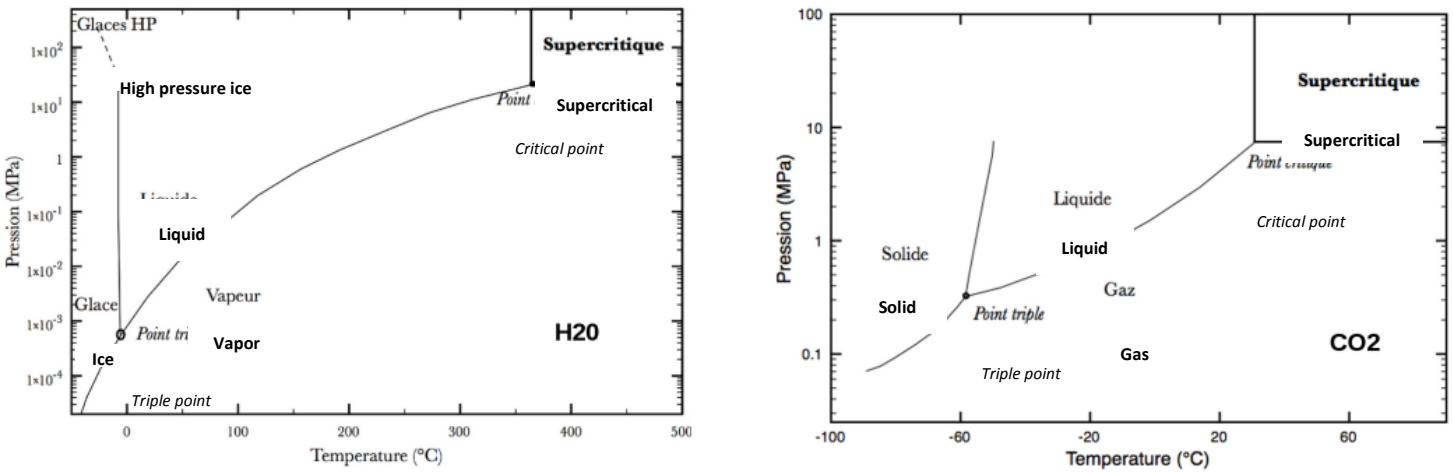


Figure 4: (P,T) diagrams for H_2O and CO_2 (source: http://planet-terre.ens-lyon.fr).

3. (P,v) diagram

In a (P,T) diagram, the phase transition occurs when we cross a boundary separating two domains. When we are on a boundary, both phases are present (liquid and gas for example) in proportions that the (P,T) diagram does not allow us to predict. This is why we also use the **(P,v) diagram**, sometimes called the **Clapeyron diagram**: it allows us to know the state of the system during the phase transition. In this type of representation, we limit ourselves to temperatures and pressures higher than those of the triple point.

The green and red curves are called **Andrews' isothermal lines** and include a flat line that represents the coexistence of the liquid and gas phases. The black curve containing the critical point C is called the **saturation curve**. This curve is the limit of the domain in which the liquid and gas phases coexist.

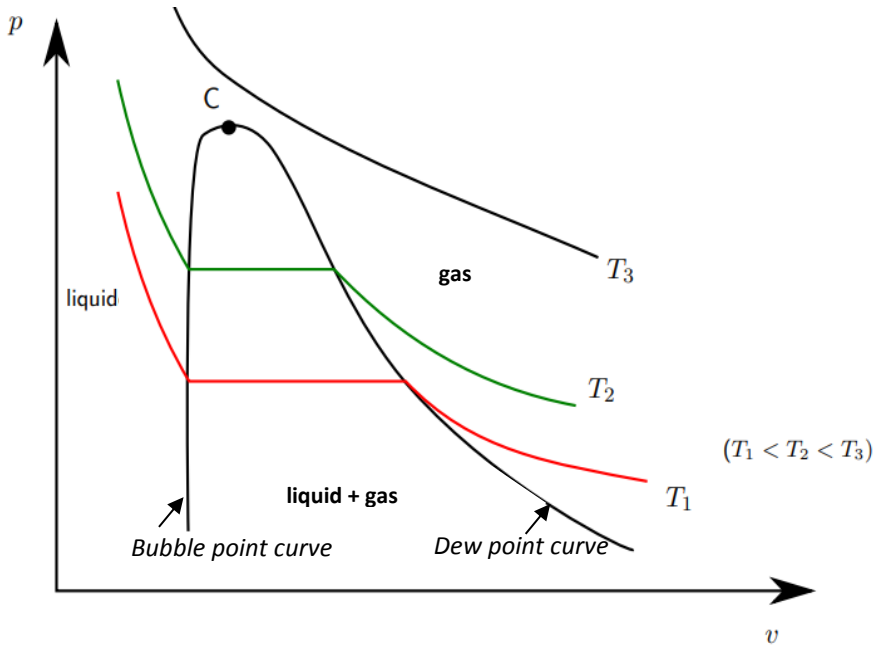


Figure 5: (P,v) diagram (source : http://planet-terre.ens-lyon.fr)

IV. Entropy and the Second Law of Thermodynamics

1. The experiment of Joule-Gay Lussac

One of the major contributions of thermodynamics is the introduction of a new concept, called **entropy** S, based on which the second law of Thermodynamics is postulated, as we will see below. Entropy is a quantity measurable on the macroscopic scale that describes the disordered nature of matter on the microscopic scale. Here we will discuss it briefly since a more detailed description would require statistical physics, which is beyond the scope of this course.

The first law of Thermodynamics, which is a law describing the conservation of energy, says nothing about the reversibility of transformations. Let us take the experiment of Joule-Gay Lussac to illustrate our point: in 1806, Gay-Lussac carried out an experiment regarding the expansion of a gas into a vacuum. Two containers with adiabatic walls, one filled with a gas and the other in vacuum, are connected by a pipe fitted with a tap (Figure 6). When the pipe is opened, the gas expands from container 1 to container 2.

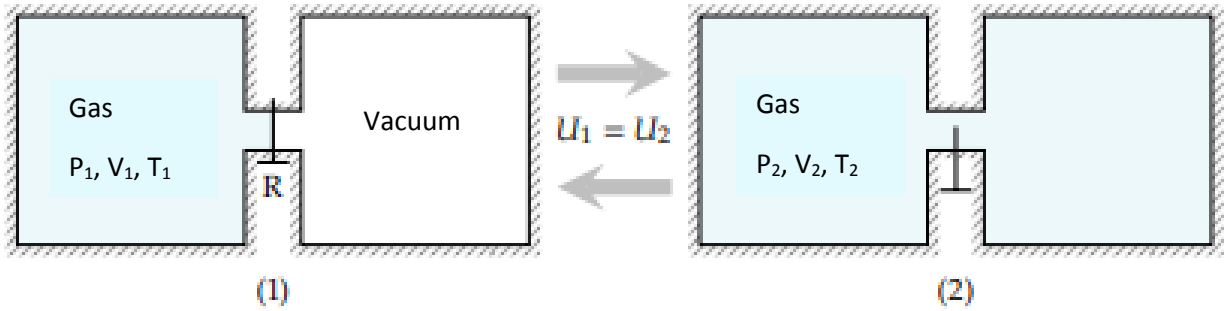


Figure 6: Experiment of Joule-Gay Lussac (source: femto-phyisque.fr)

The thermodynamic process from state (1) to state (2) is irreversible, because the particles will not spontaneously return to container 1. The process (2)→(1) is said to be impossible. The first law is necessary but not sufficient to model what is observed. We need a law imposing the direction of evolution of a system, which is why the second law of Thermodynamics was introduced.

When a system undergoes a thermodynamic process from an initial state to a final state, the change in entropy is:

$$\Delta S = S_{exchanged} + S_{created}$$

The first term describes the change in entropy because of heat exchange and is given by the expression:

$$S_{exchanged} = \frac{Q}{T}$$

The second term describes any entropy created during the process which in general is

$$S_{created} \geq 0$$

It is this second term that forces the system to evolve in a precise direction. If $S_{created}= 0$, the process is reversible. If, in addition, the process is adiabatic, i.e. Q = 0, then $S_{exchanged} = 0$ as well, and the transformation is called **isentropic**: $\Delta S = 0$.

V. Heat engines

1. Definition and methodology

Heat engines are thermodynamic systems that undergo a sequence of thermodynamic processes thus creating devices that result in energy conversions. For example, engine motors, refrigerators, heat pumps, air conditioners etc., are all heat engines.

Here we will discuss heat engines known as **dithermal**. These exchange:

- Heat Q_c with a cold source T_c
- Heat Q_h with a hot source T_h
- Work W with the environment

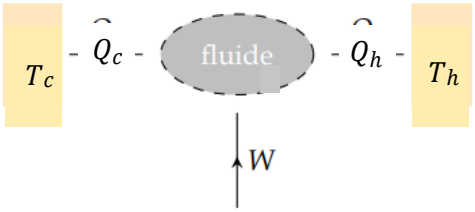


Figure 7: Energy diagram of a dithermal heat engine (source: femto-physique.fr)

In Figure 7, the arrows represent the energy exchanges, which are all oriented from the outside towards our system. The exchanges are positive if they are received by the engine (which is often a fluid contained in the engine), i.e. in the same direction as the arrows in Figure 7.

The **efficiency** of a heat engine is described by the ratio

$$\rho = \left|\frac{\text{useful energy}}{\text{energy cost}}\right|$$

To calculate these energy values, we need to apply the two laws of Thermodynamics for the case a cyclic process. In this case, the initial state of the fluid is the same as the final state and therefore the changes in internal energy and in entropy are zero over a whole cycle:

$$\begin{cases} \Delta U = Q_c + Q_h + W = 0 \\ \Delta S = \dfrac{Q_c}{T_c} + \dfrac{Q_h}{T_h} + S_{created} = 0 \end{cases}$$

2. Combustion engine

The purpose of a combustion engine (a motor) is to produce work and therefore $W < 0$. To do that it uses heat from the hot source, i.e. $Q_h > 0$.

Using the first law we find for a whole cycle:

$$W = -(Q_c + Q_h)$$

Assuming that the cold source is the atmosphere, the efficiency is:

$$\rho = \left|\frac{\text{useful energy}}{\text{energy cost}}\right| = -\frac{W}{Q_h} = 1 + \frac{Q_c}{Q_h}$$

Using the second law we find:

$$\frac{T_c}{T_h} + \frac{Q_c}{Q_h} + \frac{T_c\, S_{created}}{Q_h} = 0$$

We deduce that the efficiency can be written as:

$$\rho = 1 - \frac{T_c}{T_h} - \frac{T_c\, S_{created}}{Q_h}$$

If the process is reversible, then $S_{created} = 0$, and we obtain:

$$\rho = 1 - \frac{T_c}{T_h}$$

We note that to maximize efficiency, the temperature of the hot source must be much higher than the temperature of the cold source.

3. Refrigerating machine

The purpose of a refrigerating machine (a refrigerator) is to produce cold. It is therefore a question of taking heat from the cold source, i.e. the quantity of interest here is Q_c. The energy used to achieve this is the work of the engine W. The **efficiency of a refrigerating machine** is thus given by:

$$e = \left|\frac{\text{useful energy}}{\text{energy cost}}\right| = \frac{Q_c}{W}$$

Using the first law we find $W = -(Q_c + Q_h)$, thus

$$e = -\frac{Q_c}{Q_h + Q_c} = -\frac{1}{1 + Q_h/Q_c}$$

Using the second law we find:

$$\frac{T_h}{T_c} + \frac{Q_h}{Q_c} + \frac{T_h\, S_{created}}{Q_c} = 0$$

Thus, the efficiency can be written as:

$$e = \frac{1}{T_h/T_c - 1 + T_h\, S_{created}/Q_c}$$

According to the second law $S_{created} \geq 0$. For a refrigerating machine the cold source gives heat, therefore $Q_c > 0$, and $\frac{T_h\, S_{created}}{Q_c} \geq 0$. Thus, we deduce that

$$e \leq \frac{1}{T_h/T_c - 1} = \frac{T_c}{T_h - T_c}$$

We note that the closer the temperatures are, the better the efficiency is. It can also exceed the value of 1, which means that for 1J of electricity consumed, the air inside the refrigerating machine can be cooled by 5J if, for example, the efficiency is 5.

4. Heat pump

The purpose of a heat pump is to heat the hot source. The useful quantity is therefore Q_h, and the energy used to achieve that is the work W. The **coefficient of performance** (COP) of a heat pump is:

$$COP = \left|\frac{\text{useful energy}}{\text{energy cost}}\right| = -\frac{Q_h}{W}$$

Using an analysis similar to the one above for the refrigerating machine, we obtain that:

$$COP \leq \frac{T_h}{T_h - T_c}$$

We note that the efficiency of a heat pump is improved as the temperatures get closer. It can also exceed the value of 1, which means that for 1J of electricity consumed, we can heat the air inside the heat pump by 5J if, for example, the efficiency is 5. This is therefore a much more efficient means of heating than a conventional radiator which, at best, can have an efficiency equal to 1.

5. Example of a cycle: the Carnot cycle for an ideal gas

The Carnot cycle corresponds to a repetition of the following 4 stages:

- A → B: reversible isothermal expansion at T_h
- B → C: reversible adiabatic expansion
- C → D: isothermal at T_c so again $P \propto 1/V$ but now it is a compression (since we want a cyclic operation)
- D → A : reversible adiabatic compression

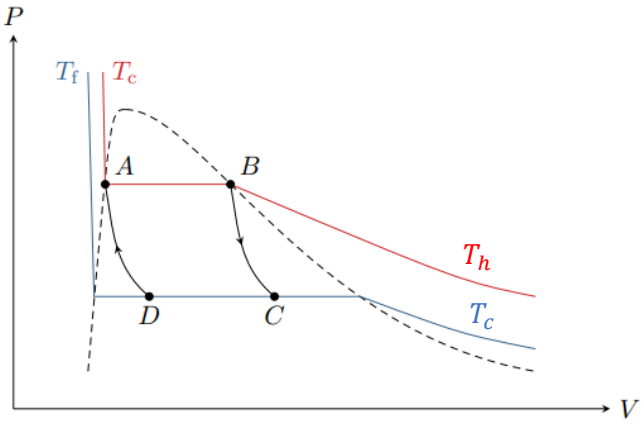


Figure 8: (P,V) diagram of the Carnot cycle.

Calculations will be carried out in the exercise sets (TD).