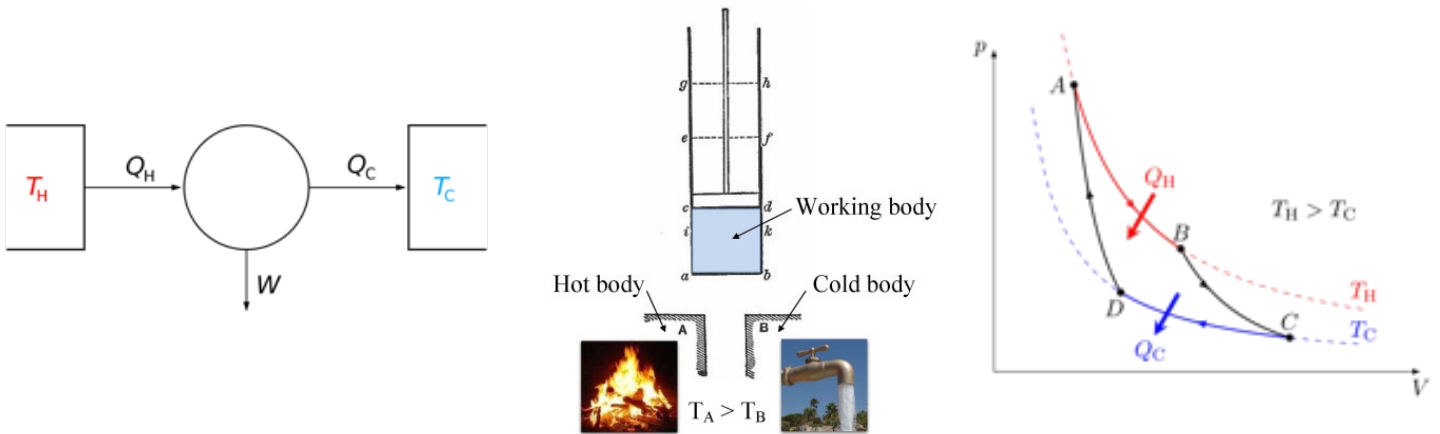


Thermodynamics



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Institut National des Sciences Appliquées de Lyon

SCAN FIRST



General introduction

This handout brings together all documents, for the Element Constitutif (EC) “Thermodynamics”.

Lectures and tutorials will give a linear view of contents of this EC. They are organised in 6 chapters. A summary the chapter and associated Learning Objectives (O) is provided at the beginning of each chapter.

The contents of this handout is divided into “blocks” :

- a main part with the learning Objectives and methodological benchmarks: they bring together all the concepts that need to be understood (definitions, principles, *etc.*), often presented on the basis of observations. Many explanations of the different concepts discussed are provided; they are not, of course, to be known by heart. Important formulas and statements are framed and/or written in bold. In addition, all the know-how required and apply the tools. They present the methodologies that will be used to solve the problems posed.
- stakes (S): they shed technological light on the major current energy challenges, which the basics of Thermodynamics make it possible to understand.

The colour version of the handout is available on the Moodle Thermodynamics page.

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Chapter 1

Energies and basic concepts

This chapter presents the fundamental concepts used in Thermodynamics. A reminder of the different types of energy: potential, kinetic, macroscopic, microscopic energies is made. The notion of internal energy is introduced. Primary energies are distinguished from final and useful energies. The notion of energy chain is addressed and different form of heat are introduced. The notion of thermodynamic system is defined and states variables defining the state of the system are introduced. Finally, reversible and irreversible processes are defined and explained.

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The **learning Objectives** of this chapter are to:

- Distinguish between primary, final and useful energies
- Distinguish between macro and microscopic, kinetic and potential energies
- Define internal energy
- Handle (conversion) the usual units in this field (energy, power, flow, *etc.*)
- Know how to find a few orders of magnitude by a quick calculation and discuss them
- Identify energy losses during processes and calculate efficiency
- Identify energy processes and establish an energy chain (from primary energy to useful energy) while respecting representation conventions
- For a given process:
 1. Define the system being studied
 2. Calculate or identify the state parameters characterising the initial state and the final state
 3. Specify the nature of the process involved
 4. Explain the sign of energy transfers (sign convention)

1.1 Energy

Consider a mass connected to a pulley. The axle of the pulley is connected to a small generator, which powers an electric circuit comprising of a lamp. As long as the mass is stationary, nothing happens, the lamp is switched off, no electric current flows in the circuit. If the mass is released, several processes take place: a mechanical process corresponding to the displacement of the mass which reaches a certain speed; it imparts a rotational movement to the pulley and the generator; an electric current is produced in the generator, the current passes through the lamp, which heats up and emits light. Once the mass comes to a standstill (it reaches the ground or the length of the string that holds it still), everything comes to a standstill again, the lamp goes out, a new state of rest is reached.

In this experiment, many physical phenomena are involved: mechanical, electrical, electromagnetic and thermal. They concern very varied fields of Physics, obeying very diverse laws. But a common physical quantity connects all these phenomena: energy. This energy here takes four forms specific to the four types of physical phenomena encountered: mechanical energy, with its two forms, the potential energy of the mass in the earth's gravitational field, transformed into kinetic energy when the mass moves, reaches a certain speed and drives the axis of the pulley. In the generator, a magnet is rotated by the movement of the axis and creates an electric current in the circuit. The energy here is in electrical form, *i.e.* electrical charges flow at certain rate (current) and under a certain voltage. In the lamp, the filament heats up by the Joule effect (*i.e.* heat or thermal energy), and reaches a high temperature, at which it emits light, *i.e.* visible electromagnetic radiation. In this experiment, the source of energy is the potential energy of the mass; everything stops when it is no longer available.

1.1.1 Kinetic energy and potential energy

Kinetic energy

Definition 1.1.1 — Kinetic energy. Kinetic energy is the energy that a given mass system possesses as a result of its motion. It is equal to the work required to move this system from rest to motion.

The kinetic energy of a mass system m animated by a speed v (non-relativistic) is given by the formula:

$$E_c = \frac{1}{2}mv^2$$

Potential energy

Definition 1.1.2 — Potential energy. Potential energy is the energy that a system possesses because of its position relative to another system with which it interacts, *i.e.* which applies a force to it.

If \vec{F} is the force exerted on the system, the change in potential energy of the system between 2 positions is equal to the opposite of the work done by \vec{F} to move the system between these two positions, independent of the path taken. Beware, the potential energy can only be defined for forces such that the work is independent of the path followed (it is then said that the *force* is *conservative*). For example, it is not possible to define a potential energy for a frictional force.

If the force applied to the system is conservative, then for an elementary displacement \vec{dl} of the system, the variation in potential energy is given by:

$$dE_p = -\delta W(\vec{F}) = -\vec{F} \cdot \vec{dl}$$

■ **Example 1.1** The potential energy due to weight is called gravitational potential energy. For an elementary point mass m of altitude z , it is written:

$$E_p(z) = - \int_{z_0}^z m\vec{g} \cdot \vec{dl} = mg \int_{z_0}^z dz = mg(z - z_0)$$

with a vertical axis pointing upwards, and z_0 the (arbitrary) reference zero for which the potential energy of gravity is zero. ■

■ **Example 1.2** The potential energy due to the force exerted by a spring is called elastic potential energy. For a material point fixed to a frame via a spring, it is written:

$$E_p = - \int -k(x - x_0)\vec{u}_x \cdot \vec{dl} = \int k(x - x_0)dx = \frac{1}{2}k(x - x_0)^2$$

with k the spring constant of the spring, \vec{u}_x the unit vector bearing an axis along the spring and x_0 the position such that the extension is zero. ■

■ **Example 1.3** The potential energy due to the force exerted by a charged particle Q on another charged particle q , separated at the distance r is called electrostatic potential energy. It is written:

$$E_p = - \int \frac{Qq}{4\pi\epsilon_0 r^2} \vec{u}_r \cdot \vec{dl} = - \frac{Qq}{4\pi\epsilon_0} \int \frac{dr}{r^2} = \frac{Qq}{4\pi\epsilon_0 r}$$

with ϵ_0 the vacuum permittivity and \vec{u}_r the unit vector of the spherical basis.

Other potential energies can be defined, provided that the force is conservative. ■

1.1.2 Total energy, macroscopic and microscopic nature of energy

This paragraph and the following one are largely inspired by the article: "Energie interne", Wikipedia, the free encyclopedia, https://fr.wikipedia.org/wiki/Energie_interne (page consulted on 5 December 2019).

The total energy of a thermodynamic system consisting of particles, molecules or atoms can be classified into two categories:

1. The kinetic energies correspond to the movement of the system as a whole as well as to the movements of the individual particles that make it up.
2. The potential energies due to the interactions of the system with the surroundings through fields, gravitational, electric or magnetic, but also due to the interactions between molecules, ions, atoms, electrons, nuclei... which make up this system.

Each of these categories can be separated into two levels:

- A macroscopic level, sensitive to our senses, *i.e.* our human scale, corresponding to the macroscopic kinetic energy ($E_{c,macro}$) of the moving system in a given frame of reference and the macroscopic potential energies ($\sum E_{p,macro}$) of the system placed, for example, in gravitational, electric or magnetic fields.
- A microscopic level not perceived by our senses, corresponding to the microscopic kinetic energies ($\sum E_{c,micro}$) that can be assimilated to the thermal agitation of particles (the mean microscopic kinetic energy of atoms/molecules is related to the temperature (*cf.* O4)) and to all the potential energies of microscopic interactions ($\sum E_{p,micro}$) which can be assimilated, among others, to the energies of chemical bonding and to the energies of interactions between nuclei (*i.e.* nuclear energies).

The total energy of a system is therefore written:

$$E_{total} = E_{c,macro} + \sum E_{p,macro} + \sum E_{c,micro} + \sum E_{p,micro}$$

1.1.3 Internal energy

Definition 1.1.3 — Internal energy. The sum of microscopic energies constitutes *the internal energy* U of the system: $U = \sum E_{c,micro} + \sum E_{p,micro}$

Given the complexity of the interactions at the microscopic level, the internal energy U cannot be easily calculated in an absolute manner (this is also the case for potential energies that depend on a reference). It is however possible to calculate its variation.

The internal energy is a state function of the system. Its variation depends only on the final and initial state of equilibrium and not on the nature of the process. Its differential dU is therefore an exact differential. It is an *extensive quantity* (*i.e.* it depends on the amount of material making up the system).

1.1.4 Primary sources of energy

In everyday life, we rarely talk about kinetic, potential or internal energy; yet we buy and consume energy on a daily basis, which we call electricity, petrol... How can we relate the energy of “everyday life” to the energy of “Physics”? This requires first of all defining the notion of primary source of energy, the source of our daily energies, and relating it to the forms of energy described above.

Definition 1.1.4 — Primary energy source. A primary energy source is a form of energy available in nature before any process. It may be directly usable, or it may require transformations in order to be usable and easily transportable. Primary energy is stored energy.

There are four forms of primary energy; three are of microscopic origin, one is of macroscopic origin:

- **Nuclear energy:** it is generated by the processes of fission (fissile *uranium* used as fuel) or fusion (not controllable, as the source of energy transmitted by the *sun*); it is a microscopic potential energy.

- **Chemical energy:** this includes all *fuels of fossil origin* (coal, natural gas, oil, lignite, *etc.*) and *biomass*; it is also a microscopic potential energy.
- **Thermal energy:** of terrestrial origin, it is called geothermal. It is supplied by underground water or hot gas and it is a microscopic kinetic energy (thermal agitation of molecules).
- **Mechanical energy:** this includes energy from different natural forces as hydraulic energy that can be macroscopic potential energy (*waterfalls, dams*) or macroscopic kinetic energy (*rivers*). Other macroscopic kinetic energies are tidal energy (*tides*) and wind energy (*winds*).

Note 1: Here we have chosen to classify solar energy as a primary energy source of a nuclear nature. It could also be considered as a source of thermal energy, since nuclear fusion in the sun provides heat (which is also the case for the fission of uranium in a nuclear reactor, which generates heat). It can also be seen as a source of radiation.

Note 2: Human and animal mechanical energy is not taken into account as a primary energy source because it is obtained through the metabolism of biomass, the primary chemical energy.

Note 3: Biomass, fossil fuels, water, wind... might not be considered as primary energies because they result from processes induced by solar energy...

Renewable nature of certain primary energies

Renewable energies (**RE** for short) are energy sources whose natural renewal is fast enough to be considered inexhaustible on the human time scale. They come from cyclical or constant natural phenomena induced by the stars: the Sun mainly for the *heat and sunlight* it generates, but also the attraction of the Moon (*tides*) and the heat generated by the Earth (*geothermal energy*). The Sun and the Earth are also at the origin of photosynthesis allowing the growth of *biomass*. The non-uniform distribution of solar energy also heats air masses unevenly: warmer air rises, colder air falls, which causes *winds*. The presence of *waterfalls and rivers* on Earth is also a source of renewable energy.

All fossil fuels and uranium are considered non-renewable.

Note: the renewable nature of an energy source depends on the speed at which the source is consumed, on the one hand, and on the speed at which it renews itself, on the other hand. Intensive land use and deforestation induced by the massive and rapid removal of biomass can thus make its renewable character questionable in some cases.

1.1.5 Final energy

The final energy is the energy available to the user, *i.e.* the energy that is consumed and/or purchased. The electricity available at the socket, the litre of unleaded petrol that you put in your vehicle... are final energy. They are the result of multiple processes (conversions, transfers (see section 1.2)) of primary energies, leading to energy losses (*cf.* S1). Final energy is only a fraction of the initial primary energy, once it has been transformed, stored, transported and finally distributed to the final consumer. Electrical energy is the result of more or less numerous processes of different primary energies:

- Nuclear energy (uranium) → thermal energy → mechanical energy → electrical energy
- Mechanical energy (water from a dam) → electrical energy
- Solar energy (radiation) → electrical energy

Each arrow above represents the action of an energy converter (see section 1.2), operating with a certain conversion efficiency (*cf.* S1).

Some primary energies are final energies: biomass, natural gas. Although they do not undergo process, they often have to be transported, with devices that are also characterised by a transport efficiency (*cf.* S1).

The shorter the process circuit (*e.g.* an individual solar water heater), the closer the amount of final energy will be to the amount of primary energy drawn from the stock (*cf.* S1).

The final energy is therefore available in the form of electricity (noted W_e) and chemical energy (W_c).

1.1.6 Useful energy

Useful energy is the one providing the required service. For example, it is the heat for heating or the light energy for lighting; mechanical work for working the land in the agricultural sector or for moving vehicles in the transport sector.

The useful energy is therefore available in the form of mechanical work (noted W_m) and heat (noted Q). The latter can be further divided in convection or conduction heat (noted Q_c) and radiation heat (noted Q_r).

We also speak of calorific energy for heat, and non-calorific energy for work. Useful energy is the last link in an energy chain (see section 1.2). Figure 1.1 give the energy flow diagram of France in 2017, showing primary, final and useful energies.

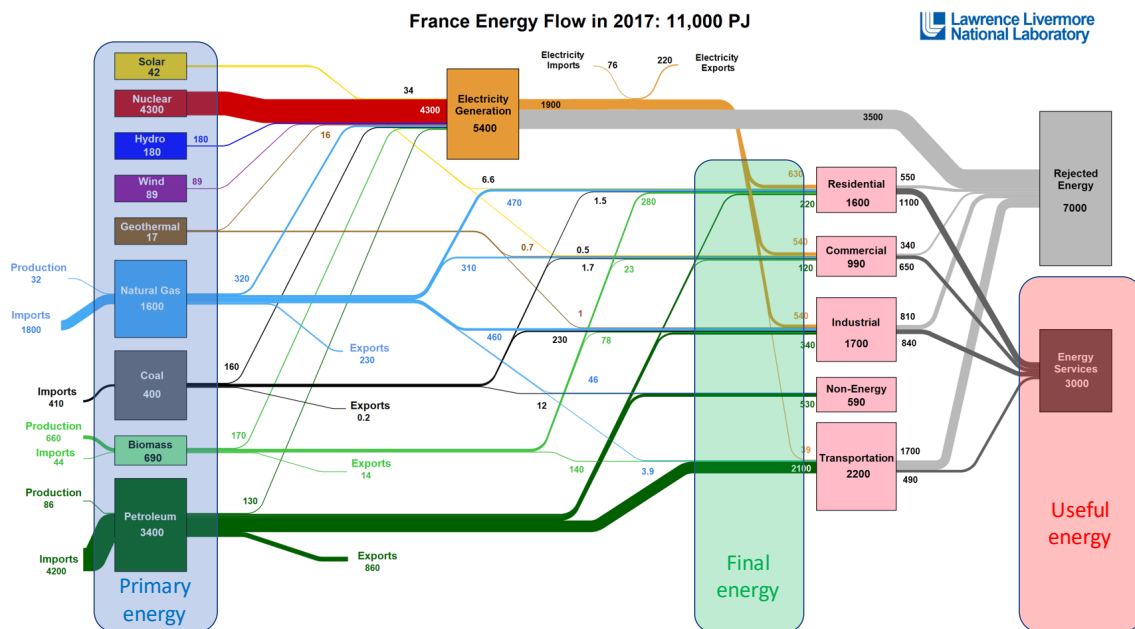


Figure 1.1: Energy flow diagram of France in 2017 (from Lawrence Livermore National Laboratory)

■ **Example 1.4** Heating a building - Useful energy is the heat supplied to the building's occupant. The final energy may be electricity (electric heating), in which case the possible sources of primary energy are uranium, fossil fuels, wind, solar, hydro, biomass or a mix of some of these. The final energy can also be fuel oil burnt directly in a boiler; in which case the primary energy is fossil energy. If the final energy comes from the incineration of household waste, the primary energy includes all the sources used to manufacture the products from which this waste originated... ■

1.1.7 Units

The unit of the international system for quantifying energy is the **Joule**. One Joule represents the work of a force of 1 N whose point of application moves 1 m in the direction of the force.

It is a quantity of energy that is perceived as small in the current activity of a human being, which handicaps its use in certain circumstances. The kilojoule ($1 \text{ kJ} = 1 \times 10^3 \text{ J}$), the megajoule ($1 \text{ MJ} =$

Order of Magn. (J)	Item
10^{-14}	Sound energy transmitted to the eardrums by listening to a whisper for one second
10^{-9}	Energy required to raise a grain of sand by 0.1mm (the thickness of a piece of paper)
10^{-2}	Use of a typical LED for 1 second
10^0	Kinetic energy produced as an apple falls 1 meter against Earth's gravity
10^1	Kinetic energy of a punch
10^2	Energy to melt 1 g of ice
10^3	1 food Calorie (large calorie)
10^4	Energy released by the metabolism of 1 gram of fat
10^5	Kinetic energy of an automobile at highway speeds
10^6	Approximate food energy of a snack such as a Snickers bar
10^7	Energy from the combustion of 1 cubic meter of natural gas
10^8	Kinetic energy of a 55 tonne aircraft at typical landing speed
10^9	Energy in an average lightning bolt
10^{12}	Maximum fuel energy of an Airbus A330-300
10^{14}	Yield of the Little Boy atomic bomb dropped on Hiroshima in World War II
10^{16}	Energy released by a severe thunderstorm
10^{17}	Total energy from the Sun that strikes the face of the Earth each second
10^{21}	Total world annual energy consumption in 2010
10^{23}	Total global uranium-238 resources using fast reactor technology
10^{69}	Estimated total mass-energy of the observable universe

Table 1.1: Order of magnitude of various energies (data from wikipedia)

1×10^6 J) and even the exajoule ($1 \text{ EJ} = 1 \times 10^{18} \text{ J}$) are therefore commonly used to quantify world energy consumption (*cf.* S1).

■ **Example 1.5** To climb stairs (about 3 m high), a 75 kg man expends 2.2 kJ of energy. ■

Conversely, to quantify very low values of energy, such as the energy of the elementary particles making up the atoms, the **electron-volt** is used: 1 eV measures the kinetic energy gained by an electron accelerated by a potential difference of 1 V, *i.e.*: $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

The **calorie** (cal) is an ancient unit of energy. It represents the amount of heat needed to raise the temperature of 1 g of water by 1 °C, so $1 \text{ cal} = 4.1855 \text{ J}$. It is the unit that is still used to measure the energetic power of food.

In industry (and on electricity bills), it is the **kilowatt-hour** (kW·h or kWh) that quantifies energy. 1 kWh corresponds to the energy consumed by an appliance delivering 1000 watts of power operating for 1 hour. We therefore have: $1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$

We also use the watt-hour (Wh) and the multiples of thousands of the kWh which are the megawatt-hour (MWh) and gigawatt-hour (GWh). Finally, the **tonne of oil equivalent** (toe), corresponding to the calorific energy obtained from the combustion of 1 tonne of "average" oil, is also used: $1 \text{ toe} = 4.186 \times 10^{10} \text{ J}$.

1.1.8 Orders of magnitude

Order of magnitude of various energies are listed on table 1.1.

1.2 Energy chain

1.2.1 Definitions and conventions

The aim of an energy chain is to describe the energy transfers between a primary source and the consumer (useful energy), by explaining the different forms that energy takes during transfers. The conventional schematisation is as follows:

- Energy reservoirs are represented by rectangles: both the name of the reservoir and the form of the stored energy (*e.g.* oil, chemical energy, microscopic potential energy) are indicated in the rectangle.
- Energy converters (which do not store) by ovals.
- “Thick” arrows indicate the direction of the transfers: the form of the transferred energy is indicated in the arrow.
- Remember that any conversion is accompanied by heat transfer to the surrounding air.
- The transport of energy (and therefore transport losses) is not indicated in an energy chain.

1.2.2 Implementation

The beginning of the chain is inevitably a reservoir since we start with primary energy (see section 1.1.4 for the list of primary energies and the corresponding form of energy). The end of the chain is an arrow since it is a transfer to the consumer’s use (useful energy, section 1.1.6). In the middle of the chain there will necessarily be energy converters, and possibly also intermediate storage tanks (*cf.* S3 for the storage of intermittent energy). Converters are characterised by their efficiency: the ratio of useful energy over input energy. The difference between useful energy and input energy is called energy losses (often in the form of heat). Energy Losses are represented by an arrow pointing outside the chain (see Figure 1.2). Some examples of converters:

- Steam Turbine: Heat $Q_c \rightarrow$ Mechanical work W_m
- Alternator: Mechanical work $W_m \rightarrow$ Electricity W_e
- Lamp: Electricity $W_e \rightarrow$ Radiation Q_r
- Electric motor: Electricity $W_e \rightarrow$ Mechanical work W_m
- Combustion engine: Chemical energy $W_c \rightarrow$ Mechanical work W_m
- ...

For intermediate reservoirs, they may be the same as those for primary energies and there are others, such as:

- Battery (Chemical energy = microscopic potential energy)
- Flywheel (Macroscopic kinetic energy)
- Capacitor (electrical potential energy) or coil (magnetic potential energy)
- Compressed gas (Microscopic potential energy)
- Phase change material (Chemical energy = microscopic potential energy)
- Gasoline (Chemical energy = microscopic potential energy)
- ...

An example of an energy chain, respecting all the conventions, is shown in Figure 1.2.

1.3 System and state variables

1.3.1 System and surroundings

We call system (σ) the part of the universe being studied. The system is defined by its constituents (quantity and nature of matter) and by the portion of space it occupies (limited by a real or fictitious surface, deformable or not). The rest of the universe is the surroundings (σ_1). Thermodynamics is the science that studies the exchange of energy and matter between the system (σ) and the surroundings (σ_1). Depending on the possibilities of exchange, the system (σ) will be referred to as:

- **isolated system:** this system cannot exchange neither energy nor matter with the surroundings;

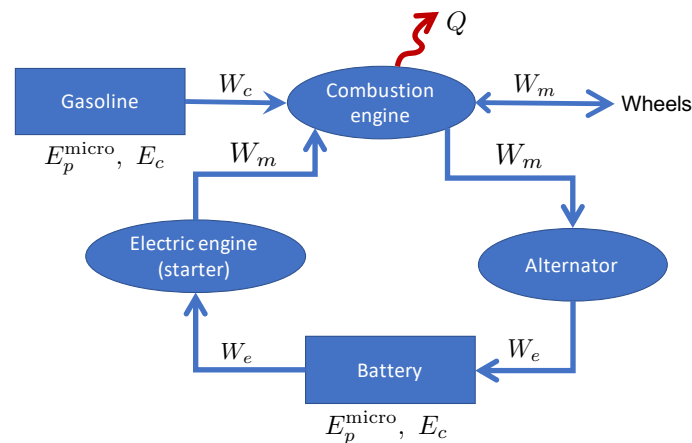


Figure 1.2: Example of the energy chain of a petrol car (including the role of the electric starter during the start-up phase).

- **closed system**: this system can exchange only energy (but not matter) with the surroundings;
- **open system**: this system can exchange energy and matter with the surroundings.

The sign convention used to qualify the exchanges is the so-called “convention du banquier”. The system is the reference and:

- *what is received by the system is counted positively;*
- *what is given by the system is counted negatively.*

Among the various forms that the surroundings (σ_1) can take, the case of an **ideal heat source** or **thermostat** should be defined as follows:

Definition 1.3.1 — Ideal heat source. An ideal heat source exchanges only heat with the system (σ) and its temperature remains constant throughout the process.

In a bithermal machine, the two sources that exchange heat with the fluid constituting the system, are called hot and cold source, depending on their respective temperatures.

1.3.2 State variables of a system

State variables are used to completely define the state of a system on a macroscopic scale at a given time. State variables are measurable quantities. A state variable can be defined locally (in a homogeneous part of the system) or for the entire system if it is completely homogeneous.

When a system is in a **state of equilibrium**, the state variables are uniform and constant over time in any homogeneous part of the system.

There are two types of state variables:

- **extensive variables** are variables that depend on the extent of the system (e.g. mass, volume...). These quantities are additive;
- **intensive variables** are variables that are independent of the extent of the system (e.g. density, concentration, pressure, temperature...).

The number of state variables needed to study the process of a system from an initial equilibrium state to a final equilibrium state will generally be limited. For example, in the case of a process undergone by a closed, homogeneous system, initially in equilibrium (uniform variables) and which will not undergo any change in its composition, the number of state variables necessary to characterise the state of the system will be limited to two. These variables will have to be

independent, *i.e.* they will be able to vary independently of each other (e.g. P and T , or P and V , or T and V).

Temperature

The particles (atoms, molecules, ions) that form matter are in perpetual motion. These are either disordered movements in the case of fluids (gas or liquid) or oscillations around an equilibrium position in the case of solids. The temperature of a system is a macroscopic measure of the degree of microscopic agitation of the particles in that system: the higher the temperature, the more intense the microscopic agitation of the particles.

The temperature of a substance is related to the mean microscopic kinetic energy $\langle E_{c,micro} \rangle$ of its atoms or molecules. The temperature T of an gas is defined by:

$$n_f \frac{1}{2} k_B T = \langle E_{c,micro} \rangle$$

where n_f is the number of degrees of freedom, *i.e.* $n_f = 3$ for a monoatomic gas (3 translational degrees), $n_f = 5$ for a diatomic gas (3 translational + 2 rotational degrees). The constant $k_B = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$ is the Boltzmann (1844-1906) constant. It is related to the Avogadro number N_A and the ideal gas constant $R = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ by the relationship:

$$R = N_A k_B$$

Pressure

The pressure exerted by a gas/object on a wall is defined as the averaged net force F of all atoms/molecules of this gas/object on the wall per unit surface S . The force is applied perpendicular to the wall and:

$$P = F/S$$

The pressure is measured in Pa ($1 \text{ Pa} = 1 \text{ N} \cdot \text{m}^{-2}$). Other common units are bar ($1 \text{ bar} = 1 \times 10^5 \text{ Pa}$), atmosphere ($1 \text{ atm} = 101\,325 \text{ Pa}$), millimetres of water column ($1 \text{ mm H}_2\text{O} = 9.8 \text{ Pa}$), millimetres of mercury ($760 \text{ mm Hg} = 1 \text{ atm}$) and torr ($1 \text{ torr} = 1 \text{ mm Hg}$).

For a gas, pressure is due to the impact of its molecules on a surface. A simple model of an instrument for measuring the pressure of a gas is the mercury barometer designed by Torricelli in the 17th century (Figure 1.3). With this apparatus, the pressure of the gas is exerted on the mercury in the container and causes it to rise in a closed tube under vacuum. The pressure is expressed directly by the height of the mercury in the column.

Exercise 1.1 Starting from the fundamental law of hydrostatics ($dP = -\rho g dz$), with P being the pressure, ρ density and z the altitude of the point considered, show that the mercury height BC is equal to 760 mm if the Torricelli barometer is placed in an atmosphere of pressure $P = 1 \text{ atm} = 1013.25 \text{ mbar} = 101\,325 \text{ Pa}$ (the density of mercury is $13.6 \text{ g} \cdot \text{cm}^{-3}$)

Volume

The volume of a system can be fixed or can vary during a process.

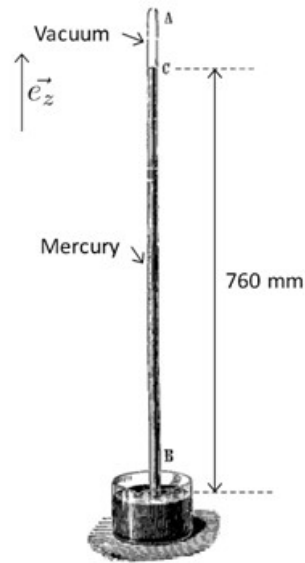


Figure 1.3: Torricelli's barometer.

Usually, volume variations of a system made of condensed phases (solid and/or liquid) and subjected to variations in temperature and pressure, may be considered negligible. On the other hand, volume variations of a system having at least one gaseous phase (in the initial or final state) must be considered.

1.4 Processes of a system

A process of a system is an evolution from one **state of equilibrium** (called the initial state) to another **state of equilibrium** (called the final state).

A system is at equilibrium if (and only if) the state variables describing it have constant values over time.

A disturbance from surroundings may cause a system to evolve. During the process, there is a change of some state variables, and there may be an exchange of heat and/or work (see Chapter 3), an exchange of matter, a modification of matter phase or composition (see Chapter 3 and 5).

Different types of processes are possible:

- **cyclic (or closed)**: if the initial state is identical to the final state;
- **isochoric**: if the volume of the system is constant during process;
- **isobaric**: if the system pressure is constant during the process;
- **monobaric**: if the system pressure is the same in the initial and final states but varies during the process;
- **isothermal**: if the temperature of the system is constant during the process (note that the process may be accompanied by heat exchange even if the temperature is constant);
- **monothermal**: if the temperature of the system is the same in the initial and final states but varies during the process;
- **adiabatic**: if there is no heat exchange between the system and the surroundings during the process. Note that the temperature of the system may vary, even if the system does not exchange heat with the surroundings. From a practical point of view, any process carried out in a very rapid manner can be considered adiabatic, as heat transfers between the system and the surroundings do not have time to take place.

1.5 Irreversibility

A **reversible process** is an **ideal process** for which (see more in Chapter 3):

- it is assumed that the system follows a infinite succession of equilibrium states (system and surroundings) at all times of the process. This process can be described as quasi static;
- an evolution of the process in the opposite direction is possible and will cause the system and the surroundings to pass through the same states of equilibrium again;
- there is continuity of the intensive quantities describing the system, absence of dissipative phenomena.

At the opposite, **irreversible processes** are all processes carried on in a not reversible way. Some sources of irreversibility are described in Chapter 4. The quantification of irreversibilities will be described by the second law of Thermodynamics and the manipulation of the entropy state function (see Chapter 4).

Chapter 2

Physical properties of pure substances and changes of state

Ideal gas model is experimentally established recalling historical experiments performed by Boyle, Mariotte, Charles and Gay-Lussac. It is then demonstrated from point mechanics using 2nd Newton's law. Partial pressure and relative density of gases are introduced.

The notion of vapour pressure is introduced for pure substance and mixtures. The experimental measurement of water vapour pressure is described and analysed leading to an experimental proof of Clausius-Clapeyron equation. The determination of relative air humidity and dew point serves as an application example.

The main properties associated with the three states of matter are recalled, as well as the vocabulary associated with changes of state.

Then the change of liquid-vapour state is described on the basis of the isothermal compression of a gas. The diagram (P, V) is used to describe all the stages of processing and the phases present at each stage.

The 3-dimensional change of state diagram (P, V, T) is presented, then the diagram (P, T) is detailed (fields, borders, phases).

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The **learning Objectives (O)** of this chapter are:

- Compare the properties of gaseous, liquid and solid states
- Cite the assumptions of the ideal gas model
- Write down the ideal gas equation and handle it with attention to the units (conversion of T , P and V)
- Express and calculate in the case of a mixture of gases: average molar mass, molar fractions, partial pressures, density, *etc.*
- Explain the concept of saturation vapour pressure P^* or P_{VS} , know its evolution according to temperature and know how to calculate it in given contexts
- Use the concept of saturated vapour pressure to predict the existence of a liquid/vapour equilibrium and to explain some observations from everyday life
- Distinguishing between evaporation and boiling
- Define the notions of dry air, wet air. Know how to express and calculate relative humidity
- To know the names of the changes of state at constant temperature
- Place the different fields (solid, liquid, vapour, super critical fluid) and name the curves on a diagram (P , V) of a pure substance
- Place the different fields (solid, liquid, vapour, super critical fluid) and name the curves on a diagram (P , T) of a pure substance
- To know the particularities of changes in water states

2.1 The Ideal Gas model

2.1.1 What is a gas?

A gas is a set of very weakly bonded atoms or molecules that has no volume of its own, but extends throughout the available volume. One can generally associate a temperature and a pressure to the gas which result from the movement of the atoms or molecules; the pressure is related to the force exerted by the atoms/molecules on the walls of the container containing the gas whereas the temperature is related to the kinetic energy of the atoms/molecules (see section 1.3.2).

2.1.2 Experimental observations

Around 1670 in England, Robert Boyle (1627-1691) observed that the air opposes an increased force as it is compressed. He then planned to study the elasticity of air using a very simple device (Figure 2.1), but without taking any particular precautions to keep the gas at a constant temperature. A U-shaped tube, with the large branch open to the atmosphere, contains air in the closed part. Equal levels in each of the legs indicates that the pressure exerted on the gas sample is equal to atmospheric pressure. The pressure of the gas can then be increased by adding mercury to the tube, and with each addition, the difference in level corresponds to the overpressure and the changes in volume of the gas can be measured. Boyle obtained the experimental results shown in Figure 2.1.

Boyle-Mariotte's Law

At the same time, in France, Abbot Edme Mariotte (1620-1684) obtained identical results. All this work led to the formulation of a law:

For a fixed quantity of the same gas at constant temperature, the product of pressure and volume is constant: $PV = \text{constant}$.

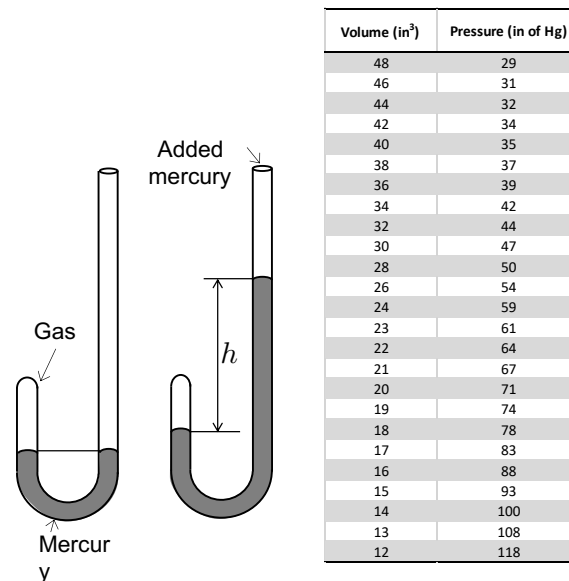


Figure 2.1: Boyle's experiment.

Exercise 2.1 Using Boyle's results (Figure 2.1), prove Boyle-Mariotte's Law by representing Boyle's data on a carefully chosen graph. ■

Charles's law and Gay-Lussac's law

A hundred years after Boyle and Mariotte's work, Jacques Charles (1746-1843) measured the effect of temperature variations on the volume of an air sample maintained under constant pressure (Figure 2.2). He showed the following relationship:

$$V = c(T + T_0) = V_0(1 + \alpha T)$$

where T is the temperature, $T_0 = 273.15^\circ\text{C}$ a constant, c a constant of proportionality, V_0 the volume of gas at 0°C , and $\alpha = 1/T_0$, the coefficient of expansion of the gas at constant pressure.

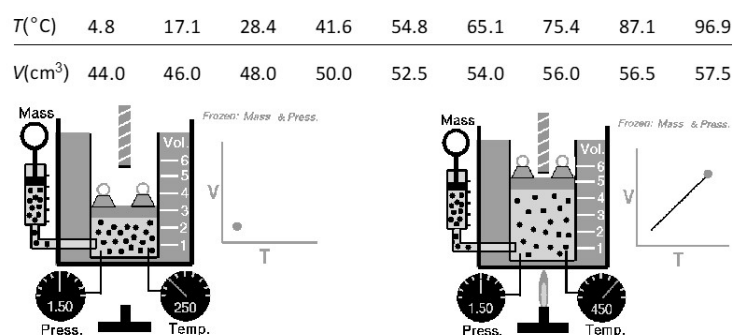


Figure 2.2: Charles' experiment.

Exercise 2.2 Draw Charles's experimental points on the graph below. Prove the validity of Charles' law and find the value of the constant T_0 . ■

Gay-Lussac completed Charles' work with the following law:

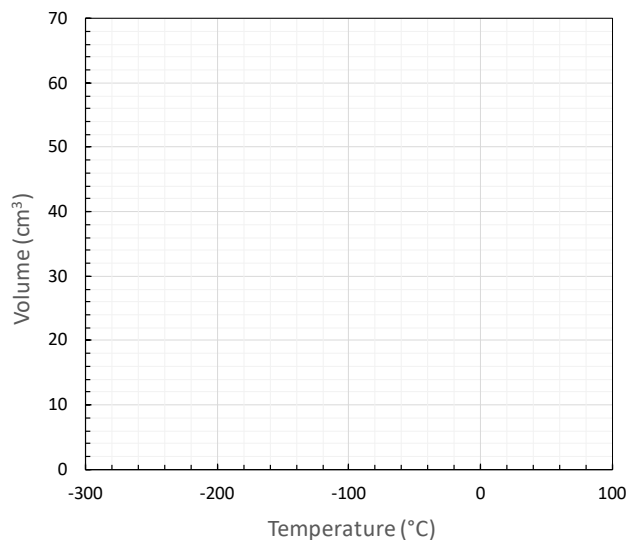


Figure 2.3: Plot here Charles's experimental results.

At constant volume, the heating of a mass of gas produces an increase in pressure proportional to the increase in temperature: $P = P_0(1 + \beta T)$

where P is the pressure of the gas at 0°C and the coefficient β is $\beta = \alpha = 1/T_0$.

These results led Lord Kelvin to believe that the point of intersection at $T_0 = -273^\circ\text{C}$ had to correspond to a minimum of the temperature below which it was impossible to go down. Hence came the idea of an absolute temperature scale, which is now universally used:

$$T_0 = 0^\circ\text{C} = 273.15\text{ K}$$

The notion of absolute temperature, proportional to the average kinetic energy of translation of the molecules, therefore necessarily positive or null is experimentally proven here, in agreement with the definition given in previous chapter (see section 1.3.2).

Charles's law can therefore be written in the form of $V = k_1 T$ (at constant pressure), where T is the absolute temperature. At constant pressure, the volume of a mass of gas is therefore proportional to its absolute temperature. In the same way, we can say that at constant volume, the pressure of a mass of gas is proportional to its absolute temperature: $P = k_2 T$.

The temperature T , which is independently proportional to the pressure and the volume, is therefore proportional to their product according to the following combined law:

$$PV = k_3 T$$

2.1.3 Ideal Gas Law

Following the work of Gay-Lussac, who observed that during chemical reactions the volumes of gas that are formed or that react are in a simple ratio (law of equivalent volumes), Avogadro interpreted these results by making the hypothesis that *equal volumes of gas, under the same conditions of temperature and pressure, contain the same number of molecules*. It can therefore be said that, under the same temperature and pressure conditions, the volume of a gas is proportional to the

number of molecules N , hence number of moles n which it contains. This leads to the so called “ideal gas law”:

$$PV = nRT = nN_A k_B T$$

expression in which R is the constant of ideal gases ($R = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, N_A is the Avogadro number ($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$) and k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$).

In the case of one mole of gas, we have: $R = PV/T = P_0 \bar{V}_0 / T_0$, expression in which $P_0 = 1 \text{ atm} = 1013.25 \text{ mbar} = 101325 \text{ Pa}$, $T_0 = 0^\circ \text{C} = 273 \text{ K}$ and \bar{V}_0 is the molar volume at pressure P_0 and temperature T_0 , which is 22.4 L .

More precise measurements than those made by Charles and Gay-Lussac have shown that gases only approach the behaviour described by the previous equations: they deviate from it especially at high pressures and temperatures, where molecules interactions modify their macroscopic behaviour.

Gases are therefore called “ideal” when ideal gas law applies. Another definition can also be proposed:

Definition 2.1.1 An ideal gas is a gas for which the potential interaction energy of the molecules is negligible compared to their kinetic energy.

Thus, in general, real gases tend towards the behaviour of ideal gases when their pressure becomes low, i.e. when chocs (interactions) between molecules become rare.

Exercise 2.3 Demonstration of ideal gas law.

Let's consider a parallelepipedic container of size $L_x \times L_y \times L_z$ in a coordinate system $(O, \vec{u}_x, \vec{u}_y, \vec{u}_z)$. We will calculate the pressure exerted by moving particles (gas molecules) of mass m on the container walls.

First, we study the bounce of one particle on the left wall perpendicular to \vec{u}_x axis. During the choc (lasting δt), the particle is submitted to a force $\vec{F} = F \vec{u}_x$. Its initial velocity is \vec{v} and final velocity is \vec{v}' (after the choc).

Second Newton's law gives: $\delta \vec{p} = \vec{F} \delta t$. Projections of this equations on \vec{u}_x , \vec{u}_y , \vec{u}_z and energy conservation lead to:

$$\begin{cases} m(v'_x - v_x) = F \delta t \\ m(v'_y - v_y) = 0 \\ m(v'_z - v_z) = 0 \\ v_x^2 + v_y^2 = v'^2_x + v'^2_y \end{cases}$$

This system gives: $v'_x = -v_x$, $v'_y = v_y$ and $v'_z = v_z$.

We now calculate the average pressure applied on the container walls by this particle. It makes a round trip to the same container wall (distance $2L_x$) during a time $\Delta t = 2L_x / v_x$.

The average force (time average over $\Delta t + \delta t \approx \Delta t$) is: $\langle F \rangle = \delta t / (\Delta t + \delta t) F = -mv_x^2 / L_x$. The average pressure exerted by N particles on the wall is then: $P_x = \sum_{i=1}^N m v_{xi}^2 / (L_x L_y L_z)$.

The product PV averaged over all container walls is then: $PV = V(P_x + P_y + P_z)/3$, leading to: $PV = \sum_{i=1}^N m(v_{xi}^2 + v_{yi}^2 + v_{zi}^2)/3 = N \langle mv^2 \rangle / 3$.

From the definition of temperature given in previous chapter ($\langle mv^2 \rangle = 3k_B T$), we finally get: $PV = nN_A k_B T = nRT$. ■

2.1.4 Ideal gas mixture: partial pressure

Given the laws of Gay-Lussac and Avogadro, it can be concluded that a mixture of ideal gases behaves like an ideal gas.

Partial pressure P_i of a gas i (n_i moles) in a mixture (n moles) is the pressure that this gas would have if it occupied alone the entire volume occupied by the mixture under the same temperature conditions.

If P is the total pressure of the mixture: $PV = nRT$ and $P_iV = n_iRT$. Hence:

$$\frac{P_i}{P} = \frac{n_i}{n}$$

$$P_i = x_i P$$

where $x_i = n_i/n$ is *the molar fraction of the gas in the mixture*.

The partial pressure of a gas in a mixture is equal to the product of its molar fraction ($x_i = n_i/n$) by the total pressure.

2.1.5 Density – Relative density of a gas

Density

Density ρ of a gas is its mass per unit volume: $\rho = m/V$.

Exercise 2.4 Using the ideal gas law, show that the expression of the density of a gas in state 2 (pressure P_2 , temperature T_2) can be expressed in terms of state 1 (pressure P_1 , temperature T_1) as $\rho_2 = \rho_1 \frac{P_2}{P_1} \frac{T_1}{T_2}$ ■

Relative density (or specific gravity) of a gas

The density of gas 1 relative to gas 2 is equal to the ratio of the masses of each gas occupying the same volume under the same temperature and pressure conditions. Thus, we have:

$$d_{1/2} = \left(\frac{m_1}{m_2} \right)_{T,P,V} = \left(\frac{n_1 M_1}{n_2 M_2} \right)_{T,P,V} = \frac{M_1}{M_2} = \frac{\rho_1}{\rho_2}$$

where M_1 and M_2 are the molar masses of these gases.

Usually, the air ($M_{air} = 28.8 \text{ g} \cdot \text{mol}^{-1}$ see below) is taken as the reference gas, we then have:

$$d_{1/air} = \frac{M_1}{M_{air}}$$

Average molar mass of an ideal gas mixture

In the case of a mixture of ideal gases, the previous results remain valid by considering the average molar mass of the mixture defined from the molar fractions x_i and molar masses M_i by:

$$\bar{M} = \sum x_i M_i$$

Exercise 2.5 Show that the molar mass of the air (78% N₂, 21% O₂, 1% Ar) is equal to 28.8 g·mol⁻¹. ■

2.1.6 A word about real gases

The actual gases deviate from the ideal behaviour in the general case. Depending on the nature of the gas and/or the pressure, positive or negative deviations from the ideal gas law will be observed. To describe the behaviour of these gases, equations of state are proposed from experimental results. One of the best known is the **Van der Waals equation** (1873), which uses corrective terms for pressure and volume (A and B are constants):

$$\left(P + A \frac{n^2}{V^2}\right)(V - nB) = nRT$$

2.2 Vapour pressure

At the surface of a liquid, due to thermal agitation, some molecules eventually evaporate even below the boiling point. This happens when the laundry dries on the clothesline at room temperature. At equilibrium, the same amount evaporate and condensate (see figure 2.4). The partial pressure of the gas is then called vapour pressure, and noted P^* or P_{vs} .

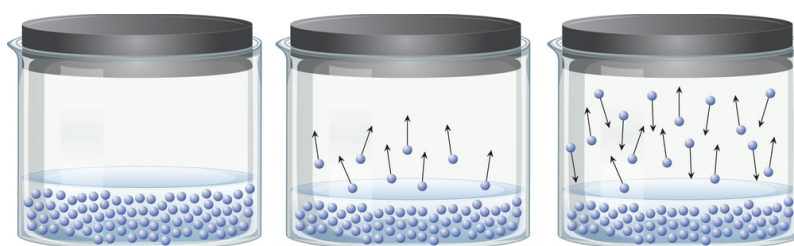


Figure 2.4: Due to thermal agitation, molecules of a liquid evaporate and eventually re condensate. At equilibrium, the same amount evaporate and condensate. The partial pressure of the gas is then called vapour pressure and noted P^* or P_{vs} (image from <https://pharmacyscope.com/vapour-pressure/>).

The higher the vapour pressure of a substance, the more likely it evaporates (*i.e.* the more “volatile” it is).

Vapour pressure depends on temperature: the higher the temperature, the more molecules evaporate, and the higher is the vapour pressure.

2.2.1 Case of the pure substance

Definition 2.2.1 A substance, whether solid, liquid or gaseous, is called a “pure substance” if, unlike a mixture, it consists of only one chemical species.

Definition of the vapour pressure in the case of a pure substance

Definition 2.2.2 In the case of a *pure substance*, the vapour pressure (P^* or P^*) is the pressure of that substance when it is at equilibrium in both liquid *and* gaseous form.

At equilibrium:

- If $P > P^*$ only liquid is present;
- If $P < P^*$ only gas is present;

- If $P = P^*$ gas and liquid are both present.

Note: for the solid-gas state change (called sublimation), a vapour pressure of sublimation can be defined, but as this is much lower than the vapour pressure of vaporisation, we will not consider it this year.

Experimental measurement of water vapour pressure

A flask is partly filled with liquid water at room temperature. Water is then heated until it boils. After a few minutes, all the air initially present into the flask is gone and only liquid and gaseous water remain. The cap is then closed and heating system is switched off. Temperature and pressure are then recorded during the cooling of the water (cap still closed) (see figure 2.5) .

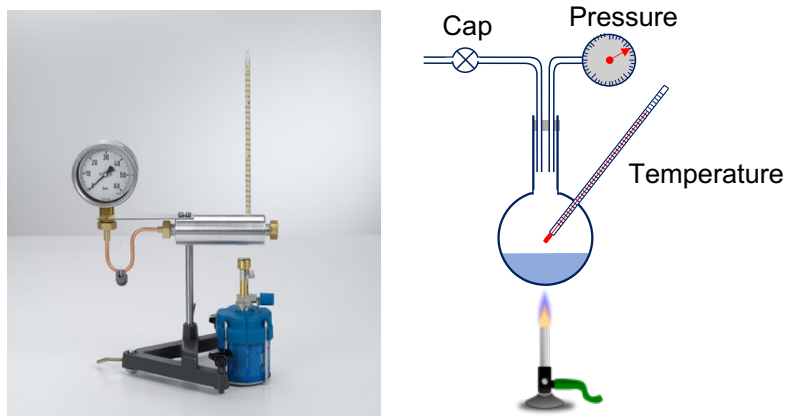


Figure 2.5: Experimental set-up for measuring vapour pressure as a function of temperature (left image from <https://www.leybold-shop.com/vp2-4-2-2.html>).

Figure 2.6 shows the evolution of the pressure inside the flask (pressure of the gas and liquid are equal inside the flask) when temperature drops from 373 K to 300 K.

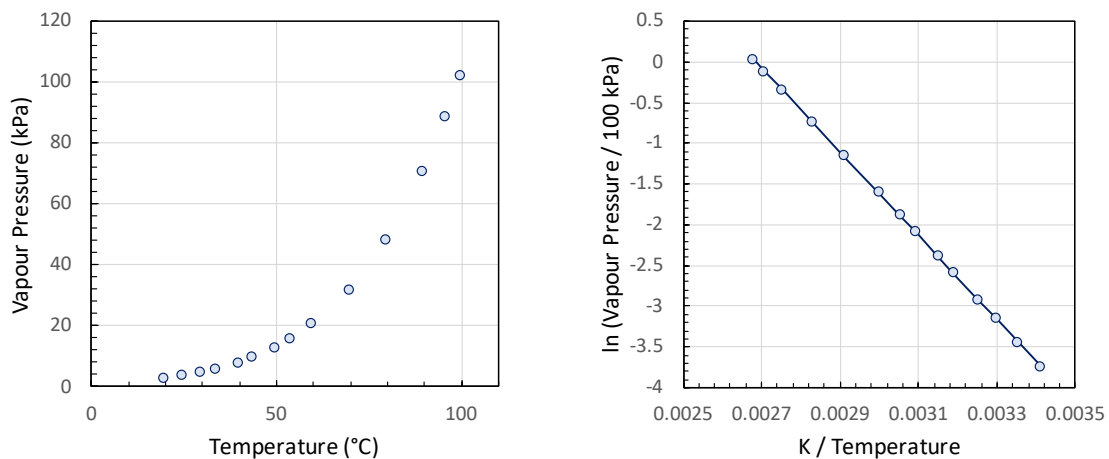


Figure 2.6: Water vapour pressure P^* versus temperature T (left) and $\ln(P^*/100\text{kPa})$ versus $1/T$ (right). The linear relation between $\ln(P^*/100\text{kPa})$ and $1/T$ proves experimentally the Rankin equation, derivation of the Clausius-Clapeyron equation: $P^* = P_0 \exp[-Q/R(1/T - 1/T_0)]$.

We can observe that at $T_{100} = 100^\circ\text{C}$, the vapour pressure of water is equal to $P_0 = 1\text{ atm} =$

101 kPa. This means that, at 100 °C, liquid water and vapour water at 1 atm are at equilibrium. In other words, under a pressure of 1 atm, water boils at 100 °C.

Now, if we plot $\ln(P^*/100\text{kPa})$ versus $1/T$ (see figure 2.6-right), we can observe a nice linear relation, leading to the experimental law:

$$\ln(P^*/100\text{kPa}) = \frac{a}{T} + b$$

where $a = 5149\text{K}$ and $b = 13.83$. Assuming $Q = -aR$ ($Q = 42.79\text{kJ}$), where R is the ideal gas constant and $P^*(T_{100}) = P_0$ (where $T_{100} = 100^\circ\text{C}$ and $P_0 = 1\text{atm} = 101\text{kPa}$), we finally get the vapour pressure of water dependency on temperature, also known as Rankin equation, a derivation of the Clausius-Clapeyron equation:

$$P^* = P_0 \exp \left[-\frac{Q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

2.2.2 Case of a gaseous mixture

Consider for example the Earth's atmosphere, which is mainly made up of 20% of O_2 and 80% of N_2 , but also other gases such as water vapour. The propensity of liquid water to evaporate is totally independent of the total atmospheric pressure but will depend solely on the **partial pressure of water vapour** $P_{\text{H}_2\text{O}}$. We recall the definition of partial pressure by considering all gases as ideal gases: $P_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}RT/V$. In very dry air (*i.e.* with $P_{\text{H}_2\text{O}} \approx 0$) the liquid water will evaporate very easily, and in a humid atmosphere ($P_{\text{H}_2\text{O}}$ relatively high) much less: in some climates it is very difficult to dry clothes.

Use of the concept of vapour pressure for gas mixtures

It can be observed that in the case of a gas mixture, the propensity to evaporate or liquefy is related to the comparison between the vapour pressure defined for a pure substance and the partial pressure of the gas (not the total pressure!).

Definition 2.2.3 The vapour pressure of a substance i as the partial pressure of the gas i such that there liquid and gas i are at equilibrium.

Assuming P_i as the partial pressure of gas i in the mixture ($P_i = n_iRT/V$ if ideal gas mixture) and P_i^* the vapour pressure of pure substance i :

- if $P_i > P^*$ the system is not in equilibrium, the gas will liquefy and P_i will decrease until it reaches P^* at liquid-gas equilibrium;
- if $P_i < P^*$ the system is not in equilibrium, the liquid will evaporate and P_i will increase until it reaches P^* at liquid-gas equilibrium;
- if $P_i = P^*$ we have equilibrium with the co-existence of the gaseous and liquid phase.

Boiling vs. evaporation

Above we have compared P_i with P^* to forecast the evolution of the system. It is also interesting to compare P^* with the system total pressure P_{tot} , *i.e.* the total pressure of the gas and of the liquid that are in mechanical equilibrium.

As long as $P_{\text{tot}} > P^*$ (the system pressure is higher than the saturation vapour pressure), a vapour bubble cannot form within the liquid because its pressure would be P^* , that is lower than the pressure of the liquid, and it would be automatically “crushed”. The liquid molecules that turn into gas necessarily do so on the upper surface of the liquid, a process called **evaporation**.

It is only when $P_{tot} = P^*$ that vapour bubbles can form inside the liquid at pressure P^* and be stable: this is the **boiling** process. The change of state is faster than during evaporation because the contact surface between gas and liquid is multiplied by the presence of bubbles.

If $P_{tot} < P^*$ the liquid-vapour equilibrium is impossible because boiling is immediate and the transition from liquid to gas is rapid.

■ **Example 2.1** For water, $P_{vs}(100\text{ °C}) = 101.4\text{ kPa}$ and $P^*(20\text{ °C}) = 2.3\text{ kPa}$. So, under normal atmospheric pressure water boils at 100 °C , but at 20 °C (as well as at any temperature below 100 °C) it evaporates! Conversely, if the partial pressure of the water in the atmosphere becomes higher than 2.3 kPa it's raining! ■

2.2.3 Evolution of vapour pressure with temperature

We observe that P^* increases with the temperature for all substances. This can easily be imagined at the microscopic level because, when the temperature rises, so does the agitation of the molecules in the liquid and, as a result, they are more likely to be "torn" out of the liquid and become gaseous.

The increase of the vapour pressure with temperature has several applications:

1. the boiling temperature of the water increases with the pressure. For example, $P^*(116\text{ °C}) = 1.8\text{ bar}$ in a pressure cooker, the boiling temperature will be above 100 °C . Conversely $P^*(84\text{ °C}) = 0.54\text{ bar}$, at the top of the Mont Blanc the boiling will take place at less than 100 °C !
2. The fact that P^* increases with temperature is what is known as "positive" feedback in climate change, *i.e.* it accelerates global warming. Indeed, water vapour is one of the gases with the strongest greenhouse effect (much more than CO_2) and, therefore, the interest is to keep the amount of water vapour in the atmosphere as low as possible. The amount of water vapour present in the atmosphere is limited by P^* ($n_{\text{H}_2\text{O}-\text{vap-max}} = P^*V/(RT)$). Since P^*/T increases with T , the amount of water in the form of vapour will increase with warming and increasing thus the greenhouse effect.

2.3 Humid air

2.3.1 Introduction

The air that surrounds us always contains a proportion of water in vapour form; this air is referred to as "humid air" as opposed to the idealized case of "dry air" that does not contain water vapour. Humid air therefore contains a variable but limited quantity of water vapour; when this quantity is at its maximum, it is called "saturated air". The maximum amount of water that can be contained in "saturated" air depends on the temperature and pressure conditions in which it is located.

2.3.2 Quantities used to study humid air

Humid air is considered to be an ideal mixture of gases: dry air and water vapour.

Relative humidity

In air saturated with water in vapour form, at the temperature T , the partial pressure of water vapour (noted as $P_{\text{H}_2\text{O}}^*(T)$) is equal to the vapour pressure of water at the same temperature: $P_{\text{H}_2\text{O}} = P_{\text{H}_2\text{O}}^*$.

By contrast, in humid unsaturated air at the same temperature T , we have that $P_{\text{H}_2\text{O}} \leq P_{\text{H}_2\text{O}}^*$.

It may be interesting to define a quantity to compare the amount of water in gaseous form contained in the air with the maximum quantity that may be present in saturated conditions. This leads us to define the **relative humidity** (or hygrometric degree).

Definition 2.3.1 The relative humidity (RH) is defined as:

$$RH = \frac{P_{\text{H}_2\text{O}}(T)}{P_{\text{H}_2\text{O}}^*(T)}$$

It can be noted that RH is a dimensionless quantity that is most often expressed in %.

We consider a volume V of humid air, at the pressure P and temperature T which contains a number of moles of water $n_{\text{H}_2\text{O}}$ in gaseous form. If the air is saturated, under the same conditions of temperature and pressure, it will contain a quantity, $n_{\text{H}_2\text{O}}^*$ of water vapour. The following relationships can be written:

$$n_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}V}{RT}$$

$$n_{\text{H}_2\text{O}}^* = \frac{P_{\text{H}_2\text{O}}^*V}{RT}$$

And therefore, we can express the relative humidity from the molar quantities: $RH = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}}^*}$.

By extension, it is also possible to express relative humidity from mass quantities, which is regularly the case in industry. Indeed, with the ideal gas law:

$$m_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}}M_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}V}{RT}M_{\text{H}_2\text{O}}$$

$$m_{\text{H}_2\text{O}}^* = n_{\text{H}_2\text{O},\text{sat}}M_{\text{H}_2\text{O}} = \frac{P_{\text{H}_2\text{O}}^*V}{RT}M_{\text{H}_2\text{O}}$$

This makes it possible to write now: $RH = \frac{m_{\text{H}_2\text{O}}}{m_{\text{H}_2\text{O}}^*}$

Dew point

Definition 2.3.2 The dew point of moist air is the temperature at which it must be cooled down for the first drop of liquid water to appear. The dew point is therefore the temperature at which the partial pressure of the water vapour is equal to its vapour pressure.

2.4 Changes of the phase of pure substances

2.4.1 General reminders

Pure substance

Definition 2.4.1 A substance, whether solid, liquid or gaseous, is called a “pure substance” if, unlike a mixture, it consists of only one chemical species.

Pure substances are a sample of matter with constant composition and specific chemical properties (*e.g.* H_2O , *etc.*). When they are made up of a single element in the atomic or molecular state (*e.g.* Cu , Fe , H_2 , O_2) they are specified as simple elements. The characteristics of changes of state of a pure substance are different from those of changes of state of a mixture (binary mixtures fall out of the scope of this book).

Comparative properties of the three states of matter

The characteristics of the three states of matter are summarised in Figure 2.7. In this figure the crystallised solid state is considered, as opposed to the amorphous (or glassy) solid state, which is an out-of-equilibrium state, which is similar to the liquid state from a thermodynamic point of view.

From a thermodynamic perspective, changes of state are accompanied by exchanges of work and heat, associated respectively with variations in volume (particularly between the gaseous state

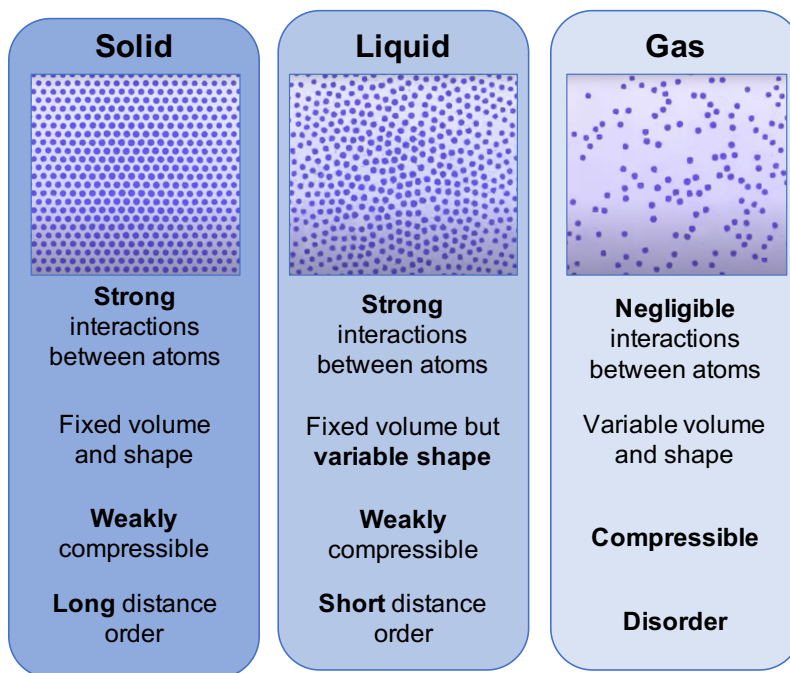


Figure 2.7: Summary of the characteristics of the physical states of matter (crystallised solid state).

and the liquid and solid states) and with the breaking or creation of bonds between atoms or molecules of the pure substance. The calculations of these quantities, resulting from the application of the 1st law, are detailed in Chapter 3. The heat exchanged during a change of state is called **latent heat**. It corresponds to the *amount of heat that is supplied or released to a mass unit of matter to change its physical state*. There are three types of latent heat of process:

1. the **latent heat of fusion or melting** L_{fus} linked to the transformation from the solid to the liquid state;
2. the **latent heat of vaporisation** L_{vap} linked to the transformation from the liquid state to the gaseous state;
3. the **latent heat of sublimation** L_{sub} linked to the transformation from the solid state to the gaseous state.

The associated reverse processes (respectively solidification or freezing, condensation, deposition) involve the same amount of heat, but, of course, **with an opposite sign**.

Latent heat is an intensive quantity, with dimensions $[\text{J}\cdot\text{kg}^{-1}]$ or $[\text{J}\cdot\text{mol}^{-1}]$.

In addition to the changes of state associated with the three physical states of matter (solid, liquid or gas), there are also solid to solid transformations, known as allotropic transformations. These are transformations from one state to the same state, but with different atomic organisation (*e.g.* from body centred cubic to face centred cubic). All the terms associated with the changes of state are grouped together in Figure 2.8.

2.4.2 Experimental observations

Heating curve when heating a pure substance at constant pressure

When a pure substance is heated regularly at constant pressure and its temperature T is measured as a function of time, a thermal analysis curve such as the one shown in Figure 2.9 is obtained for pure water.

Figure 2.9 shows the different stages encountered during the change of state of pure water under a pressure of 1 atm:

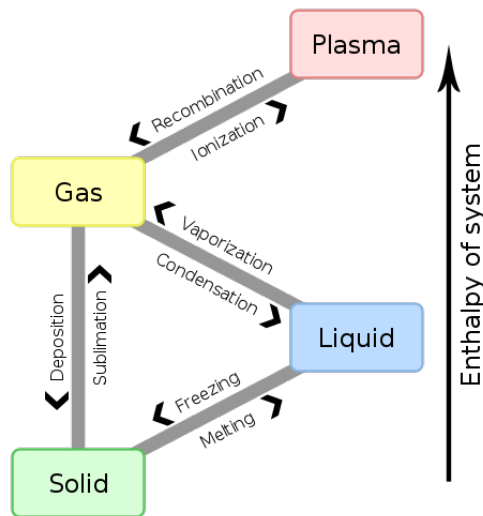


Figure 2.8: Denomination of changes of state.

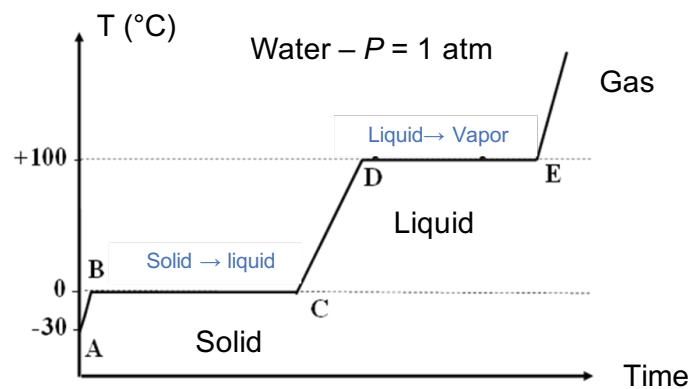


Figure 2.9: Idealised heating curve when heating pure water under atmospheric pressure.

- *Stage AB*: rise of the temperature of the solid; at B, the first drop of liquid appears establishing the solid/liquid equilibrium;
- *Stage BC*: here there is the the solid/liquid equilibrium and the provided heat is entirely used to melt the solid (so the temperature remains constant during this stage); at C, the melting of the solid is finished;
- *Stage CD*: the temperature of the liquid rises; at D, the first vapour bubble appears establishing the solid/liquid equilibrium;
- *Stage DE*: here there is the the liquid/gas equilibrium and the provided heat is entirely used to vapourise the liquid (so the temperature remains constant during this stage); at E, the vaporisation of the liquid is finished;
- *Stage E...*: beyond the point E, the gas temperature rises as long as we provide heat to the system.

Compression of a pure gaseous substance at constant temperature: case of CO_2

Now consider one mole of carbon dioxide at $T = 0^\circ\text{C}$ and $P = 1\text{ atm}$. Let's compress this gas in an isothermal and reversible way. In a pressure - volume diagram ($P = f(V)$), the curve obtained has a hyperbolic shape according to the ideal gas law ($PV = \text{const}$), although CO_2 does not behave

exactly like an ideal gas. If we compress until the pressure reaches 34 atm (the molar volume of the gas \bar{V}_{gas} is then close to $450 \text{ cm}^3/\text{mol}$), a first drop of liquid appears (point *B* on the diagram in Figure 2.10). If we compress again, the volume will obviously decrease but the pressure will remain constant as long as the two phases, liquid and gas, are present, hence the horizontal step on the diagram. When the total volume is equal to $\bar{V}_{liq} = 45 \text{ cm}^3/\text{mol}$ (point *A* on the diagram in Figure 2.10), the CO_2 will be entirely in the liquid state and further compression will result in a further pressure increase, the absolute value of the slope of the curve being very large due to the very low compressibility of liquids.

At 20°C , the phenomena observed would be the same: under an equilibrium pressure equals to 56 atm, liquid (of molar volume $\bar{V}_{liq} = 50 \text{ cm}^3/\text{mol}$) will appear in contact with vapour phase (of molar volume $\bar{V}_{gas} = 220 \text{ cm}^3/\text{mol}$).

At 31°C , \bar{V}_{gas} and \bar{V}_{liq} are equal ($95 \text{ cm}^3/\text{mol}$), so that the horizontal liquefaction step is reduced on the isothermal curve at point *C* ($P_c = 73 \text{ atm}$). At temperatures above 31°C (the critical temperature of CO_2), gas can be continuously transformed into liquid without phase transition.

All of the above experimental findings can be summarised in a Clapeyron diagram (Figure 2.10). On each isotherm, the horizontal plateau corresponds to the gas-liquid mixtures in such a way that the area of the plane below the saturation curve (obtained by joining the ends of the plateau together up to point *C*, shown as a dotted line in Figure 2.10) is a two-phase (liquid/vapour) equilibrium area. The part between *A* and *C* of the saturation curve is called the **boiling curve** and the *C* – *B* part is called the **dew curve**. At a given temperature, the equilibrium pressure in the two-phase range is the **vapour pressure** of the pure substance.

Consider states *R* and *S* in Figure 2.10. One can change from *R* to *S* by following the 0°C isotherm according to *R* – *B* – *A* – *S*. But one can also follow the path *R* – *E* (heating at constant volume), *E* – *F* (compressing at constant temperature) and *F* – *S* (cooling at constant pressure), reaching thus *S* without any without any phase change, contrary to the first case. This possibility of a continuous transition from the states *R* to *S* makes the terms liquid and gas somewhat imprecise. There is no natural criterion for distinguishing liquid from gas. If one follows the *R* – *E* – *F* – *S* path: where does the gas end, where does the liquid begin? It is because of this ambiguity that we introduce the **fluid state** without specifying whether it is liquid or gaseous. For temperatures above T_c and pressures above P_c , this is called the **supercritical state**.

2.4.3 State change diagrams

Pressure - Volume diagram

The pressure - volume diagram representing the liquid-vapour change of state is given in Figure 2.10 in the case of CO_2 . The liquid-vapour change of state for all pure substances will have the same characteristics in one diagram (P, V). In the two-phase field, characterised by a fixed temperature and pressure (vapour pressure), the proportions of each phase (liquid or vapour) vary.

Pressure - Temperature diagram

The pressure - temperature diagram of change of state is obtained by projecting the diagram (P, T, V) on the plane (T, P). An example is given in Figure 2.11. It shows the domains of existence of the solid, liquid and gaseous phases, as well as the triple point (*A* in Figure 2.11) and the critical point *E*.

The vaporisation curve, in the case of water in Figure 2.6-left, gives the evolution of the vapour pressure, $P_{\text{H}_2\text{O}}^*$, depending on the temperature between the triple point and the critical point. If we represent this evolution in the form $\log(P_{\text{H}_2\text{O}}^*) = f\left(\frac{1}{T}\right)$ the result is a straight line (Figure 2.6-right). This linear evolution can be modelled by taking into account 3 hypotheses and using the Gibbs free energy function *G* (see Chapter 6). The evolution of the saturated vapour pressure as a function of temperature can also be represented on a diagram plotted on a logarithmic scale (see Figure

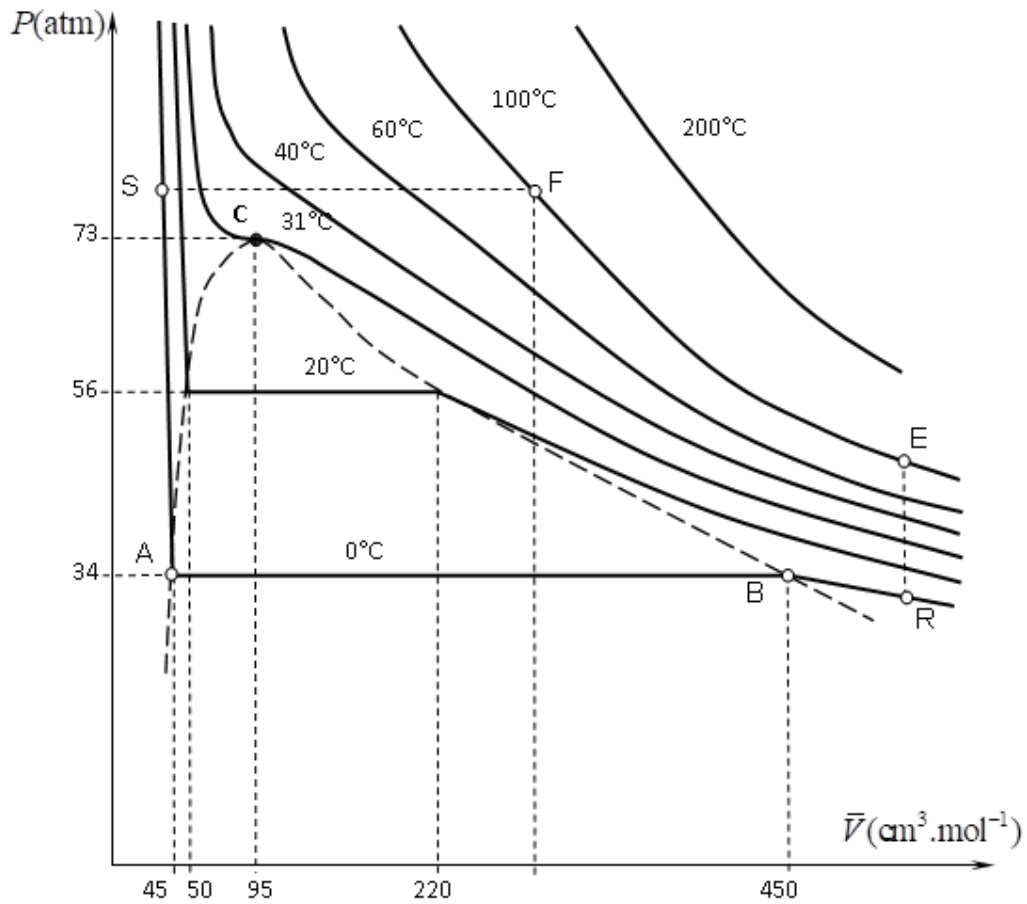


Figure 2.10: Pressure - Volume diagram of CO₂ vaporisation at different temperatures. The horizontal pressure plateaus in the two-phase range give the values of the CO₂ vapour pressure for the different test temperatures.

2.6-right).

For water the melting curve has a negative slope, whereas the melting curve of most other pure substances has a positive slope.

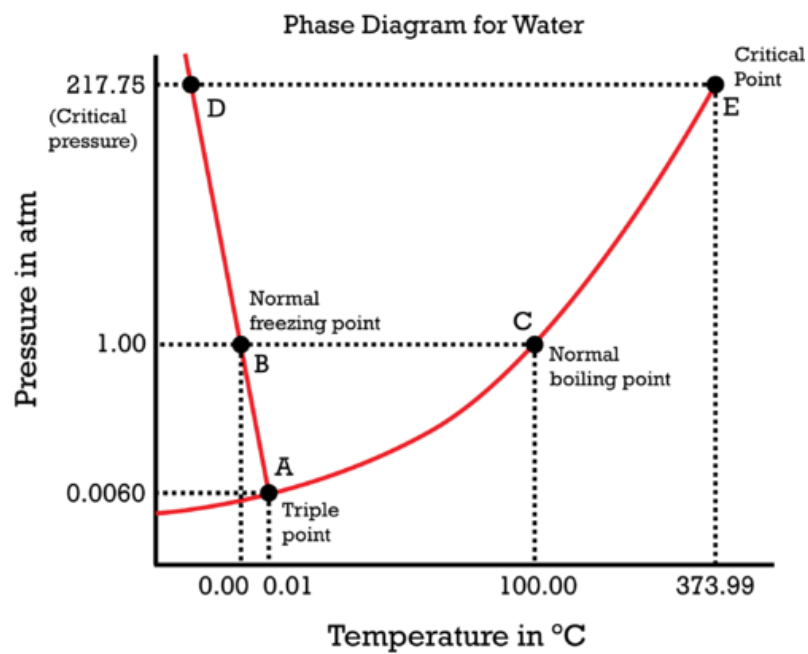


Figure 2.11: Pressure - temperature diagram of water state change.

Chapter 3

First law of Thermodynamics

This chapter presents the first law of thermodynamics (or law of energy conservation). Its application is studied for different systems (isolated, closed and open) and processes (isothermal, isochoric, isobaric and adiabatic) involving compressible (ideal gases) and incompressible (liquid and solid) phases. The notion of enthalpy is introduced. Heat capacities are defined depending on the processes and the phases of the matter. The notions of work and heat are defined as forms of exchanging energy. The notion of state and path functions is introduced allowing the calculation of internal energy and enthalpy variations, heat and work for reversible processes. Finally, thermal machines are introduced and their performance is defined for driving and receiving machines.

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The **learning Objectives (O)** of this chapter are:

- State the first law of Thermodynamics for isolated, closed and open systems
- Calculate the work of pressure forces for different reversible processes
- Propose a Clapeyron diagram representation for a reversible process, discuss the non-reversible case and graphically estimate the work involved
- Calculate the heat exchanged during the different reversible processes
- Distinguishing a reversible, or ideal, process from an irreversible process
- Distinguishing heat and temperature
- Distinguish: state function and path function
- Defining the enthalpy function
- State the expressions of internal energy and enthalpy variations for different processes using heat capacities
- Demonstrate and state Mayer's relationship to ideal gases
- Demonstrate and apply (with knowledge of the associated assumptions) the relation $PV^\gamma = \text{const}$
- Apply the first law to typical processes
- Applying the first law to changes of state
- Applying the first law to thermal machines
- Distinguish between efficiency and coefficient of performance in thermal machines

3.1 The First Law of Thermodynamics

3.1.1 Experimental observations

1) A lamp of mass m , defining a system σ is suspended from the ceiling of a room at a height h with respect to the ground (Figure 3.1-left: initial state A). The suspension wire breaks and the lamp falls in free fall onto a stone floor and breaks (Figure 3.1-right: final state B). It is considered that this fall has very little effect on the stone floor, which can be considered identical in states A and B. The ground is considered to be at altitude 0.

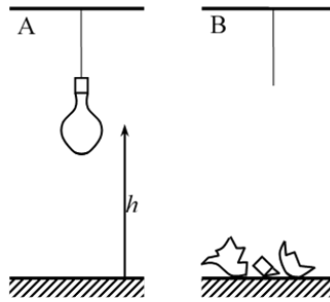


Figure 3.1: Example of a lamp falling to the ground due to the wire breaking.

In state A, the internal energy is equal to U_A , the kinetic energy $E_{c,macro,A} = 0$ and the potential energy $E_{p,macro,A} = mgh$. In state B, the internal energy is worth U_B , the kinetic energy $E_{c,macro,B} = 0$ and the potential energy $E_{p,macro,B} = 0$.

The total macroscopic mechanical energy variation is therefore non-zero, while the system is at rest in its initial state and in its final state. Mechanical energy has therefore been transferred to the system as internal energy. The increase in internal energy in σ is mainly due to the structural modification of the lamp (the lamp has broken and the creation of the new surfaces due to the breaks required energy). It may also be incidentally due to the temperature variation of the lamp parts, which may have heated up slightly during the impact.

2) In a famous experiment, James P. Joule showed how it is possible to vary the internal energy of a substance by the exchange of work or heat between the substance, *i.e.* the system, and the surroundings. He put water in insulated container (no heat exchange between the fluid and the surroundings) and he agitated the fluid with a rotating stirrer. The work done on the fluid by the stirrer, *i.e.* shaft work, increased the temperature of the fluid. Joule demonstrated that the increase of internal energy of the fluid measured by the temperature variation was equal to the work transferred to the fluid measured from the rotation of the stirrer. In addition, he also showed that the initial fluid temperature could be restored by allowing the heat exchange between the fluid and a cooler object thus showing that also heat can be used to vary the internal energy of any system.

3.1.2 First law or principle of energy conservation

This law, which is a general principle of physics, can be expressed as follows:

The total quantity of energy E_{total} is constant. When energy disappears in one form it appears simultaneously in other forms.

The total energy E_{total} is a conservative quantity, the physical content of which has been stated in the first chapter:

$$E_{total} = E_{c,macro} + \sum E_{p,macro} + U = const$$

with: $U = \sum E_{c,micro} + \sum E_{p,micro}$ the system's internal energy.

To apply the first law to any process, we need to remind that the total energy considered is the

energy of the system σ and of the surroundings. Therefore, for any process the first law requires that:

$$\Delta_t E_\sigma + \Delta_t E_{\text{surroundings}} = 0$$

where the term Δ_t indicates the temporal variation of the energy between an initial and final state ($\Delta_t = E_{\text{final}} - E_{\text{initial}}$).

In the context of thermodynamics, heat and work represent energy *in transit* across the boundary dividing the system from its surroundings. They are never stored or contained in the system and they can be seen as energy flows to or from a system. Conversely, internal, potential or kinetic energy represent quantities of energy contained in the system.

3.1.3 First law in isolated systems

Applied to an isolated system, *i.e.* a system that cannot exchange energy or mass with its surroundings (for example the universe), the first law states that its total energy cannot change:

$$\Delta_t E_\sigma = 0 \quad \rightarrow \quad \Delta_t E_{c,macro} + \sum \Delta_t E_{p,macro} + \Delta_t U = 0$$

with:

- $\Delta_t E_{c,macro}$ is the temporal variation in the overall (macroscopic) kinetic energy of the system between an initial state and a final state.
- $\sum \Delta_t E_{p,macro}$ is the temporal variation in the potential energies of external conservative forces.
- $\Delta_t U$ is the temporal variation of internal energy of the system (*i.e.* of all the microscopic potential and kinetic energies between the initial state and the final state).

If the system is mechanically at rest, the kinetic and macroscopic potential energy variations are zero and the first law of thermodynamics is reduced to:

$$\Delta_t U = 0$$

Unless otherwise specified, the system will henceforth be assumed to be at rest.

The last equation means that the internal energy of an isolated system is conserved.

3.1.4 First law in closed systems

Applied to a closed system the first law states that the temporal variation of the total energy of the system is equal to the energy exchanged with the surroundings. We have seen that the two ways of transferring energy are work W and heat Q . So that:

$$\Delta_t E_\sigma = W + Q \quad \rightarrow \quad \Delta_t E_{c,macro} + \sum \Delta_t E_{p,macro} + \Delta_t U = W + Q$$

If the system is mechanically at rest, the kinetic and macroscopic potential energy variations are zero and the first law of thermodynamics is reduced to:

$$\Delta_t U = W + Q$$

As stated before, the system will henceforth be assumed to be at rest unless otherwise specified.
For an elementary (**infinitesimal**) process, the first principle is written:

$$dU = \delta W + \delta Q$$

with d and δ indicating the differential of the quantity respect to the **time**.

Important note: the internal energy differential is noted with a "d" because it is the differential of a state function (see S7) (thus a small inventory change). Small exchanges of work and heat are not exact differential forms in the sense of OMSI (cf. semester 1) but, they are energy transfers and not stock variations and they are noted with a delta (δ).

3.1.5 Work

Work is one of the two ways that a system has to exchange energy with the surroundings (the other being heat, see next sections). You have studied in high school that work occurs when a force acts through a distance along the trajectory of a point. Work is the dot product of force and displacement. In the case where a constant external force \vec{F} allows the displacement of a solid from one position A to another position B, the work of this constant force is given by: $W = \vec{F} \cdot \vec{AB} = \|\vec{F}\| \cdot \|\vec{AB}\| \cdot \cos \alpha$ (Figure 3.2).

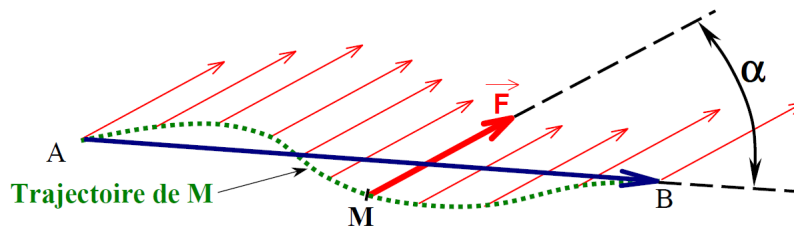


Figure 3.2: Work of a constant force along a path AB.

When the force \vec{F} varies during the movement (e.g. electrostatic force between two charges at a distance of r which varies in $\frac{1}{r^2}$), we generalize the previous expression, and the work of the force \vec{F} along a path AB is given by:

$$W_{A \rightarrow B} = \int_A^B \vec{F} \cdot d\vec{l}$$

Different types of work are possible depending on the type of force acting on the point. For example, we can find the work done by the gravity, by a spring, by the electric field or by a fluid. The latter is called work of pressure forces and it is a type of mechanical work.

Work of pressure forces

The work of pressure forces, w_{pf} is one of the two types of mechanical work that will be encountered most often in the course. It is done when an external pressure acts on a surface and displaces a volume of fluid, i.e. a liquid or a gas. An example is the movement of a piston with surface S in a cylinder which causes the compression or the expansion of the fluid (system) contained in the cylinder (Figure 3.3). The external pressure force acting on the system has a magnitude $P_{ext}S$ and is directed to the left, so $\vec{F} = -P_{ext}S \cdot \vec{u}_x$. The piston displacement can be written $d\vec{l} = dx \cdot \vec{u}_x$. If the piston moves to the left, $dx < 0$ otherwise $dx > 0$. So we have:

$$W_{pf} = \int \vec{F} \cdot d\vec{l} = - \int P_{ext} S dx$$

Here, Sdx corresponds to the variation in volume dV of the fluid, (which is negative if there is compression, *i.e.* when the piston moves to the left, and positive when there is expansion, *i.e.* when the piston moves to the right). This means that we can finally write the **general mathematical expression** of the work of pressure forces W_{pf} :

$$W_{pf} = - \int P_{ext} dV$$

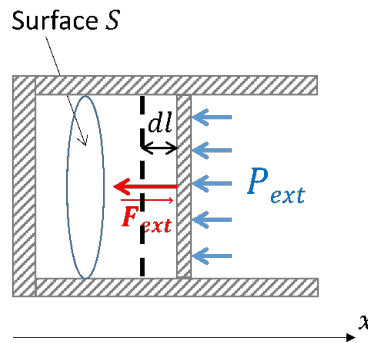


Figure 3.3: Compression of a fluid contained in a tank closed by a moving piston.

In the case of compression, the work exchanged by the fluid (= system) with the surroundings is positive: it receives energy in the form of mechanical work. In the case of fluid expansion, the work exchanged by the fluid with the surroundings is negative and so the fluid provides work to the surroundings.

Attention: W_{pf} is the work of external pressure forces, it is therefore the external pressure (*i.e.* the pressure of the surroundings) that leads to an exchange of work, and not the pressure of the fluid. The latter is equal to the external pressure only in reversible processes otherwise the two pressures are different.

Shaft work

The shaft work (W_s) is the other type of mechanical work considered in this course. It is called shaft work because it is often transferred by means of a rotating shaft, like that in a turbine or compressor. In this case, the shaft work corresponds to the work of a torque and it can be expressed by the product between the torque Γ and the angle of rotation θ as it will be seen in Physics in the 2nd semester.

$$W_s = \int \Gamma d\theta$$

However, the term shaft work is used more broadly to include any mechanical work (except the work of pressure forces) transferred to the system. For this reason we will not calculate the shaft work using the previous formula unlike the work of pressure forces.

Non mechanical works

The work of pressure forces and the shaft work represent transfers of mechanical energy. In this course we will consider only this two types of work but, however, other forms of work are possible. For example, energy can also be transferred in the form of electrical work: $W_e = \int U dq$ (seen in Physics in the 1st semester), with U the voltage (not the internal energy) at the terminals of the dipole through which the electric charge q passes. This is the case of batteries (that you will see more in details in Chemistry 2nd year) where the energy associated to a chemical reaction is transferred to the surroundings in this form.

3.1.6 Heat

We know from experience that a hot object brought into contact with a cold object becomes cooler, whereas the cold object becomes warmer. Something is transferred from the hot object to the cold one, and we call that something heat Q . Thus heat always flows spontaneously from a higher temperature to a lower one. This leads to the concept of temperature as driving force for the transfer of energy as heat. Without a temperature difference, no spontaneous heat transfer occurs. Like work, heat exists only as energy in transit from a system to or from its surroundings. In spite of the transient nature of heat, it is often viewed in relation to its effects on the system from which or to which it is transferred.

Heat effects refer to physical and chemical phenomena that are associated with heat transfer to or from a system. In this course we will study the following three heat effects that can be observed in a system due to heat transfer:

- heating or cooling, *i.e.* temperature changes of a substance;
- phase changes that are accompanied by latent heats;
- chemical reactions characterized by heats of reaction.

In any system these three heat effects can be observed separately or coupled together, for example when heating water to increase its temperature and to induce its vaporisation or a chemical reaction which releases heat and increases the temperature of the system. The mathematical expressions of the first two heat effects will be seen throughout this chapter whereas the expression of the last case will be provided in the fifth chapter on the thermochemistry.

3.1.7 State and path functions

The microscopic kinetic energy depends only on the thermal agitation speed of the particles. The microscopic potential energy depends only on the position of all the particles. The internal energy U therefore depends only on the state of the system, it is said to be a state function. This means that the variation in internal energy ΔU of the system depends only on the initial and final states of the system. For a system at rest in the initial state A and final state B, write:

$$\Delta_i U = W + Q = U_B - U_A$$

Let two different states A and B of the same system σ , be represented by two points in the space of the independent state variables used to describe the evolution of σ (Figure 3.4). One can go from state A to state B in an infinite number of ways (there is an infinite number of possible processes linking points A and B).

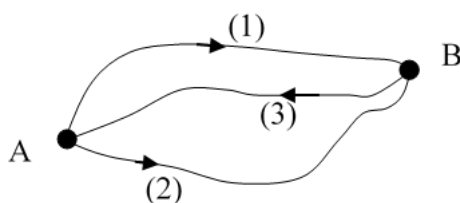


Figure 3.4:

Then let (1) and (2) be the paths corresponding to two different evolutions leading from state A to state B, and (3) the path corresponding to an evolution leading from state B to state A, and:

- W_1 and Q_1 the work and heat exchanged between σ and the surroundings during (1).
- W_2 and Q_2 the work and heat exchanged between σ and the surroundings during (2).
- W_3 and Q_3 the work and heat exchanged between σ and the surroundings during (3).

As it can be guessed from Figure 3.4, the works (W_1 , W_2 and W_3) and the heats (Q_1 , Q_2 and Q_3) exchanged along the three different paths are all different ($W_1 \neq W_2 \neq W_3$ and $Q_1 \neq Q_2 \neq Q_3$). Indeed, the work and the heat depend on the path chosen to go from the initial state A to the final state B. They are called **path functions**.

However, consider the closed process (1) + (3). We can write: $W_1 + W_3 + Q_1 + Q_3 = 0$.

Consider the closed process (2) + (3). We can write: $W_2 + W_3 + Q_2 + Q_3 = 0$.

Comparing the two previous expressions, it comes: $W_1 + Q_1 = W_2 + Q_2 = \text{const}$.

So, for any evolution i of the system σ from the initial state A to the final state B, we have:

$$W_i + Q_i = \text{const} = \Delta_i U$$

Consequently, the internal energy does not depend on the path chosen to go from A to B, but it depends only on the choice of the initial and final state. It is called a **state function**. In this case the first law can also be expressed as follows:

Whatever the process undergone by a system between a given initial state and a given final state, the total amount of energy $W + Q$ exchanged by this system with the surroundings during the process depends only on its initial state and its final state.

Case of a cycle

Because U is a state function, it is possible to write for a cycle going from state A to state B and then again to state A

$$\Delta U_t = (U_B - U_A) + (U_A - U_B) = 0$$

For a system undergoing a cycle, the total variation of internal energy is zero. Regarding the quantities of work W and heat Q exchanged with the surroundings during this process, they are different than zero but the sum of these two quantities is zero: $\Delta_t U = W + Q = 0$.

3.1.8 Reversible processes

The development of thermodynamics is facilitated by the introduction of a special kind of process characterized as reversible.

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions.

The reversible process is **ideal**; it represents a limit to the performance of an actual process that is never fully realized. Work is often calculated for hypothetical reversible processes, because the choice is between this calculation and no calculation at all. The reversible work may then be combined with an appropriate *efficiency to calculate the real work* involved in a real process.

The concept of reversible processes plays also a key role in the derivation of thermodynamics relationships. In this context, we often compute changes in thermodynamic state function (U but not only as we will see later) along the path of a hypothetical reversible process. If the result is a relationship involving only state functions, then this relationship is valid for *any process* starting from the same initial state and arriving to the same final state. Indeed, the primary use of the reversible process concept is for derivation of generally valid relationships among state functions. The mathematical definition of a reversible process needs the knowledge of the concept of entropy, a state function that will be introduced in the next chapter. However, we can provide here a list of features characterizing in a general way a reversible process that:

- can be reversed at any point by an infinitesimal change in external conditions;

- is never more than minutely removed from equilibrium;
- traverses a succession of equilibrium states meaning that the temperature and pressure of the system are the same of those of the surroundings;
- is frictionless;
- proceeds infinitely slowly;
- when reversed, retraces its path, restoring the initial state of system and surroundings.

3.2 General applications of the first law in closed systems

We present here the very general analysis of reversible processes for **any type of closed system**. Although of little interest for practical applications, they provide a very simple way of calculating changes in state functions for a specific change of state (from a certain initial to a final state). Indeed, for a complex industrial process that brings about a particular change of state, the calculation of changes in state functions are not made for the path of the actual process. Rather, they are made for a simple closed-system reversible process that brings about the same change of state. This is possible because changes in state functions are independent of the process, they depend only of the initial and final state. We will see later in this chapter how to obtain the specific mathematical expressions of $\Delta_i U$, Q and W depending on the considered substance (ideal gas, liquid or solid) and if the system experiences changes of temperature or changes of state or chemical reactions. Finally, we will see in a dedicated section at the end of this chapter how the first law is applied to open systems.

3.2.1 Adiabatic processes

Let's consider a closed system that cannot exchange heat with the surroundings ($Q = 0$). In this case, the system can exchange only work with the surroundings and the first law becomes:

$$\Delta_i U = W \quad (\text{adiabatic})$$

Here the exchanged work is the sum of the work of pressure forces and of the shaft work ($W = W_{pf} + W_s$). However, we will consider usually that only the work of pressure forces is applied and other types of work are nil. In this case, the calculation of work can be done either using the work definition $W_{pf} = - \int P_{ext} dV$ or calculating the variation of internal energy.

3.2.2 Isochoric processes

If the volume of the system remains constant during a process (isochoric process), there can be no work of external pressure forces, $W_{pf} = 0$, because $dV = 0$ and $W_{pf} = - \int P_{ext} dV$. Hence:

$$\Delta_i U = Q + W_s \quad (\text{const } V)$$

If we also consider that the closed system is subjected to no other work than that of pressure forces, we have:

$$\Delta_i U = Q \quad (\text{const } V)$$

In this case, the heat exchanged by the system with the surroundings during a constant volume (isochoric) process is equal to the variation of the internal energy of the system and therefore depends only on the initial and final state of the system in this particular case:

Having established that heat is equal to the variation of internal energy of the system in isochoric processes, we need now to find a mathematical expression for the internal energy in order to calculate the heat.

Important note: We will see that **more expressions are available** depending on the effect induced by the heat. For example, in the section on the heat capacity we will see the mathematical expression in the case where the heat induces only a change of temperature of the system. In addition, keep always in mind that **more effects coupled together are possible**.

3.2.3 Isothermal processes

A process is defined isothermal if it is reversible and the system keeps its temperature constant during the entire process. During an isothermal process, the system can exchange both heat and work with the surroundings and the first law becomes:

$$\Delta_t U = Q + W \quad (\text{const } T)$$

We will see later that the expressions of Q and W depend on the type of system and process chosen.

Note 1: an isothermal process is a very good example to highlight that the heat exchanged by a system is not forcibly coupled to the temperature of the system. Indeed, if it is true that heat can modify the temperature of a system, it is also true that a system can exchange heat without modifying its temperature (case of an isothermal process).

Note 2: keep in mind that the difference of temperature needed to have heat exchange is between the temperature of the surroundings (usually kept constant) and the temperature of the system. The latter can change or not, the only important thing is that remains different from the surroundings temperature in order to have heat exchange.

3.2.4 Isobaric processes

Let's consider a closed system subjected an isobaric process (reversible process at constant pressure). In this case the work of pressure forces is equal to:

$$W_{pf} = - \int P_{ext} dV = - \int P dV = -P \int dV = -P \Delta_t V = -P(V_f - V_i)$$

considering that the surroundings pressure (P_{ext}) is always equal to the system pressure (P) in a reversible process. Then we can calculate the variation of internal energy:

$$\Delta_t U = Q + W = Q + W_{pf} + W_s \quad (\text{const } P)$$

where we divided the global work as the sum between the work of pressure forces and shaft work. Considering that shaft work is nil ($W_s = 0$), the heat exchanged during an isobaric process is equal to:

$$Q = \Delta_t U - W_{pf} = \Delta_t U + P \Delta_t V \quad (\text{const } P)$$

The last equation shows us that, in this case heat cannot be directly determined by just knowing the variation of internal energy as in the previous case of an isochoric process. The term due to the work of pressure forces must be considered. It can therefore be more convenient to define another state function which, combining together the variation of internal energy and the work of pressure forces, would allow one to obtain immediately the heat exchanged during an isobaric process.

3.3 Enthalpy

The group $U + PV$ arises naturally in isobaric processes (see previous section) and in applications involving open systems. This suggests the definition, for convenience, of this combination as a new thermodynamic function.

Definition 3.3.1 The mathematical (and only) definition of enthalpy H is

$$H \equiv U + PV$$

Because U , P and V are all state functions, **enthalpy is a state function**. Enthalpy is an **extensive quantity**, such as U and V that it contains. Its variation is thus relative to the quantity of matter constituting the system that undergoes the process (we can also define a value of the molar enthalpy, noted \bar{H} . The amount of the system is calculated on the basis of one mole of material constituting the system).

The differential form of the enthalpy definition is:

$$dH = dU + d(PV)$$

This equation for any differential change of state. Upon integration, it becomes an equation for a finite change of state:

$$\Delta_t H = \Delta_t U + \Delta_t(PV) = \Delta_t U + P\Delta_t V + V\Delta_t P$$

In case of isobaric processes ($\Delta_t P = 0$), the last equation becomes:

$$\Delta_t H = \Delta_t U + P\Delta_t V$$

and, replacing in the previous energy balance, we find that:

$$Q = \Delta_t U + P\Delta_t V = \Delta_t H \quad (\text{const } P)$$

We finally obtain that the enthalpy change in a reversible, constant-pressure, closed-system process equals the amount of heat transferred into the system.

$$\Delta_t H = Q \quad (\text{const } P)$$

The heat exchanged by the system with the surroundings during a constant pressure (isobaric) process is equal to the variation of the enthalpy of the system and therefore depends only on the initial and final state of the system in this particular case:

The enthalpy plays a role in constant-pressure processes analogous to the internal energy in constant-volume processes. This equation suggests the usefulness of enthalpy, but its greatest use becomes fully apparent with its appearance in energy balances for flow processes (processes on open systems) as applied to heat exchangers, pumps, compressors, turbines, engines, etc., for the calculation of heat and work rates.

The numerical values calculation of Q and W for the infinite possible processes is impossible. However, it is possible to calculate the values of state functions, *i.e.* internal energy or enthalpy, as function of T and P for a substance of interest. These values can then be used to calculate Q and W for any process involving that substance. The determination of numerical values for these functions, in particular enthalpy, are treated later in this and in the following chapters.

3.4 Heat capacity

Our recognition of heat as energy in transit was historically preceded by the idea that gases, liquids and solids have capacity for heat, *i.e.* they can accumulate heat. Therefore, for a given quantity of heat, the smaller the temperature change caused in the substance, the greater its capacity. Following this idea a *heat capacity* was defined as $C \equiv \frac{dQ}{dT}$. The problem with this definition is that it makes C , like Q , a process-dependent quantity (path function) rather than a state function. However, we do now know that gases, liquids and solids (any substance) have capacity for internal energy, or enthalpy, that accounts for the microscopic kinetic and potential energies. We can therefore define two quantities that, although they retain this outmoded name, are state functions independent of the process.

3.4.1 Heat capacity at constant volume

Definition 3.4.1 The constant-volume heat capacity of a substance is defined as:

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

In this notation U is considered a function of T and V and C_V represents the partial derivative of U respect to T at constant volume (as indicated by the parentheses and the subscript). This type of notation is widely used in thermodynamics. It is needed because thermodynamics state functions, like U , can be written as functions of different sets of independent variables. For example we can write $U(T, V)$ or $U(T, P)$. Usually in multivariable calculus, a set of independent variables is unambiguous, and a partial derivative with respect to one variable implies constancy of the others. Because thermodynamics reflects physical reality, one may deal with alternative sets of independent variables, introducing ambiguity unless the variables being held constant are explicitly specified. The constant-volume heat capacity is an extensive quantity. Two corresponding intensive quantities (*i.e.* independent of the total mass of the system) can be defined as:

- Constant-volume molar heat capacity related to one mole of the considered substance and expressed in $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$$\bar{C}_{V_m} = \frac{C_V}{n}$$

- Constant-volume specific heat capacity related to 1 kg of the considered substance and expressed in $\text{J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$

$$\bar{C}_V = \frac{C_V}{m}$$

Although the definition of the constant-volume heat capacity makes no reference to any process, it relates in an especially simple way to a constant-volume process in a closed system, for which we obtain:

$$dU = m \bar{C}_V dT \quad (\text{const } V)$$

Integration yields:

$$\Delta_i U = m \int_{T_i}^{T_f} \bar{C}_V dT \quad (\text{const } V)$$

The last equation refers to the most general case that keeps into account the dependence of the heat capacity with the temperature. In our course we will deal most of the time with the case where

the heat capacity can be considered as independent of the temperature. In this case the integration gives:

$$\Delta_t U = m \bar{C}_V (T_f - T_i) = m \bar{C}_V \Delta_t T \quad (\text{const } V)$$

This equation gives us a mathematical expression for the heat in a constant-volume process with $W_s = 0$ and where the only heat effect is the change of temperature of the system:

$$Q = \Delta_t U = m \bar{C}_V \Delta_t T \quad (\text{const } V)$$

Unlike the previous equation, this equation linking the heat to the internal energy variation is valid **only for isochoric processes** where $W_{pf} = 0$ and $W_s = 0$. It is not valid for other processes because Q and W are path functions and so they change if the process is different. This is the reason for emphasizing the distinction between state functions and path functions such as Q and W . The principle that state functions are path- and process-independent is an essential concept in thermodynamics.

For the calculation of property changes, but not for Q and W , an actual process can be replaced by any other process going from the same initial to the same final state. The choice is made based on convenience, with simplicity a great advantage.

3.4.2 Heat capacity at constant pressure

Definition 3.4.2 The constant-pressure heat capacity of a substance is defined as:

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_P$$

Here, C_P is defined as the partial derivative of the enthalpy respect to the temperature keeping the pressure constant. As previously seen for the constant-volume heat capacity, also constant-pressure heat capacity is an extensive quantity and two corresponding intensive quantities (*i.e.* independent of the total mass of the system) can be defined as:

- Constant-pressure molar heat capacity related to one mole of the considered substance and expressed in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$$\bar{C}_{P_m} = \frac{C_P}{n}$$

- Constant-pressure specific heat capacity related to 1 kg of the considered substance and expressed in $\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$

$$\bar{C}_P = \frac{C_P}{m}$$

As before, although the definition of the constant-pressure heat capacity makes no reference to any process, it relates in an especially simple way to a constant-pressure (isobaric) process in a closed system, for which we obtain:

$$dH = m\bar{C}_P dT \quad (\text{const } P)$$

Integration yields:

$$\Delta_t H = m \int_{T_i}^{T_f} \bar{C}_P dT \quad (\text{const } P)$$

The last equation refers to the most general case that keeps into account the dependence of the heat capacity with the temperature. In our course we will deal most of the time with the case where the heat capacity can be considered as independent of the temperature. In this case the integration gives:

$$\Delta_t H = m\bar{C}_P (T_f - T_i) = m\bar{C}_P \Delta_t T \quad (\text{const } P)$$

This equation gives us the mathematical expression of the **heat exchanged only in a constant-pressure (isobaric) process** where the only observed heat effect is the change of temperature of the system:

$$Q = \Delta_t H = m\bar{C}_P \Delta_t T \quad (\text{const } P)$$

3.4.3 Temperature dependence of the heat capacity

Heat capacities are increasing functions of the temperature. However, they vary slowly the temperature and so they are generally considered to remain independent of temperature within a restricted temperature range. For our practical use in the exercises, most of the time heat capacities will be considered constant with temperature unless otherwise specified.

Note: if a change of state (e.g. liquid to gas) takes place in the temperature range investigated, the value of the heat capacity will change abruptly at the time of the change of state.

For general knowledge, the temperature dependence of the heat capacity at constant-pressure is usually modelled by an empirical polynomial function as:

$$\frac{C_P}{R} = \alpha + \beta T + \gamma T^2 + \delta T^{-2}$$

Because the ratio $\frac{C_P}{R}$ is dimensionless, the units of C_P are governed by the choice of R . This means that in our course, being $R = 8.31 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, the previous equation becomes:

$$\bar{C}_{P_m} = A + BT + CT^2 + DT^{-2}$$

where either C or D (sometimes both) is usually zero, depending on the substance considered. The parameters are independent of temperature, but, at least in principle, depend on the value of the constant pressure especially for gases. By contrast, for liquids and solids the effect of pressure is usually negligible.

3.4.4 Heat capacity in the ideal gas state

We have previously said that an ideal gas is a gas wherein there are no interactions between molecules (or atoms). In these conditions the ideal gas has still properties due to its internal molecular configuration, just as does a real gas, but without the influence of intermolecular interactions. Accordingly, the heat capacities of ideal gases are functions of temperature, but independent of pressure. Statistical mechanics provides a basic equation for the temperature dependence of the molar internal energy of the ideal gas:

$$U^{ig} = \frac{3}{2}RT + f(T)$$

and, from the enthalpy definition we can easily obtain also the temperature dependence of the of the molar enthalpy of the ideal gas:

$$H^{ig} = \frac{5}{2}RT + f(T)$$

These two equations allow us to obtain the numerical value of the molar heat capacities for monoatomic and diatomic ideal gases.

Monoatomic gases (e.g. argon Ar)

In this case we have $f(T) = 0$ and so:

$$\begin{aligned}\bar{C}_{V_m} &= \left(\frac{\partial U^{ig}}{\partial T} \right)_V = \frac{3}{2}R = 12.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ \bar{C}_{P_m} &= \left(\frac{\partial H^{ig}}{\partial T} \right)_P = \frac{5}{2}R = 20.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

Diatomic gases (e.g. oxygen O₂, nitrogen N₂)

In this case we have $f(T) = RT$ and so:

$$\begin{aligned}\bar{C}_{V_m} &= \left(\frac{\partial U^{ig}}{\partial T} \right)_V = \frac{5}{2}R = 20.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ \bar{C}_{P_m} &= \left(\frac{\partial H^{ig}}{\partial T} \right)_P = \frac{7}{2}R = 29.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

Moreover, for ideal gases (monoatomic, diatomic and polyatomic) we define also the **heat capacity ratio** γ , also called **adiabatic index** or **Laplace coefficient**, as:

$$\gamma = \frac{\bar{C}_{P_m}}{\bar{C}_{V_m}}$$

By replacing the corresponding numerical values we find that:

$$\gamma = \frac{5}{3} = 1.67 \quad (\text{for monoatomic gases})$$

$$\gamma = \frac{7}{5} = 1.4 \quad (\text{for diatomic gases})$$

Finally, being the heat capacities of ideal gases functions only of the temperature, it is possible to obtain a simple correlation between \bar{C}_V and \bar{C}_P for an ideal gas. Indeed, starting from the definition of enthalpy we have that the enthalpy variation is:

$$\Delta_t H = \Delta_t U + \Delta_t (PV)$$

The term PV in ideal gases is equal to nRT according to the ideal gas law. Therefore:

$$\Delta_t H = \Delta_t U + \Delta_t (nRT)$$

$$n\bar{C}_{P_m} \Delta_t T = n\bar{C}_{V_m} \Delta_t T + nR\Delta_t T$$

By simplifying the moles and $\Delta_t T$ we obtain the **Mayer's relation for an ideal gas**:

$$\bar{C}_{P_m} - \bar{C}_{V_m} = R$$

3.4.5 Heat capacity in the liquid and solid state (incompressible phases)

In our course, the two heat capacities \bar{C}_V and \bar{C}_P are always used in exercises with ideal gases. Indeed, due to their compressibility, the work of pressure forces is not negligible making $\Delta U \neq \Delta H$ for a same change ΔT of temperature. The situation is different with the incompressible phases, *i.e.* liquids and solids. In this case the work of pressure forces becomes negligible because $\Delta V \approx 0$ making the difference between the change of enthalpy and the change of internal energy during isobaric processes for a same ΔT negligible. Indeed:

$$\Delta_t H = \Delta_t U + P\Delta_t V \approx \Delta_t U \quad (\text{const } P)$$

As a consequence, we will obtain:

$$C_P \Delta_t T \approx C_V \Delta_t T$$

meaning that $C_V \approx C_P$ being $\Delta_t T$ the same in both expressions. For this reason, a unique value C of heat capacity independent of the type of process is used for liquids and solids:

$$C_P \approx C_V = C$$

$$\Delta_t U = \Delta_t H = m\bar{C} \Delta_t T \quad (\text{only for liquids and solids})$$

In the last equation the intensive counterpart of the heat capacity has been used. Indeed, the heat capacity C of liquids and solids is an extensive quantity and two corresponding intensive quantities (*i.e.* independent of the total mass of the system) can be defined as:

- Molar heat capacity for any type of process related to one mole of the considered liquid or solid substance expressed in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$$\bar{C}_m = \frac{C}{n}$$

- Specific heat capacity for any type of process related to 1 kg of the considered liquid and solid substance expressed in $\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}$

$$\bar{C} = \frac{C}{m}$$

3.5 Internal energy and enthalpy variations in a general system

In order to calculate the internal energy and the enthalpy variations of a general system, we need to express these state functions as function of the state variables P , V , T :

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

with the terms in the parenthesis corresponding to the partial derivatives of the state function respect to one state variable and keeping the other variable constant. We have seen that the partial derivatives respect to the temperature are the previously given definitions of the heat capacity thus obtaining:

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (\text{for any material})$$

$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (\text{for any material})$$

The second partial derivatives depend on the system considered (*e.g.* a solid, a liquid or a gas). For homogeneous fluids (*i.e.* liquids or gases) they are equal to:

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

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

The demonstration of these relationships will be given later because it requires the knowledge of the state function entropy introduced in the next chapter. By replacing the partial derivative terms we obtain:

$$dU = C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \quad (\text{for homogeneous fluids})$$

$$dH = C_P dT + \left[V - T \left(\frac{\partial V}{\partial T}\right)_P \right] dP \quad (\text{for homogeneous fluids})$$

These are general equations relating enthalpy and entropy to temperature and pressure for **homogeneous fluids of constant composition** once that the fluid equation of state is given. This equation tells how the state variables P, V, T are related in the fluid.

Having given the general equations to calculate the internal energy and enthalpy variation of any system and of homogeneous fluids, we are going to focus in the next sections on the systems that will be considered in our course. They are ideal gases, incompressible liquids and incompressible solids.

3.6 Applications to ideal gases

Ideal gases are characterized by the state equation: $PV = nRT$. We can therefore calculate precisely the second partial derivatives:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = 0 \quad (\text{for ideal gases})$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = 0 \quad (\text{for ideal gases})$$

and we obtain that:

$$dU = n\bar{C}_{V_m}dT \quad (\text{for ideal gases})$$

$$dH = n\bar{C}_{P_m}dT \quad (\text{for ideal gases})$$

where the system moles are explicitated by using the molar heat capacities. These equations show that the internal energy and the enthalpy of an ideal gas depend only on the temperature. The physical explanation is that the ideal gas is defined as a system formed by atoms or molecules that do not have any interactions between them (*i.e.* the potential interaction energy of the molecules is negligible compared to their kinetic energy). Therefore, the term in front of dP becomes nil. From the differential equations, we can find the time integrated form of the internal energy and enthalpy variation:

$$\Delta_t U = n\bar{C}_{V_m}\Delta_t T \quad (\text{for ideal gases and any process})$$

$$\Delta_t H = n\bar{C}_{P_m}\Delta_t T \quad (\text{for ideal gases and any process})$$

In the rest of this section we will focus on applications of the first law to reversible processes involving ideal gases.

3.6.1 Isothermal processes

Having previously seen that the internal energy (and its enthalpy) of an ideal gas is a function of only the temperature, the variation of internal energy of an ideal gas is nil if the reversible process is carried on at constant temperature (isothermal).

$$\Delta_t U = 0 \quad (\text{ideal gases at const } T)$$

As a consequence we have that:

$$Q = -W \quad (\text{ideal gases at const } T)$$

Considering that only the work of pressure forces is applied to the system, we can then calculate the work of an ideal gas during a reversible isothermal process from an initial state i to a final state f :

$$W_{pf} = - \int_{V_i}^{V_f} P_{ext} dV = - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \left(\frac{V_f}{V_i} \right)$$

$$W_{pf} = -nRT \ln \left(\frac{V_f}{V_i} \right) \quad (\text{ideal gases at const } T)$$

For a compression, we have that $\frac{V_f}{V_i} < 1$ and the work will be positive (work received by the system from the surroundings). For an expansion, $\frac{V_f}{V_i} > 1$ and the work will be negative (work done by the system to the surroundings).

From the expression of the work we immediately find the expression of the heat:

$$Q = -W_{pf} = nRT \ln \left(\frac{V_f}{V_i} \right) \quad (\text{ideal gases at const } T)$$

Let's now make some considerations on the work of pressure forces during an isothermal process. In particular, we want to compare the work W_{pf}^{rev} done during the reversible isothermal process with the work W_{pf}^{irrev} done during irreversible processes at constant T going from the same initial state i to the same final state f (monothermal processes). The superscripts *rev* and *irrev* are used here and later to avoid confusion between the two works of a reversible and irreversible process respectively. In the rest of the course we will always calculate the work in reversible processes, making the use of the superscript *rev* useless.

For an irreversible monothermal process, there are infinite possibilities of calculating the work because the volume and pressure of the system can change in infinite ways during the process (keeping as only condition that pressure and volume in the initial and final state allow one to have the same temperature). We will therefore choose how the system pressure and volume change during the monothermal process in order to calculate W_{pf}^{irrev} , and the choice will be done to keep the calculation as simple as possible. It is worth to point out that this choice does not affect the universality of the results that we will obtain; it will simply allow us to do the comparison in a less abstract and more mathematical way. We choose that the pressure of the system varies instantaneously from P_i to P_f at the beginning of the monothermal process. In this way the process can be considered as monobaric in addition to monothermal with the system pressure being equal to P_f during the entire process. In these conditions the irreversible work of the monothermal process can be calculated as:

$$W_{pf}^{\text{irrev}} = - \int_{V_i}^{V_f} P_{ext} dV = - \int_{V_i}^{V_f} P_f dV = -P_f \int_{V_i}^{V_f} dV = -P_f(V_f - V_i)$$

This expression can be rewritten by replacing P_f according to the ideal gas law:

$$W_{pf}^{\text{irrev}} = -P_f(V_f - V_i) = -\frac{nRT_f}{V_f}(V_f - V_i) = -nRT \left(1 - \frac{V_i}{V_f} \right) = nRT \left(\frac{V_i}{V_f} - 1 \right)$$

considering that $T_f = T_i = T$. We can now compare the irreversible work with the reversible one previously calculated and reported here:

$$W_{pf}^{\text{rev}} = -nRT \ln \left(\frac{V_f}{V_i} \right) = nRT \ln \left(\frac{V_i}{V_f} \right)$$

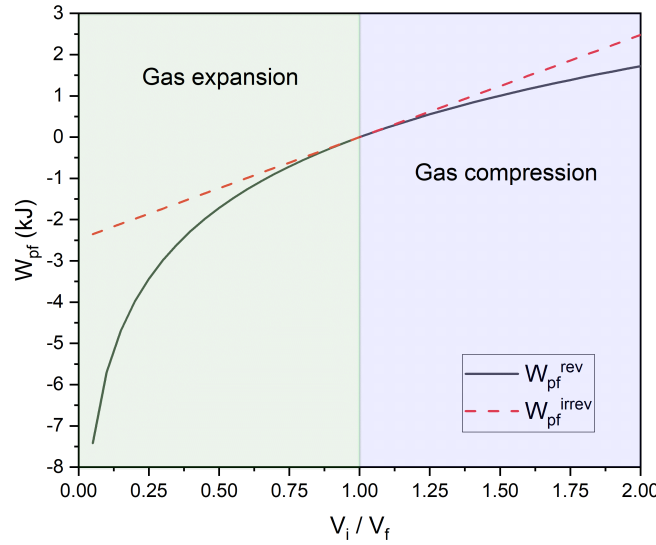


Figure 3.5: Comparison of the work of pressure forces exchanged during a monothermal (red dashed line) and isothermal (black continuous line) process. In both cases, the considered system is an ideal gas at 298 K made of 1 mole. The left green part of the graph refers to the case of a gas expansion whereas the right blue part refers to a gas compression.

In Figure 3.5 we compare W_{pf}^{rev} and W_{pf}^{irrev} as a function of the ratio $\frac{V_i}{V_f}$ calculated for a system made of 1 mole of ideal gas at 298K. Figure 3.5 shows the comparison for both cases of expansion ($\frac{V_i}{V_f} < 1$, work negative done by the system) and compression ($\frac{V_i}{V_f} > 1$, work positive received by the system) from a same initial to a same final state. In both case, $W_{pf}^{\text{rev}} < W_{pf}^{\text{irrev}}$. Therefore, less work is required to compress a gas ($W_{pf} > 0$) in a reversible way because, if we do the compression in an irreversible way, part of the energy provided is lost due to irreversibilities (*e.g.* friction), and so we must provide more work to arrive to the same final state. Similarly, during the gas expansion part of the energy transferred from the system to the surroundings is lost and for this reason the recovered irreversible work is lower than the reversible one.

These conclusions can be generalised to any type of process: a driving process ($W_{pf} < 0$) will provide more work the more it tends towards ideality (or reversibility); a receiving process ($W_{pf} > 0$) will require less work the more it tends towards ideality (or reversibility).

3.6.2 Isochoric processes

As seen previously for any type of system, if the process is carried on at constant volume ($\Delta V = 0$) the work of pressure forces from an initial state i to a final state f is nil:

$$W_{pf} = - \int_{V_i}^{V_f} P_{\text{ext}} dV = 0 \quad (\text{const } V)$$

Usually, also the shaft work is nil ($W_s = 0$) and, in this case the application of the first law gives:

$$Q = \Delta_t U = n \bar{C}_{V_m} \Delta_t T \quad (\text{const } V)$$

where the expression of the internal energy with the moles is used more often than the one with the mass (they are equivalent). For an ideal gas, we have already seen in a mathematical way that the expression $\Delta_t U = n\bar{C}_{V_m} \Delta T$ has a general validity. The same demonstration can be obtained also considering a transformation for an ideal gas from initial state i (pressure P_i and volume V_i) to final state f (pressure P_f and volume V_f). To calculate the variation of internal energy from i to f , we use the fact that U is a state function and decompose the transformation $i \rightarrow f$ into $i \rightarrow m$ and $m \rightarrow f$, where state m has the same temperature as state i and the volume as state f (see fig. 3.6). The variation of internal energy is $\Delta_t U = \Delta_t U_{i \rightarrow m} + \Delta_t U_{m \rightarrow f}$.

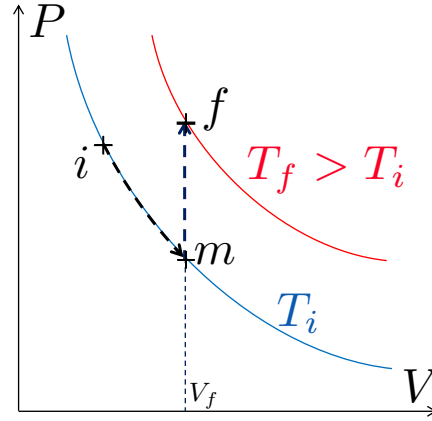


Figure 3.6: Transformation from initial state i to final state f through an intermediate state m : $\Delta_t U = \Delta_t U_{i \rightarrow m} + \Delta_t U_{m \rightarrow f}$.

As, U depends only on temperature for an ideal gas, $\Delta_t U_{i \rightarrow m} = 0$. We can deduce that $\Delta_t U = \Delta_t U_{m \rightarrow f} = W_{m \rightarrow f} + Q_{m \rightarrow f}$, where the transformation $m \rightarrow f$ is performed at constant volume, such that $W_{m \rightarrow f} = 0$. We finally get: $\Delta_t U = Q_{m \rightarrow f} = n\bar{C}_{V_m} \Delta T$ showing that:

$$\Delta_t U = n\bar{C}_{V_m} \Delta T \quad (\text{for any type of process with ideal gases})$$

3.6.3 Isobaric processes

If the reversible process from an initial state i to a final state f is carried on at constant pressure the work of pressure forces is:

$$W_{pf} = - \int_{V_i}^{V_f} P_{ext} dV = - \int_{V_i}^{V_f} P dV = -P(V_f - V_i) = -P\Delta_t V \quad (\text{const } P)$$

considering that the surroundings pressure (P_{ext}) is always equal to the system pressure (P) in a reversible process. Then we can calculate the variation of internal energy:

$$\Delta_t U = Q + W_{pf} \quad (\text{const } P)$$

considering that shaft work is nil ($W_s = 0$). Then, the heat exchanged during an isobaric process is equal to:

$$Q = \Delta_t U - W_{pf} = \Delta_t U + P\Delta_t V \quad (\text{const } P)$$

and introducing the enthalpy function we finally obtain:

$$Q = \Delta_t H = n \bar{C}_{P_m} \Delta_t T \quad (\text{const } P)$$

As previously done, for an ideal gas we can easily redemonstrate the general validity of the expression $\Delta_t H = n \bar{C}_{P_m} \Delta_t T$. Let's consider a transformation for an ideal gas from initial state i (pressure P_i and volume V_i) to final state f (pressure P_f and volume V_f). To calculate enthalpy variation from i to f , we use the fact that H is a state function and decompose the transformation $i \rightarrow f$ into $i \rightarrow m$ and $m \rightarrow f$, where state m has the same temperature as state i and the pressure as state f (see fig. 3.7). The variation of internal energy is $\Delta_t H = \Delta_t H_{i \rightarrow m} + \Delta_t H_{m \rightarrow f}$.

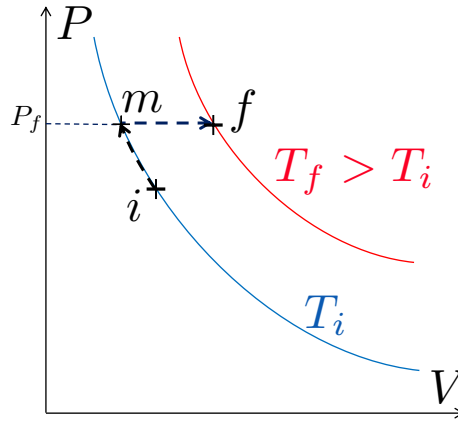


Figure 3.7: Transformation from initial state i to final state f through an intermediate state m : $\Delta_t H = \Delta_t H_{i \rightarrow m} + \Delta_t H_{m \rightarrow f}$.

As, H depends only on temperature, $\Delta_t H_{i \rightarrow m} = 0$. We can deduce that $\Delta_t H = \Delta_t H_{m \rightarrow f} = W_{m \rightarrow f} + Q_{m \rightarrow f} + \Delta_t (PV)_{m \rightarrow f}$, where the transformation $m \rightarrow f$ is performed at constant pressure, such that $W_{m \rightarrow f} + \Delta_t (PV)_{m \rightarrow f} = 0$. We finally get: $\Delta_t H = Q_{m \rightarrow f} = n \bar{C}_{P_m} \Delta_t T$ showing that:

$$\Delta_t H = n \bar{C}_{P_m} \Delta_t T \quad (\text{for any type of process with ideal gases})$$

3.6.4 Adiabatic processes

In a reversible adiabatic process the system cannot exchange heat with the surroundings ($Q = 0$). In this case the first law states:

$$\Delta_t U = W$$

Considering that only work of pressure forces is present and using the expression of U as function of T for an ideal gas we obtain:

$$W_{pf} = n \bar{C}_{V_m} \Delta_t T \quad (Q = 0)$$

However, we could calculate W_{pf} for an adiabatic process also from its definition obtaining:

$$W_{pf} = - \int_{V_i}^{V_f} P_{ext} dV = - \int_{V_i}^{V_f} P dV$$

In order to integrate the term PdV we need to know how the system pressure changes during a reversible adiabatic process, *i.e.* we need to know the equation of state of ideal gases during a reversible adiabatic process (that is **not** $PV = nRT$). We can obtain this dependence by coupling together the first law and the definition of W_{pf} expressed in the differential form:

$$\begin{aligned} dU &= \delta Q + \delta W_{pf} = \delta W_{pf} \\ \delta W_{pf} &= -P_{ext}dV = -PdV \end{aligned}$$

We obtain:

$$dU = -PdV \rightarrow n\bar{C}_{V_m}dT = -\frac{nRT}{V}dV \rightarrow \frac{dT}{T} = -\frac{R}{\bar{C}_{V_m}}\frac{dV}{V}$$

where we used the ideal gas law. Integrating both terms between the initial state i and the final state f we have:

$$\int_{T_i}^{T_f} \frac{dT}{T} = -\frac{R}{\bar{C}_{V_m}} \int_{V_i}^{V_f} \frac{dV}{V} \rightarrow \ln\left(\frac{T_f}{T_i}\right) = -\frac{R}{\bar{C}_{V_m}} \ln\left(\frac{V_f}{V_i}\right) \rightarrow T_f V_f^{\frac{R}{\bar{C}_{V_m}}} = T_i V_i^{\frac{R}{\bar{C}_{V_m}}}$$

By removing the logarithm and using the Mayer's relation together with the definition of the heat capacity ratio we finally obtain:

$$T_f V_f^{\frac{R}{\bar{C}_{V_m}}} = T_i V_i^{\frac{R}{\bar{C}_{V_m}}} \rightarrow T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

The last equation represents the equation of state of ideal gases during a **reversible adiabatic** process which can be written in three equivalent forms:

$$PV^\gamma = \text{const}$$

$$TV^{\gamma-1} = \text{const}$$

$$P^{1-\gamma}T^\gamma = \text{const}$$

It is possible to pass from one form to the others by replacing one of the state variables (P, V, T) with the ideal gas law $PV = nRT$.

At this point we can develop the integral to find W_{pf} . We replace P using the first equation rewritten between the initial state i and a generic intermediate state of the process:

$$\begin{aligned} P_i V_i^\gamma &= P V^\gamma \\ W_{pf} &= - \int_{V_i}^{V_f} \frac{P_i V_i^\gamma}{V^\gamma} dV = -P_i V_i^\gamma \int_{V_i}^{V_f} \frac{1}{V^\gamma} dV = -\frac{P_i V_i^\gamma}{1-\gamma} (V_f^{1-\gamma} - V_i^{1-\gamma}) \end{aligned}$$

We finally obtain that the work of pressure forces in a reversible adiabatic process is:

$$W_{pf} = \frac{1}{\gamma-1} (P_f V_f - P_i V_i) \quad (Q = 0)$$

For a reversible adiabatic process we have two mathematical expressions of W_{pf} that are equivalent and give the same numerical value (of course). The choice of which one should be used depends on which one is simpler to use depending on the available data.

So far, we have seen how to calculate Q and W_{pf} for reversible adiabatic processes. Let's see

now what happens in irreversible adiabatic processes. In this case, we have always that $Q^{irrev} = 0$ (definition of adiabatic process) and so by applying the first law we obtain again the same expressions also for the irreversible work:

$$W_{pf}^{irrev} = \Delta_t U = n \bar{C}_{V_m} \Delta_t T \quad (Q^{irrev} = 0)$$

In addition, by using the ideal gas law and the Mayer's relation we can see that:

$$W_{pf}^{irrev} = \frac{1}{\gamma - 1} (P_f V_f - P_i V_i) \quad (Q = 0)$$

We can therefore say that for an adiabatic process (reversible or irreversible):

$$W_{pf} = \Delta_t U = n \bar{C}_{V_m} \Delta_t T = \frac{1}{\gamma - 1} (P_f V_f - P_i V_i) \quad (\text{for adiabatic processes})$$

However, we do know by now that work is a path function and so it cannot be the same in a reversible and irreversible process. The reason why we have the same expressions is that the final state of a reversible and irreversible adiabatic process starting from the same initial state i is different. The reversible process will lead from state i to state f , whereas the irreversible process will lead from state i to the different state f' . Therefore the variation of internal energy of the two processes is different thus leading to different numerical values of the reversible and irreversible work of pressure forces ($W_{pf}^{irrev} \neq W_{pf}^{rev}$) as expected.

Reversible and irreversible adiabatic processes are both characterized by no heat exchange ($Q^{rev} = 0, Q^{irrev} = 0$). However, due to the presence of irreversibilities in the irreversible process, they lead to different final states meaning that the change of internal energy $\Delta_t U$ of the two processes is different. That's why, even if the reversible and irreversible work of pressure forces are different ($W_{pf}^{irrev} \neq W_{pf}^{rev}$), we can calculate them using the same mathematical expressions.

3.6.5 Graphical representation of work in reversible processes

Any fluid in a thermodynamic equilibrium state can be characterized by thermodynamic quantities, state variables or state functions. It can therefore be useful to represent these states in thermodynamic diagrams, as a function of two variables or state functions, in order to describe a process, but also to graphically calculate other quantities, such as work and the amount of heat exchanged. We will limit ourselves here to single-phase gaseous systems, but this type of diagram can also be used for multiphase systems, for example to study the change of state of a pure substance.

The pressure - volume (also called Clapeyron) diagram, where the volume is on the abscissa and the pressure on the ordinate, makes it possible to represent a thermodynamic state or a process, by the set of couples (P, V) when these are defined (Figure 3.8). It should be noted that the x-axis can also represent the molar volume (expressed in $\text{m}^3 \cdot \text{mol}^{-1}$ and noted \bar{V}) or the volume per unit mass (expressed in $\text{m}^3 \cdot \text{kg}^{-1}$ and noted v). In some works, this representation can be called the Watt diagram.

Representation of processes of ideal gases

A process can be completely represented in a diagram by a continuous line, only when all the thermodynamic states are known and defined, *i.e.* when the system under study follows a succession of states of equilibrium with the surroundings at all instants of the process. As presented in O3, this situation corresponds to an ideal, or reversible, process. In summary, only reversible processes can be represented by a continuous line in thermodynamic diagrams. The main processes are represented in the Clapeyron diagram as shown in Figure 3.9:

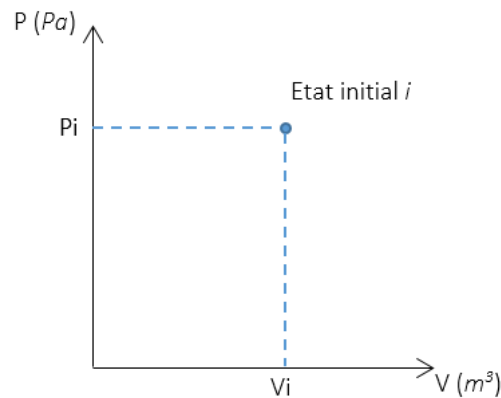


Figure 3.8: Clapeyron diagram.

- Isobaric processes are represented by horizontal lines (blue line).
- Isochoric processes are represented by vertical lines (green line).
- Isothermal processes of ideal gases are represented by equation curves: $PV = \text{const}$ (cf. O4) or, equivalently, $P = \frac{\text{const}}{V}$ (orange line). These equations are equilateral hyperboles.
- The reversible adiabatic processes of ideal gases are represented by equation curves: $PV^\gamma = \text{const}$ (see O10) or, equivalently, $P = \frac{\text{const}}{V^\gamma}$ (violet line).

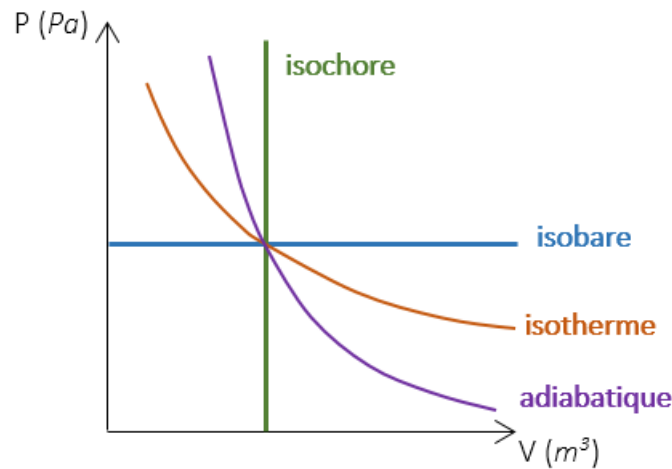


Figure 3.9: Typical process patterns in a Clapeyron diagram.

Calculation of the work exchanged during a process and a cycle

Consider a mole of ideal gas in a cylinder, closed by a piston. Initially, the gas is in a thermodynamic state I described in Figure 3.8 by the couple (P_i, V_i) . As the piston moves down, the gas is compressed, the volume decreases and the pressure increases, the point representing the thermodynamic state moves up and to the left and the work received by the gas is positive. When the piston rises, the gas expands, the volume increases, the pressure decreases, the point moves downwards and to the right. The work here is negative. This experiment allows us to “guess” that it is possible to link the work, and its sign, to the plot of a process in a Clapeyron diagram.

For example, still in the same configuration, the very slow expansion of the gas against a constant external pressure can be plotted in the Clapeyron diagram in Figure 3.10. In Figure 3.8, for a process of I to F, $\int P dV > 0$ so: $W_{pf} = W_{gas} < 0$.

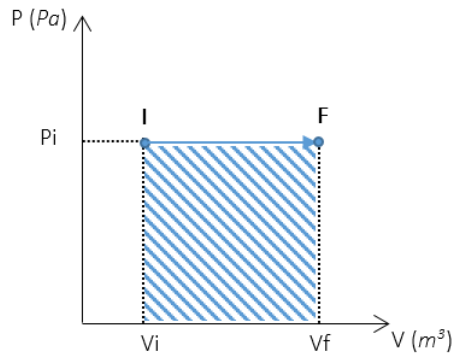


Figure 3.10: Very slow expansion of a gas against external pressure ($P_{\text{ext}} = P_i$).

In the opposite direction, from F to I, $\int P dV < 0$ so: $W_{pf} = W_{\text{gas}} > 0$.

For an isochoric process, the area under the curve is zero, and it is confirmed that the work of the pressure forces is nil. In the case of cyclic gas process (Figure 3.11), it is therefore possible to determine the total work of the pressure forces and its sign from the area of the cycle.

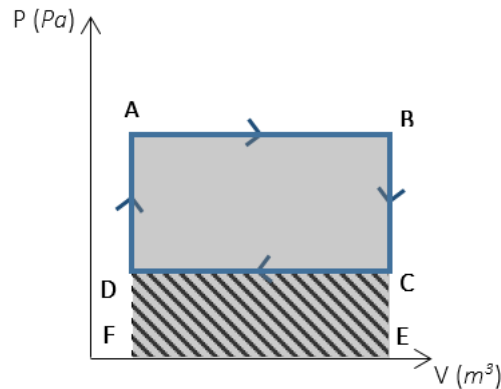


Figure 3.11: Case of a cyclical process.

The total work of the pressure forces is equal to: $W_{\text{total}} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$.

The BC and DA processes are isochoric (the area under the curves is zero), therefore $W_{BC} = W_{DA} = 0$. The work exchanged during the AB process is equal to the opposite of the area of the rectangle ABEF (shaded), and is therefore negative. The work exchanged during the CD process is equal to the area of the rectangle CDEF (hatched), and is therefore positive. Finally, the total work is therefore equal to the opposite of the area of the rectangle ABCD. The total work is negative, the gas provides work to the surroundings, this cycle is therefore called “engine”.

In summary, during a reversible cyclic process of an ideal gas, the area of the cycle in the Clapeyron diagram is equal to the absolute value of the total work of the pressure forces.
If the cycle is carried out in the direct or trigonometric direction, the total work is positive ($W_{\text{total}} > 0$) (Figure 3.12-left).
If the cycle is carried out in the indirect or clockwise direction, the total work is negative ($W_{\text{total}} < 0$) (Figure 3.12-right).

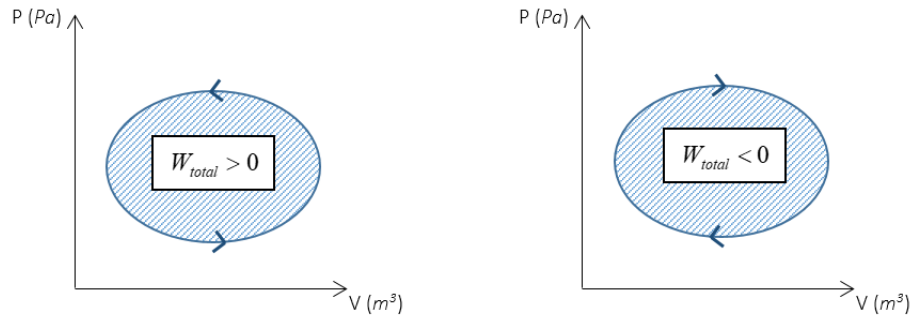


Figure 3.12: Sign of work exchanged and direction of a cycle's path.

3.7 Applications to incompressible phases

In this section we will focus in particular on applications of the first law to reversible processes involving only incompressible phases. With the term incompressible phase we refer to liquids and solids, which are considered incompressible because the effect of the pressure on their volume (and vice versa) is considered negligible in the range of pressure typically chosen.

For incompressible liquids and solids, we have that the internal energy and enthalpy variations are:

$$dU = n\bar{C}_m dT - nP d\bar{V} \quad (\text{for incompressible liquids and solids})$$

$$dH = n\bar{C}_m dT + n\bar{V} dP \quad (\text{for incompressible liquids and solids})$$

with \bar{V} the molar volume of the substance and \bar{C} the heat capacity of incompressible phases.

3.7.1 Isochoric processes

As shown for a generic isochoric process, also for incompressible phases we have that the work of pressure forces is nil because the volume is constant.

$$W_{pf} = - \int_{V_i}^{V_f} P_{ext} dV = 0 \quad (\text{const } V)$$

If also shaft work is nil, the application of the first law gives:

$$Q = \Delta_t U = m\bar{C} \Delta_t T \quad (\text{const } V)$$

where the expression of the internal energy with the mass is typically used for incompressible phases.

3.7.2 Isobaric processes

If the reversible process from an initial state i to a final state f is carried on at constant pressure the work of pressure forces is:

$$W_{pf} = - \int_{V_i}^{V_f} P_{ext} dV = - \int_{V_i}^{V_f} P dV = -P \int_{V_i}^{V_f} dV = -P(V_f - V_i) = -P\Delta_t V \quad (\text{const } P)$$

considering that the surroundings pressure (P_{ext}) is always equal to the system pressure (P) in a reversible process. Then, we apply the first law:

$$\Delta_t U = Q + W_{pf} \quad (\text{const } P)$$

considering that no other types of work are applied ($W_s = 0$). The heat exchanged during an isobaric process is equal to:

$$Q = \Delta_t U - W_{pf} = \Delta_t U + P\Delta_t V \quad (\text{const } P)$$

and introducing the enthalpy function we finally obtain:

$$Q = \Delta_t H = m\bar{C}\Delta_t T \quad (\text{const } P)$$

By comparing the last equation of the heat with the one previously found for isochoric processes of incompressible phases, we see that the heat is found with the same mathematical expression in isochoric and isobaric processes. As discussed in the section on the heat capacity of liquids and solids, the reason is that the effect of pressure on the volume of incompressible phases is negligible ($\Delta_t V \approx 0$) and therefore W_{pf} will be negligible as well.

$$W_{pf} = -P\Delta_t V \approx 0 \quad (\text{const } P)$$

Consequently we obtain that for incompressible phases the variation of internal energy and enthalpy are similar for isobaric processes:

$$\Delta_t H = \Delta_t U + P\Delta_t V \approx \Delta_t U \quad (\text{const } P, \text{ only for incompressible phases})$$

For this reason the heat expression for isobaric processes comes down to the expression of the heat for isochoric processes.

3.7.3 Isothermal processes

In isothermal processes, we have that:

$$\Delta_t U = -nPd\bar{V} \quad (\text{const } T)$$

Because the internal energy depends also on P , we still have a variation of internal energy for isothermal processes of incompressible liquids.

3.7.4 Adiabatic processes

Adiabatic processes are characterized by no heat exchange between the system and the surroundings ($Q = 0$). Therefore, the first law becomes:

$$\Delta_t U = W$$

Considering that only work of pressure forces is present and using the expression of U as function of T for an ideal gas we obtain:

$$W_{pf} = m\bar{C}\Delta_t T \quad (Q = 0)$$

However, reminding that the pressure has a negligible effect on the volume of incompressible phases, we have that:

$$W_{pf} \approx 0 \rightarrow \Delta_t T \approx 0$$

For this reason, adiabatic processes on incompressible phases can be approximated to isothermal processes.

3.8 Applications of the first law to phase transformations

3.8.1 Experimental observations

A mass of pure water is placed in a container. A moving (without friction) piston closes this container without any gas (except water vapour, of negligible volume at room temperature) overhanging the liquid (pure substance). A mass is placed on the piston, maintaining a weight and thus a constant pressure (Figure 3.13). The system (mass of water) is continuously heated and the evolution of its temperature and volume is observed. When the water is liquid, the temperature increases with the volume, while the water remains liquid (A): the expansion of the compressed liquid is measured (and considered negligible). Then, suddenly, as the volume continues to grow, the temperature stops increasing. The mixture in the cylinder is then two-phase (B): one part is liquid and the other vapour. The addition of heat does not cause any increase in temperature, but only the progressive process of the liquid into vapour: this is boiling. The system consists of a liquid-vapour mixture. Finally, when the last drop of liquid has been transformed into vapour, the temperature starts to rise again as heat is added (C-D). The fluid is then in a dry vapour state.

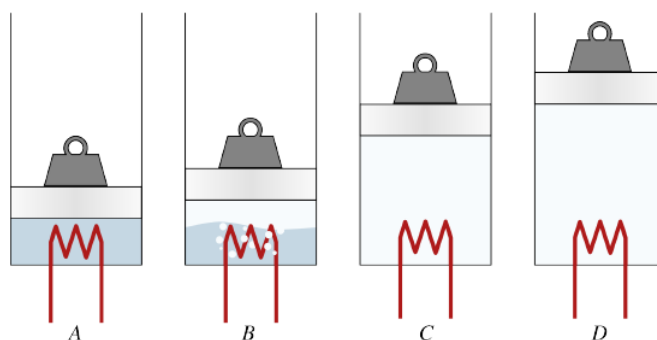


Figure 3.13: Supply of a quantity of heat to a fixed mass of water at constant pressure (A: compressed liquid; B: liquid-vapour mixture; C: saturated steam; D: dry steam). From the book: Thermodynamics of the Engineer, Olivier Cleynen, Framabook 2018.

From these observations we can conclude that:

- boiling requires a supply of heat (but the temperature of the pure substance system remains constant).
- work is exchanged during boiling as it causes the piston to move.

Any change of state is accompanied by an exchange of work and heat.

3.8.2 General considerations

A phase change is a reversible process characterized by the coexistence of two phases during the entire process. When a pure substance is melted from the solid state or vaporized from the liquid at constant pressure, no change in temperature occurs meaning that **phase changes are isothermal and isobaric processes**. In particular, the constant pressure at which the phase change occurs is equal to the vapor pressure of the substance at the temperature of the phase transition (see chapter 2). For example, liquid water vaporises at 100°C only if the pressure of the system is 1 atm that is the vapour pressure of water at 100°C ($P_{\text{H}_2\text{O}}^*(100^{\circ}\text{C}) = 1 \text{ atm}$).

In order to take place, phase changes require the transfer of a certain amount of heat to the substance. We can then see that in this case heat does not modify the temperature of the system but, it changes the state of the system. This is the second of the three heat effects previously introduced and the heat needed to induce the phase change is called **latent heat**. We have the latent heat of melting

L_{melt} for a solid to liquid transition, of vaporization L_{vap} for a liquid to vapour (or gas) transition and of sublimation L_{sub} for a solid to gas transition. Latent heats correspond to the amount of heat needed to change the phase of one gram of the considered system, a pure substance, and their units are $\text{kJ}\cdot\text{kg}^{-1}$. The corresponding molar quantity is called enthalpy of phase change and is obtained by multiplying the latent heat by the molar mass of the pure substance:

$$\Delta_{\text{phase change}}H = L \cdot M$$

where $\Delta_{\text{phase change}}H$ is the molar enthalpy of phase change not to be confused with the total variation of enthalpy of the system which depends on the mass of the system ($\Delta_t H = n \cdot \Delta_{\text{phase change}}H$). The use of the enthalpy instead of the internal energy as state function is because phase changes are isobaric processes and we know that in this case $Q = \Delta_t H$. So, we have the enthalpy of melting ($\Delta_{melt}H$), the enthalpy of vaporisation ($\Delta_{vap}H$) and the enthalpy of sublimation ($\Delta_{sub}H$) with units $\text{kJ}\cdot\text{mol}^{-1}$.

Note: the writing $\Delta_{\text{phase change}}$, *i.e.* Δ_{vap} , Δ_{sub} , Δ_{melt} , implicitly indicate that the reaction quantity is a molar quantity. It is therefore unnecessary (and redundant) to put a bar on the letter representing the quantity.

Latent heats (or enthalpies of phase change) are a physical property of the considered system and they are an increasing function of the temperature (even if they can be considered constant in restricted temperature ranges) as shown in Figure 3.14.

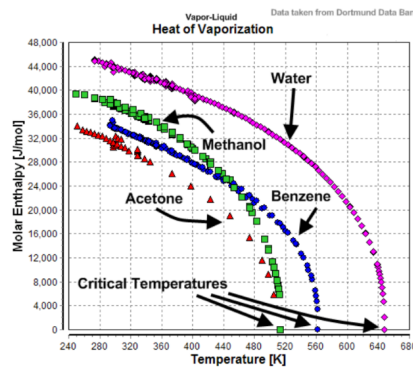


Figure 3.14: Temperature variation of the molar enthalpy of vaporization of different pure substances.

The latent heats are related to other system properties by the *Clapeyron equation* introduced in Chapter 2 and which demonstration is shown in Chapter 6:

$$\Delta_{\text{phase change}}H = T \Delta_t \bar{V} \frac{dP^*}{dT}$$

where for a pure substance at temperature T ,

- $\Delta_{\text{phase change}}H$ = molar enthalpy change accompanying the phase change;
- $\Delta_t \bar{V}$ = molar volume change accompanying the phase change;
- P^* = saturation pressure, *i.e.* the pressure at which the phase change occurs, which is function of only T .

Latent heats can be measured experimentally or calculated using this equation. Indeed, in the case of vaporization of a pure liquid, $\frac{dP^*}{dT}$ is the slope of the vapour pressure-vs-temperature curve (in the diagram $P - T$) at the temperature of interest, $\Delta_t \bar{V} = \bar{V}_{gas} - \bar{V}_{liq}$ is the difference between the molar volumes (volumes occupied by one mole) of saturated vapour (or gas) and saturated liquid, and

$\Delta_{\text{phase change}}H$ is the latent heat of vaporization. So, knowing the vapour pressure and volumetric data it is possible to obtain the latent heat.

$$\Delta_{\text{vap}}H = T(\bar{V}_{\text{gas}} - \bar{V}_{\text{liq}}) \frac{dP^*}{dT}$$

Finally, the latent heats of vaporisation, melting and sublimation are correlated in proximity of the triple point of a pure substance. Indeed, at the triple point, which coordinates P_t and T_t are perfectly determined (e.g. for water: $T_t = 273.16$ K and $P_t = 610$ Pa) for a pure substance, the three phases solid, liquid and vapour coexist. If, around this triple point, a certain quantity of matter at constant pressure passes successively from the solid state (S) to the liquid state (L) and then to the vapour state (V), before returning to the solid state (S), a cycle is obtained allowing one to write:

$$\Delta_t H_{S \rightarrow L} + \Delta_t H_{L \rightarrow V} + \Delta_t H_{V \rightarrow S} = 0 \rightarrow mL_{\text{melt}} + mL_{\text{vap}} - mL_{\text{sub}} = 0$$

By simplifying the mass of the system, we obtain that at the triple point:

$$L_{\text{melt}} + L_{\text{vap}} - L_{\text{sub}} = 0$$

and equivalently with the enthalpy of phase change:

$$\Delta_{\text{melt}}H + \Delta_{\text{vap}}H - \Delta_{\text{sub}}H = 0$$

Assuming that latent heat is independent of temperature (true in proximity of the triple point), this relationship can be applied in a small range of temperature around the triple point.

3.8.3 Heat and work in phase changes

Let's see now how we can calculate the heat and work exchanged during the vaporisation, sublimation and fusion. Regarding the work, shaft work is always nil during a phase transition.

Vaporisation

In this case as in any isobaric process, heat is equal to the total variation of enthalpy of the system that is obtained by multiplying the latent heat of vaporisation by the mass of the system (or equivalently the enthalpy of vaporisation by the moles of the system).

$$Q = \Delta_t H = mL_{\text{vap}} = n\Delta_{\text{vap}}H$$

The work of pressure forces (that is the only work present during any change of phase) can be calculated for an isobaric process:

$$W_{pf} = - \int_{V_i}^{V_f} P_{\text{ext}} dV = - \int_{V_i}^{V_f} P dV = -P \int_{V_i}^{V_f} dV = -P(V_f - V_i)$$

The volumes in the final and initial states are the volumes of the gas and liquid phase respectively. They are obtained by multiplying the molar volumes of the gas and liquid phase by the moles of the system ($V_{\text{gas}} = n\bar{V}_{\text{gas}}$ and $V_{\text{liq}} = n\bar{V}_{\text{liq}}$). Moreover, we remind the reader that the pressure of the system during a vaporisation is equal to the vapour pressure of the substance at the temperature of the phase change. We then obtain:

$$W_{pf} = -P^*(V_{\text{gas}} - V_{\text{liq}}) \approx -P^*V_{\text{gas}}$$

The volume of the liquid phase can be neglected in the calculation of W_{pf} because $V_{\text{gas}} \gg V_{\text{liq}}$.

■ **Example 3.1** The vaporization of one kilogram of water under atmospheric pressure at 100°C provides work equal to $W_{vap} = -PV_{gas} = -nRT = -\frac{10^3}{18} \times 8.314 \times 373 = -172 \text{ kJ}$ (neglecting the contribution of V_{liq}) and requires heat equal to $Q_{vap} = \Delta_{vap}H = mL_{vap} = 1 \times 2257 = 2257 \text{ kJ}$ ■

As final remark, we point out that in the case of **condensation**, *i.e.* the transition from gas to liquid, heat and work have the same absolute value of those calculated for the vaporisation but **opposite sign**:

$$Q^{cond} = -Q^{vap}$$

$$W_{pf}^{cond} = -W_{pf}^{vap}$$

Sublimation

For this case, the same considerations done for the heat and work for the vaporisation are valid and so, we have:

$$Q = \Delta_t H = mL_{sub} = n\Delta_{sub}H$$

$$W_{pf} = -P^*(V_{gas} - V_{sol}) \approx -P^*V_{gas}$$

$$Q^{dep} = -Q^{sub}$$

$$W_{pf}^{dep} = -W_{pf}^{sub}$$

with the deposition being the gas to solid transition, the opposite of sublimation.

Melting

For the transition solid to liquid, we have a similar expression for the heat:

$$Q = \Delta_t H = mL_{melt} = n\Delta_{melt}H$$

whereas the work of pressure forces is negligible in this case because $V_{sol} \approx V_{liq}$.

$$W_{pf} = -P^*(V_{liq} - V_{sol}) \approx 0$$

Finally for the opposite transition, *i.e.* freezing, we have:

$$Q^{freez} = -Q^{melt}$$

$$W_{pf}^{freez} = -W_{pf}^{melt} \approx 0$$

3.9 Applications of the first law to chemical reactions

Heat effects of chemical processes are just as important as those of physical processes. Chemical reactions are accompanied by the transfer of heat, by temperature changes or by both. The ultimate cause lies in the difference between the chemical bonds in the products and reactants. For example, for a combustion reaction, the change in chemical bonding from reactants (fuel and oxygen) to products (water and CO_2) releases heat (called heat of combustion, $\Delta_{comb}H$). Then, this heat can be entirely transferred to the surroundings without modifying the system temperature (case

of isothermal reactions) or it can be entirely used to increase the system temperature (case of adiabatic reactions). These two cases are the two extremes of the infinite combination of possible effects that a system can experience due to chemical reactions. We will see more in details in chapter 5 how to apply the first law to chemical processes occurring at constant pressure (often the atmospheric pressure), and how to calculate the changes of enthalpy of the system induced by chemical processes.

3.10 Open systems

Although the focus of the preceding sections has been on closed systems, the concepts presented find far more extensive application. The first law of thermodynamics (or law of energy conservation) apply to all processes, to open as well as to closed systems. Indeed, the open system includes the closed system as a special case. This section is therefore devoted to the treatment of open systems and to the development of equations of wide practical applications.

3.10.1 Measures of flow

Open systems are characterized by flowing streams; in our course we will use three common measures of flow:

- mass flow rate, \dot{m} , expressed in $\text{kg}\cdot\text{s}^{-1}$;
- molar flow rate, \dot{n} , expressed in $\text{mol}\cdot\text{s}^{-1}$;
- volumetric flow rate, \dot{V} , expressed in $\text{m}^3\cdot\text{s}^{-1}$.

where the $(\dot{})$ notation is a mathematical expression to indicate the rate of change of the value of a certain quantity. These measures of flow are interrelated:

$$\dot{m} = M \dot{n}$$

$$\dot{m} = \rho \dot{V}$$

with M the molar mass and ρ the density of the considered substance.

3.10.2 Control volume and steady-state flow processes

The region of space identified for analysis of open systems is called a **control volume** (see Figure 3.15). The material within the control volume is the thermodynamic system for which the energy balance is written and the surroundings is everything that is outside of the control volume. **Steady-state** flow processes are those for which conditions within the control volume do not change with time. These are an important class of flow processes (and the only one treated in this course) often encountered in practical applications. In a steady-state process the control volume contains a constant mass of fluid implying that the inflows of mass (called *inlets*, \dot{m}_1 and \dot{m}_2 in Figure 3.15) is exactly matched by the outflows of mass (called *outlets*, \dot{m}_3 in Figure 3.15).

$$\sum_{\text{inlets}} \dot{m}_i = \sum_{\text{outlets}} \dot{m}_j \rightarrow \dot{m}_1 + \dot{m}_2 - \dot{m}_3 = 0 \quad \text{in steady-state processes}$$

As a particular case, when there is a single inlet and a single outlet in the control volume, the mass flow rate \dot{m} is the same for both streams. The same is not necessarily true for the molar and volumetric flow rate as heat and work exchanges between the surroundings and the control volume may induce changes of these two rates.

3.10.3 First law in open systems

For open systems, energy transfers between the control volume and the surroundings can take place not only through heat and work as in closed systems but also through the mass flows entering

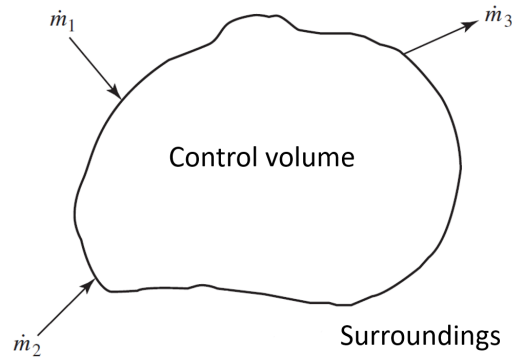


Figure 3.15: Example of control volume of an open system with two inlets and one outlet.

and leaving the control volume. Indeed, streams flowing into and out of the control volume have associated with them energy in its internal, potential and kinetic form, and all may contribute to the energy change of the system (see Figure 3.16).

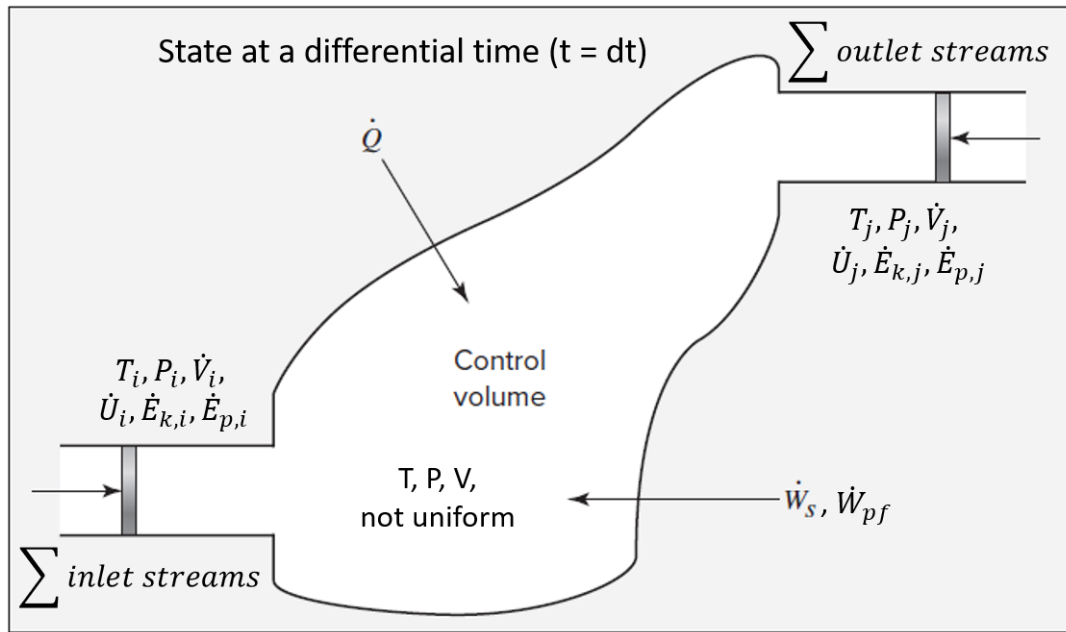


Figure 3.16: Example of control volume of an open system with all energy exchanges

Let's now carry on the energy balance on the control volume of Figure 3.16 by considering that during the differential time considered the rate of state functions and the state variables do not vary. For this open system characterized by i inlets and j outlets, the first law states:

$$dU + dE_{k,macro} + dE_{p,macro} = \delta\dot{Q} + \delta\dot{W} + \sum_i (\dot{U}_i + \dot{E}_{k,macro,i} + \dot{E}_{p,macro,i}) + \\ - \sum_j (\dot{U}_j + \dot{E}_{k,macro,j} + \dot{E}_{p,macro,j})$$

with \dot{Q} and \dot{W} the rate of heat and work (*i.e.* amount of heat and work per unit of time) transferred between the control volume and the surroundings, and the two sum terms showing the energy provided by the inlets (\sum_i) and the outlets (\sum_j) respectively.

As we have already seen, the work rate may include several types of mechanical work. Among them, the most interesting for us are:

- the work of pressure forces (\dot{W}_{pf}) due to a possible change of volume (compression or expansion) of the entire control volume during the process;
- the shaft work (\dot{W}_s) due to the rotation of a shaft in the control volume (for example in compressors or turbines);
- the work of pressure forces induced by all streams flowing into and out of the control volume. This term is calculated as the product between the stream pressure P and the variation of the stream volume inside the control volume. However, the stream volume inside the control volume is zero meaning that $\dot{W}_{pf,i} = -P_i(0 - \dot{V}_i) = P_i\dot{V}_i$ and $\dot{W}_{pf,j} = -P_j(\dot{V}_j - 0) = -P_j\dot{V}_j$.

We can then rewrite the first law by explicating the different types of works:

$$dU + dE_{k,macro} + dE_{p,macro} = \delta\dot{Q} + \delta\dot{W}_{pf} + \delta\dot{W}_s + \sum_i P_i\dot{V}_i - \sum_j P_j\dot{V}_j + \sum_i (\dot{U}_i + \dot{E}_{k,macro,i} + \dot{E}_{p,macro,i}) - \sum_j (\dot{U}_j + \dot{E}_{k,macro,j} + \dot{E}_{p,macro,j})$$

and then regroup together the different sum terms:

$$dU + dE_{k,macro} + dE_{p,macro} = \delta\dot{Q} + \delta\dot{W}_{pf} + \delta\dot{W}_s + \sum_i (\dot{U}_i + P_i\dot{V}_i + \dot{E}_{k,macro,i} + \dot{E}_{p,macro,i}) - \sum_j (\dot{U}_j + P_j\dot{V}_j + \dot{E}_{k,macro,j} + \dot{E}_{p,macro,j})$$

As last step, we replace the enthalpy definition $H = U + PV$ in the equation

$$dU + dE_{k,macro} + dE_{p,macro} = \delta\dot{Q} + \delta\dot{W}_{pf} + \delta\dot{W}_s + \sum_i (\dot{H}_i + \dot{E}_{k,macro,i} + \dot{E}_{p,macro,i}) - \sum_j (\dot{H}_j + \dot{E}_{k,macro,j} + \dot{E}_{p,macro,j})$$

Finally, we can integrate the equation between an initial and final state and then we call the difference between the energy due to the flowing streams as $\Delta_s = E_{outlets} - E_{inlets}$. We obtain the most general form of the first law applied to open systems:

$$\Delta_t U + \Delta_t E_{k,macro} + \Delta_t E_{p,macro} = \dot{Q} + \dot{W}_{pf} + \dot{W}_s - \Delta_s (\dot{H} + \dot{E}_{k,macro} + \dot{E}_{p,macro})$$

that is typically found in the form:

$$\Delta_t U + \Delta_t E_{k,macro} + \Delta_t E_{p,macro} + \Delta_s (\dot{H} + \dot{E}_{k,macro} + \dot{E}_{p,macro}) = \dot{Q} + \dot{W}_{pf} + \dot{W}_s$$

In this equation we remind the reader to pay attention to the different Δ terms:

- Δ_t indicating a variation of the quantity respect to the time (between final and initial states);
- Δ_s indicating a variation of the quantity respect to the space (between outlets and inlets streams);

3.10.4 First law in steady-state flow processes

In practical applications many processes are carried on in steady-state conditions which means that:

- the mass of the system within the control volume is constant;
- no changes occur with time in the properties of the fluid within the control volume nor at its entrances and exits;

- no expansion of the control volume is possible ($\dot{W}_{pf} = 0$).

As a consequence, because energy is conserved, the net rate of energy transfer into the control volume must be equal to zero in steady-state processes ($\Delta_t U = 0$, $\Delta_t E_{k,macro} = 0$ and $\Delta_t E_{p,macro} = 0$). In these conditions the first law applied to open systems can be simplified to:

$$\Delta_s(\dot{H} + \dot{E}_{k,macro} + \dot{E}_{p,macro}) = \dot{Q} + \dot{W}_s$$

which is the mathematical expression of the **first law applied for a steady-state process**. This type of processes are very common in industrial applications as for example, turbines, compressors, heat exchangers. In addition, in many applications kinetic and potential-energy terms are omitted because they are negligible compared with other terms leading to:

$$\Delta_s \dot{H} = \dot{Q} + \dot{W}_s$$

The last expression of the first law for a steady-state process is analogous to the equation of the first law for closed systems. However, enthalpy rather than internal energy is the thermodynamic property of importance for open systems, and Δ_s refers to a change from inlet to outlet, rather than from before to after an event. The calculation of the enthalpy variation in the space is done by using the same relationships found for enthalpy variation in the time by replacing initial and final state with inlet and outlet respectively. In this way we can calculate enthalpy variations for ideal gases and incompressible phases as well as during changes of phase.

Let's now see some practical applications of the first law in open systems. We will show two typical cases often encountered in industrial applications: the case of heat exchangers and the case of turbines and compressors.

Heat exchanged in steady-state flow processes

Heat exchangers allow the transfer of heat between two fluids flowing in adjacent pipes as shown in Figure 3.17. In this case shaft work is not present and the first law for both fluids is:

$$\Delta_s \dot{H} = \dot{Q} = \dot{m} \bar{C}_P \Delta_s T$$

Moreover, being the outer pipe adiabatic with the external surrounding all the heat given by the hotter fluid is taken by the colder fluid without any loss:

$$\dot{Q}_C + \dot{Q}_H = 0 \rightarrow \dot{Q}_C = -\dot{Q}_H$$

We can then write:

$$\dot{m}_C \bar{C}_P (T_C^{out} - T_C^{in}) = -\dot{m}_H \bar{C}_P (T_H^{out} - T_H^{in})$$

where the subscript H and C refer to the hot and cold fluid respectively. The last equation put in relation the inlet and outlet temperatures of the two fluids exchanging heat.

Shaft work exchanged in steady-state adiabatic flow processes

In adiabatic compressors, pumps and turbines, a fluid can exchange only shaft work with the surroundings ($\dot{Q} = 0$). As shown in Figure 3.18 a turbine is a rotary mechanical devices able to extract energy from a fluid flow and converts it into useful mechanical work. In a similar way, a compressor or a pump is a rotary device able to provide energy to a fluid flow in the form of mechanical work. In this case the first law becomes:

$$\Delta_s \dot{H} = \dot{W}_s = \dot{m} \bar{C}_{P_m} (T_{out} - T_{in})$$

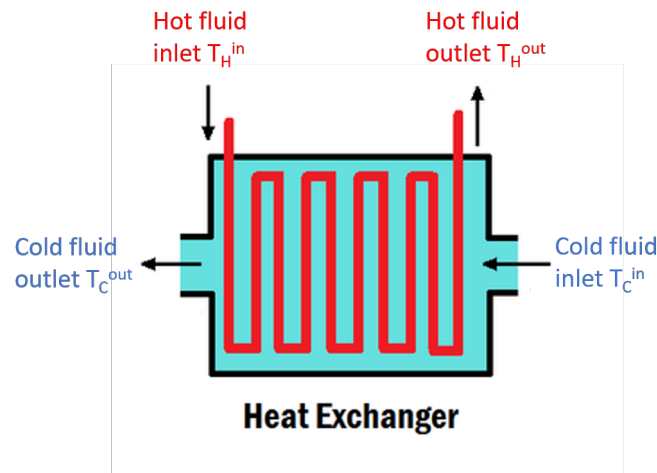


Figure 3.17: Example of heat exchanger. The hotter fluid flows in the inner red pipe while the colder fluid flows in the outer blue pipe. The two fluids are not in a direct contact (no mass exchange between them). The heat exchange between the two fluids is carried on through the wall of the inner red pipe.

allowing us to calculate the shaft work once that the inlet and outlet temperature are known. Depending on the type of fluid that is processed (ideal gas or liquid), the last equation can be developed more. In the case of **ideal gases** (case of turbines and compressors), the inlet and outlet temperature are related for an ideal adiabatic process:

$$P^{1-\gamma}T^\gamma = \text{const} \rightarrow P_{in}^{1-\gamma}T_{in}^\gamma = P_{out}^{1-\gamma}T_{out}^\gamma \rightarrow T_{out} = T_{in} \left(\frac{P_{in}}{P_{out}} \right)^{\frac{1-\gamma}{\gamma}}$$

and replacing in the first law we obtain:

$$\dot{W}_s = \dot{n} \bar{C}_{P_m} T_{in} \left[\left(\frac{P_{in}}{P_{out}} \right)^{\frac{1-\gamma}{\gamma}} - 1 \right] \quad \text{case of ideal gases}$$

By contrast, if the fluid is a **liquid** (case of pumps), we can use the relation valid only for ideal processes $dH = VdP$ (that will be explained in chapter 4):

$$\dot{W}_s = \int_{in}^{out} d\dot{H} = \int_{P_{in}}^{P_{out}} \dot{V} dP = \dot{V} (P_{out} - P_{in}) \quad \text{case of liquids}$$

The last two equations allow one to calculate the shaft work for ideal gases and liquids in steady-state adiabatic flow processes.

3.11 Applications of the first law to thermal machines

3.11.1 Definitions

A thermal machine is a technological object designed to achieve a conversion between work and heat. From a thermodynamic point of view, a thermal machine is a device that causes a fluid to undergo *transformations during a cycle in which this fluid exchanges energy with the surroundings in the form of work and heat.*

Driving and receiving machines, thermodynamic system

It is possible to classify these machines into two categories:

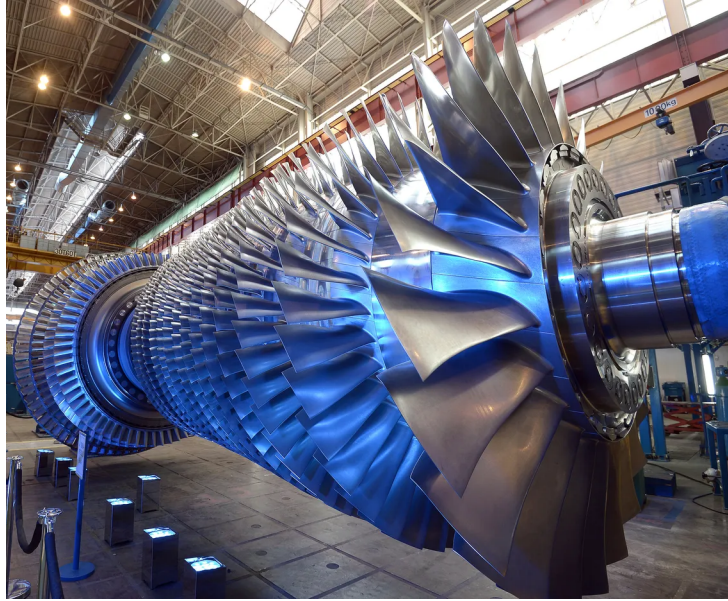


Figure 3.18: Example of a gas turbine.

- **Driving machines**, whose purpose is to provide mechanical work from heat. With the conventions used in the course, the overall result will therefore be $W < 0$ for these machines. There are many different technological forms of prime movers, volumetric engines (energy transfer through a change in volume) such as automobile engines, and turbomachines (energy transfer through flow forces), such as turbo-jets or steam engines.
- **Receiving machines**, which receive mechanical energy from the surroundings ($W > 0$), for example by a compressor or an electric motor. The purpose of these machines is generally to allow energy transfer from a cold source to a hot source. This is for example the case of refrigerating machines (air conditioner, refrigerator) and heat pumps.

We will limit ourselves to the study of ***machines operating cyclically***. In this case, the system is periodically in the same thermodynamic state.

The thermodynamic system is made up of the substance that undergoes the various transformations, not of what contains it, *i.e.* the technological elements of the practical device are excluded from the system (cylinder, piston, compressor, heat exchanger). We generally speak of a ***transformation agent*** to qualify this substance which constitutes the ***thermodynamic system***.

Reminder of the conventions used

Mastery of the conventions used in thermodynamics is fundamental for the study of thermal machines because several systems exchange energy, in mechanical or thermal form. With the "banker's" convention (see Chapter 1), when a thermodynamic system receives energy, this energy is counted positively. This convention is illustrated in Figure 3.19, in which three systems exchange heat. It is therefore possible to define three different references.

For a thermal machine, a single thermodynamic reference is generally used: the transformation agent. In our example, if σ_a is the transformation agent, the quantities of heat involved in the system are Q_1 and Q_3 with $Q_1 < 0$ and $Q_3 > 0$.

Keeping the same reference, it will therefore be necessary to use $-Q_1$ for the system σ_b and $-Q_3$ for the system σ_c whatever the sign of Q_1 , Q_2 and Q_3 .

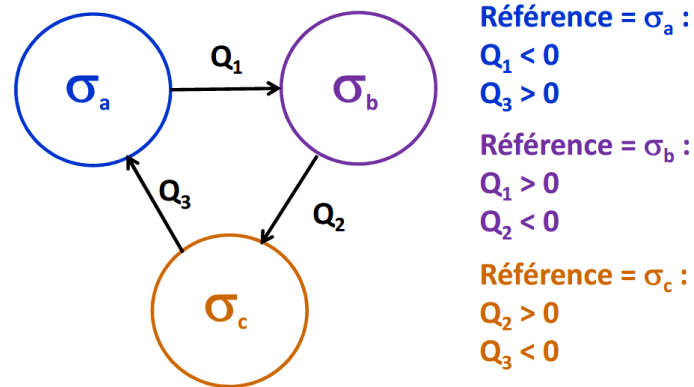


Figure 3.19: Sign conventions for thermal machines.

3.11.2 Thermal machines

Let us apply the first principle to a thermal machine operating according to any cycle, *i.e.* the various transformations undergone by the fluid (system σ) follow a thermodynamic cycle. Taking the fluid as a system, one can write:

$$\Delta U_t = \sum_i (Q_i + W_i)$$

As internal energy is a state function, its variation does not depend on the path followed, it is therefore necessarily zero over a cycle:

$$\sum_i (Q_i + W_i) = 0$$

Depending on the number of heat sources exchanging with the fluid (=system), we will speak of monothermal machine (1 heat source), bithermal (2 sources), trithermal, etc... It will be assumed that each heat source works like a thermostat (cf. O2).

Monothermal machines

This is the simplest configuration is shown in Figure 3.20 in which the transformation agent (system σ) exchanges heat with only one thermostat (system σ_1). However, the interest of this type of machine is very limited because it only converts mechanical energy into heat (see demonstration in chapter 4).

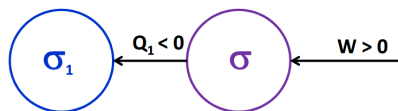


Figure 3.20: Diagram of a single-temperature machine.

Bithermal machines

A bithermal machine integrates a fluid (system σ), which exchanges heat with a hot source (σ_1) and a cold source (σ_2).

Whatever the signs of W , Q_1 and Q_2 , the internal energy can always be written for cyclic operations:

$$\Delta U_t = W + Q_1 + Q_2 = 0$$

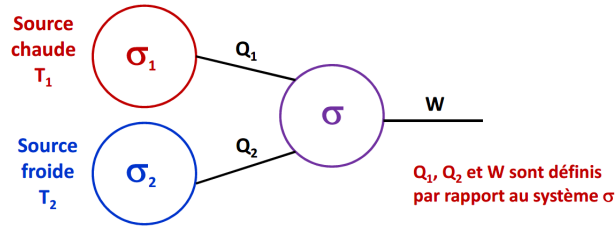


Figure 3.21: Diagram of a bithermal machine.

3.11.3 Characterisation of the performance of a thermal machine

Driving bithermal machines: engines

A representative diagram of the operation of an internal combustion engine is given in Figure 4.11. For an engine, the efficiency is defined by:

$$\eta_{\text{engine}} = \frac{-W}{Q_1}$$

The 1st law allows one to write $-W = Q_1 + Q_2$ from where:

$$\eta_{\text{engine}} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

Knowing that $Q_2 < 0$, $Q_1 > 0$ and $|Q_2| < |Q_1|$, the efficiency of a motor is always between 0 and 1. This shows that an engine always supplies less mechanical energy than the heat received from the hot source, even when the operation is thermodynamically "perfect", *i.e.* reversible (or ideal).

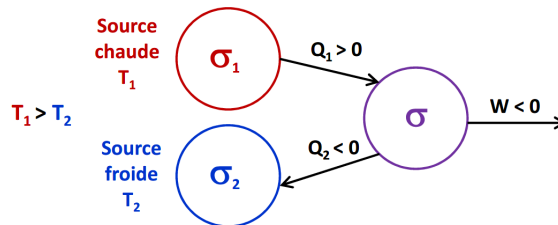


Figure 3.22: Representative diagram of an internal combustion engine operation.

Receiving bithermal machines

The representative diagram of the operation of a receiving machine is shown in Figure 4.12. For refrigerating machines and heat pumps, the mechanical energy is always positive but the

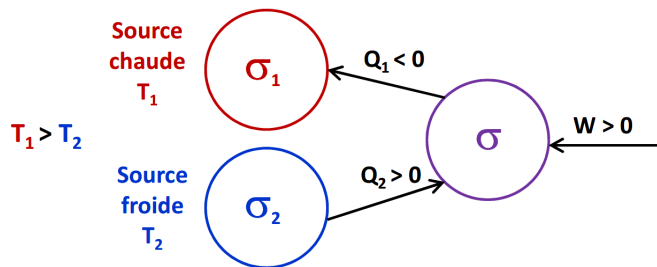


Figure 3.23: Representative diagram of the operation of a receiving machine.

useful energy is exchanged at the cold source (refrigerator, air conditioner) or the hot source (heat

pump) respectively. For receiving machines the performance of a thermal machine is given by the **coefficient of performance (CoP)** that is defined as:

$$CoP = \frac{\text{useful energy}}{\text{supplied energy}} = \frac{\text{useful power}}{\text{supplied power}} = \frac{\text{what interests me}}{\text{what I pay}}$$

By convention, the coefficient of performance is always positive and greater than 1 (unlike the efficiency). According to the 1st law the **CoP of any refrigerating machine** is:

$$CoP_{\text{fridge}} = \frac{Q_2}{W}$$

whereas the **CoP of any heat pump** is:

$$CoP_{\text{HP}} = \frac{-Q_1}{W}$$

Note: The coefficient of performance should not be confused with the efficiency (cf S1). The efficiency takes into account all the energies in the system, with or without cost to the user, and therefore represents the useful energy at the output of the machine in relation to the total energy required for its operation.

Chapter 4

Second law of Thermodynamics and entropy

Based on every day life examples, the limits of the first law are made explicit and the concept of irreversibility is introduced.

The quantification of irreversibilities is carried out through the introduction of the entropy function.

Calculations of created entropy make it possible to predict the direction of processes and their (ir)reversibility.

Finally, entropy calculations are proposed on typical processes, and both principles are applied to the case of heat engines and motors.

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The **learning Objectives** of this chapter are:

- To understand the second law of Thermodynamics and the concept of irreversibility

- To understand the notion of entropy, know its unit and its nature as a “state function”, understand that it represents a qualitative measure of disorder at a microscopic scale
- To calculate entropy variations of a system ΔS_σ on a given process
- To calculate the exchanged entropy (ΔS_{exc}) with the surroundings
- To calculate the created entropy (ΔS_{cre}) and conclude on the reversibility of a process
- To represent a cycle of processes on a diagram $T - S$
- To understand the main sources of irreversibility
- To express the coefficient of performance (CoP) of heat pumps and the efficiency η of engines

4.1 The Second Law of Thermodynamics

In previous chapter, it has been shown that energy can be transferred from one form (*i.e.* microscopic/macroscopic, kinetic/potential) to another one, but the total amount of energy is conserved. neither creation, nor destruction of energy is possible.

In this chapter, we are going to discover that each form of energy is not equivalent: there is a hierarchy among the different forms of energy. In other words even if the energy *quantity* is conserved, its *quality* will be irreversibly degraded.

4.1.1 Some experiments to start

Experiment #1: hot and cold water

A hot water container is put in contact with a cold water container. After reaching equilibrium, both containers will contain warm water (see figure 4.1).

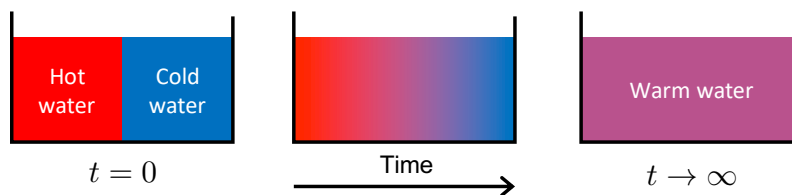


Figure 4.1: Hot and cold water are transformed into warm water.

Heat has therefore been transferred from the hot water to the cold water so that, at equilibrium, both containers are warm.

Experiment #2: braking a racing car

A race car at high velocity breaks hard to a sudden stop. A picture of the front wheels shows (see figure 4.2) shows that they turned red hot, proving that they reached very high temperature.

Macroscopic kinetic energy of the race car has therefore been transferred into heat.

Experiment #3: pouring ink into water

A few drops of ink are poured into a glass of water (see figure 4.3). Ink and water spontaneously mix leading to an homogeneous solution.

Diffusion of ink molecules into water leads to a homogeneous solution.

Experiment #4:

A glass of wine on the edge of a table falls and breaks splitting wine all over the floor (see figure 4.4).



Figure 4.2: When a race car breaks, macroscopic kinetic energy is transformed into heat.

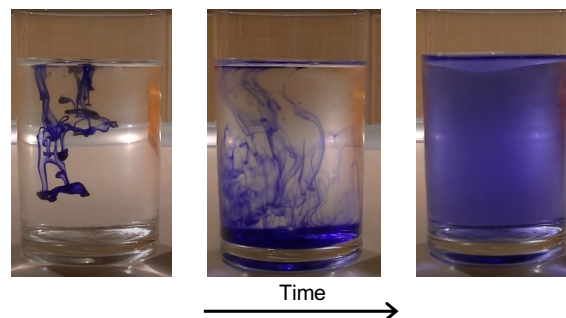


Figure 4.3: Ink and water spontaneously mix leading to an homogeneous solution.

It is possible for the glass to fall and break, but impossible for the glass fragments and the wine on the floor to spontaneously gather together into a full glass on the table.

4.1.2 Statements of the second law of thermodynamics

From these experiments, we can conclude that even if energy is always conserved, systems evolve in a spontaneous direction so that the *quality* of energy decreases. Energy degrades from high quality forms (mechanical, electrical) to low quality form (heat).

The reason for this behaviour can be understood from a microscopic point of view. High quality forms of energy are indeed more ordered. For example, mechanical energy (macroscopic kinetic energy) is the simultaneous motions of a set of atoms **in the same direction**. At the other end, low quality forms of energy are more disordered. For example, heat is the erratic/random motion of atoms/molecules.

From these observations, several expressions of the second law of thermodynamics can be proposed.

Clausius statements

The most simple expression of the second law of thermodynamics was expressed by Clausius. It is directly connected to experiment #1.

Heat only moves spontaneously from a higher to a lower temperature. The heat transfer from a lower to a higher temperature cannot take place without energy input.

Kelvin statements

Another expression of the second law of thermodynamics can be deduced from experiment #2: work can transform into heat, but the opposite is impossible!

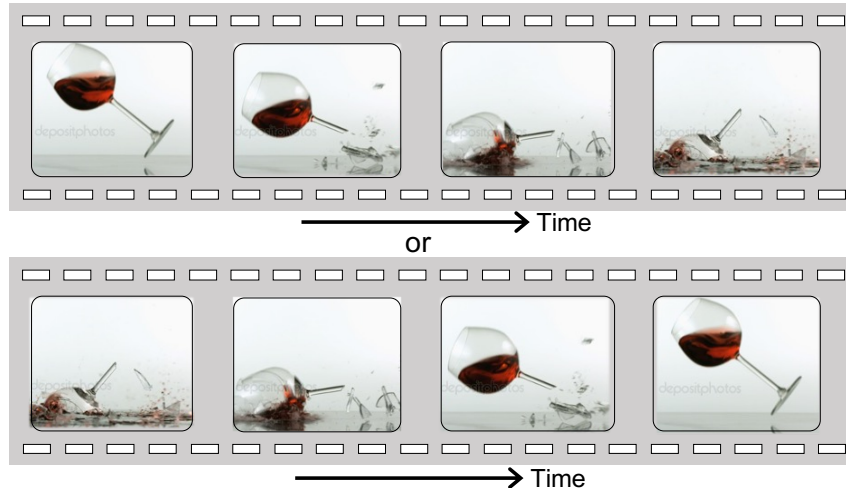


Figure 4.4: Does the glass of wine falls and breaks or do the glass fragments and wine spontaneously gather together into a full glass?

No engine can continuously convert heat into work from a single heat source.

Generalisation

The most general form of the second law of thermodynamics involves the microscopic point of view.

Transformations of an isolated system always proceed in a direction for which disorder increases. Irreversible processes define the arrow of time.

4.1.3 Needs for a state function to quantify energy degradation

We have illustrated that it is not possible to convert energy under any conditions on the sole principle of its conservation. Our intuition and daily experience teach us that many processes can only take place in one direction. Thus, energy conservation (1st law) is not entirely sufficient to determine what is possible. We need a tool (a state function) to quantify energy degradation in order to determine in which direction energy can or cannot be transformed and what kind of process is feasible in practice.

4.2 Entropy and the second law

4.2.1 The concept of entropy

What is the purpose of entropy?

Entropy has been designed to answer the questions set out in the previous section. With entropy, we will have a tool to calculate the direction of an evolution, *i.e.* to mathematically predict the arrow of time for irreversible processes.

Irreversible processes generally lead to states where the temperature is greater than what it would have been with a reversible process. To quantify the irreversibility of an evolution, we will quantify the heat that would have to be removed from the substance to bring it back to its initial state in a reversible way. By subtracting from it the heat that has actually been transmitted, we obtain the heat that has been uselessly created during evolution. However, the lower the temperature at which this heat is created, the less it can be transformed into work (*cf.* S5 - Carnot's engine). We will thus "penalise" the cost in heat by dividing it by the temperature. In this way, we will obtain a magnitude

in joules per kelvin (the entropy created during evolution) which will be zero during reversible processes and will always be positive during irreversible processes. It is this creation which will be the manifest sign that any irreversible process is possible in only one direction.

Definition

Let us begin by admitting that **entropy is a state function**, *i.e.* something that characterises the state of a system. Put it in another way: if we consider a portion of the Universe at a given moment (a system), we find that this system has a mass, a volume, a temperature and these properties describe its current state (which is why they are called state variables). Entropy (noted S) is a state variable in addition to P , T and V . In contrast, we have seen that heat and work are not state functions: they are not quantities that describe the state of a system, but rather a transfer between two systems (path quantities). So we will always think of entropy as the entropy of “something” (as we would say the pressure, the temperature of “something”). For example, we will say “this substance has entropy” or “the entropy of this substance is increasing/decreasing”, and not “we take/give entropy to this substance”. Strictly speaking, we say that entropy is an additive state quantity.

Definition 4.2.1 The entropy S of a system is a state function. Its variation dS during any process is given by:

$$dS = \delta S_{exc} + \delta S_{cre}$$

- δS_{exc} is the **exchanged entropy**. It is given by:

$$\delta S_{exc} = \frac{\delta Q}{T_{ext}}$$

where δQ is the heat exchanged by the system with the surroundings and T_{ext} is the external temperature, *i.e.* the temperature at the system external boundary.

- δS_{cre} is the **created entropy**.
 - if $\delta S_{cre} = 0$, the process is reversible;
 - if $\delta S_{cre} > 0$, the process is irreversible;
 - if $\delta S_{cre} < 0$, the process is impossible (the arrow of time is reversed).

The SI unit of entropy is $\text{J}\cdot\text{K}^{-1}$.

We will see in the following that this definition has many important consequences.

Consequence #1: reversible processes

For reversible processes, $T = T_{ext}$ and $\delta S_{cre} = 0$, leading to:

$$dS = \frac{\delta Q_{rev}}{T}$$

Consequence #2: a path independent state variable

As entropy is a state function, the entropy variation ΔS between states A and B does not depend on the process path. Among all possible path, choosing a reversible path between A and B (that always exists!), we can get:

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T}$$

where the “rev” index specifies that integration takes place along a reversible path.

Consequence #3: cyclic processes

As entropy is a state function, the entropy variation ΔS when system leaves state A and comes back to state A , whatever the process path, is null:

$$\Delta S(A \rightarrow A) = \oint dS = 0$$

Consequence #4: adiabatic processes

For adiabatic processes, $Q = 0$ and $\delta S_{exc} = 0$, leading to:

$$\Delta S_{adiab} = \int \delta S_{cre} \geq 0$$

For adiabatic reversible processes, $Q = 0$, $\delta S_{exc} = 0$ and $\delta S_{cre} = 0$, leading to:

$$\Delta S_{adiab}^{rev} = 0$$

A trick to calculate entropy

When a system follows an irreversible evolution between A and B (as for all real processes), then it is necessary to find a reversible path between these two states and carry out the above integration to calculate ΔS . There is always a reversible way (in fact, there are even an infinite number of such ways) to make a system evolve between A and B (see figure 4.5. For this to happen, the work that is transferred to it must be transferred infinitely slowly (quasi-static equilibrium) and the heat that is transferred to it must be transferred with an infinitesimal temperature difference (succession of an infinite number of infinitely small temperature variations).

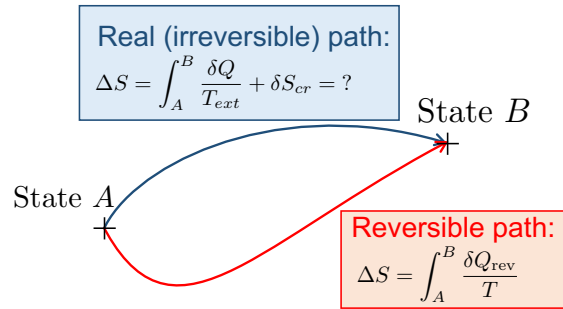


Figure 4.5: Even if a system undergoes a real (irreversible) process between states A and B , it is possible to calculate its entropy variation, assuming a reversible path between A and B .

Exchanged heat with an ideal source (heat reservoir or thermostat)

Definition 4.2.2 An ideal heat source (HS), heat reservoir, or thermostat, is a system of infinite capacity with a temperature T_{HS} that remains constant during the entire heat exchange with its surroundings.

When a system exchange heat with an ideal heat source, the external temperature of the system is the temperature of the heat reservoir ($T_{ext} = T_{HS}$).

The exchanged entropy δS_{exc} between the system and an ideal heat source of temperature T_{HS} is:

$$\delta S_{exc} = \frac{\delta Q}{T_{HS}} \text{ or } \Delta S_{exc} = \frac{Q}{T_{HS}}$$

A heat reservoir supplies or absorbs heat at constant temperature without internal imbalance due to heterogeneity. It is therefore considered to work at equilibrium without entropy creation in a reversible manner.

The entropy variation of an ideal heat source, considered as a system, is:

$$\delta S_{HS} = \frac{\delta Q}{T_{HS}} \text{ or } \Delta S_{HS} = \frac{Q}{T_{HS}}$$

Another definition of entropy: the microscopic point of view

From a microscopic point of view, the concept of entropy was revisited by Ludwig Boltzmann in the 1870s, as a direct measure of disorder.

Definition 4.2.3 The entropy of a system is given by the natural logarithm of the number Ω of possible microscopic configurations of the individual atoms and molecules of the system that could cause the observed macroscopic state of the system.

$$S = k_B \ln \Omega$$

where $k_B = 1.38 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant.

This definition is more general than the previous macroscopic definition. The equivalence of these two definitions can be demonstrated using statistical physics.

4.2.2 Predicting the direction of change: entropy balance

In this section, we are going to use entropy to analyse the experiments presented in section 4.1.1.

Irreversibilities during heat transfer (see experiment #1)

Let's consider an infinitely large system σ , that can be considered as an ideal cold heat source of temperature T_C . It is brought into contact with another ideal hot heat source of temperature T_H . The system σ exchanges heat Q with the source (see figure 4.6).

To predict the direction of change, we are going to calculate the created entropy ΔS_{cre} from the

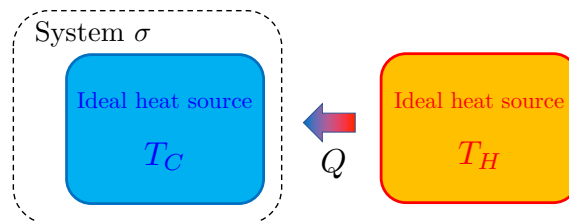


Figure 4.6: An ideal heat source (system σ) of temperature T_C is exchanging heat Q with another ideal heat source of temperature T_H .

entropy variation of the system ΔS_{σ} and the exchanged entropy ΔS_{exc} .

As the system is an ideal heat source, considered as reversible, its entropy variation is given by:

$$\Delta S_{\sigma} = \frac{Q}{T_C}$$

The exchanged entropy ΔS_{exc} is given by:

$$\Delta S_{exc} = \frac{Q}{T_H}$$

The created entropy is finally given by:

$$\Delta S_{cre} = \Delta S_{\sigma} - \Delta S_{exc} = Q \left[\frac{1}{T_H} - \frac{1}{T_C} \right] = \frac{Q}{T_H T_C} (T_H - T_C)$$

We can conclude that:

- if $T_H = T_C$, then $\Delta S_{cre} = 0$, so that the process is reversible.
- if $T_H > T_C$ and $Q > 0$, then $\Delta S_{cre} > 0$, the process is irreversible: the heat goes from the hot to the cold source.
- if $T_H > T_C$ and $Q < 0$ or if $T_H < T_C$ and $Q > 0$, then $\Delta S_{cre} < 0$, the process is impossible: the heat cannot go from the cold to the hot source.

From kinetics energy to heat (see experiment #2)

Our system is now a car of mass M , racing at velocity v (state A). It slows down (see figure 4.2) until complete stop (state B); the kinetics energy of the car has been transformed into heat in the carbon brake disks. After a few minutes, the disks are cooled by the ambient air supposed to be an ideal heat source of temperature T_{ext} (state C).

We want to calculate the created entropy during the processes $A \rightarrow B \rightarrow C$. The first law of thermodynamics applied to our system leads to:

$$W^{A \rightarrow B} + Q^{A \rightarrow B} + W^{B \rightarrow C} + Q^{B \rightarrow C} = \Delta U^{A \rightarrow C} + \Delta E_c^{A \rightarrow C}$$

As state C is identical to state A in a microscopic point of view (same temperature, same bounds), $\Delta U^{A \rightarrow C} = 0$. Moreover, $A \rightarrow B$ process is adiabatic ($Q^{A \rightarrow B} = 0$) and the car does not provide any work to the surrounding during the two processes $W^{A \rightarrow B} = W^{B \rightarrow C} = 0$, leading to:

$$Q^{B \rightarrow C} = -\frac{1}{2}mv^2$$

The exchanged entropy is given by:

$$\Delta S_{exc} = \Delta S_{exc}^{A \rightarrow B} + \Delta S_{exc}^{B \rightarrow C} = 0 + \frac{Q^{B \rightarrow C}}{T_{ext}}$$

From a microscopic point of view the entropy of the car is identical at state C as at state A , so that $\Delta S_{\sigma}^{A \rightarrow C} = 0$. The created entropy is finally given by:

$$\Delta S_{cre} = \Delta S_{\sigma}^{A \rightarrow C} - \Delta S_{exc}^{A \rightarrow C} = -\frac{Q^{B \rightarrow C}}{T_{ext}} = \frac{mv^2}{2T_{ext}}$$

The created entropy is positive. The process is irreversible. It is reversible only if $v = 0$. The reverse process (brake disks are heated leading to an acceleration of the car) is therefore impossible.

Irreversibilities during mixing (see experiment #3)

When two systems are mixed together so that molecules or atoms can diffuse and explore a larger volume, the number of configuration Ω_{1+2} is larger than when the systems (Ω_1 and Ω_2) were separated: $\Omega_{1+2} > \Omega_1\Omega_2$, or, $\ln\Omega_{1+2} > \ln\Omega_1 + \ln\Omega_2$.

Using Boltzmann microscopic definition of entropy, we have: $S_{1+2} > S_1 + S_2$.

There is a net positive variation of the entropy of the system after mixing: $\Delta S_\sigma > 0$. As there is no heat exchanged during mixing, we can conclude that $\Delta S_{cre} > 0$, the process of mixing is irreversible.

Irreversibilities during failure (see experiment #4)

When an object breaks into pieces, the number of configuration increases. Indeed, before failure, there is only one piece and therefore, one configuration. After failure, there are many possible configurations. The net increase of Ω leads to a net increase in S_σ . As the failure is brutal, and therefore adiabatic ($Q = 0$ and $\Delta S_{exc} = 0$), the created entropy is positive when the object breaks into pieces. The re-creation of the object from the debris is therefore impossible.

Demonstration of Clausius statement

Let's assume a thermal machine (our system σ) in contact with two ideal heat sources at temperatures T_H and T_C . The machine is based on a cycle, so that at each cycle the system is back to its initial state (see figure 4.7).

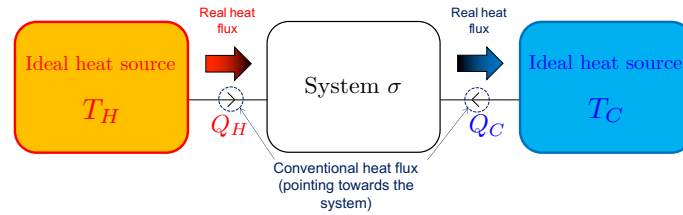


Figure 4.7: Clausius stated that heat goes spontaneously from higher to lower temperature. Calculation of ΔS_{cre} confirms this statement.

By convention, the arrows defining the signs of heat transfers Q_H and Q_C are pointing to the system, meaning that Q_H and Q_C are positive when heat is transferred to the system and negative when heat is given by the system. They may not correspond to the real heat flux.

As the system is performing a cycle, $\Delta S_\sigma = 0$. Moreover, the exchanged entropy is given by:

$$\Delta S_{exc} = \frac{Q_H}{T_H} + \frac{Q_C}{T_C}$$

The first principle applied to the system gives: $Q_H + Q_C = 0$. The created entropy is then given by:

$$\Delta S_{cre} = \Delta S_\sigma - \Delta S_{exc} = \frac{Q_H}{T_H T_C} (T_H - T_C)$$

The created entropy is positive if $T_H > T_C$ and $Q_H > 0$, meaning that heat transfer is only possible from hot to cold source through the system, in a irreversible manner, proving thus Clausius statement.

Demonstration of Kelvin statement

Now, let's consider a heat engine (our system σ transforming heat into work. The machine is based on a cycle, so that at each cycle the system is back to its initial state (see figure 4.8).

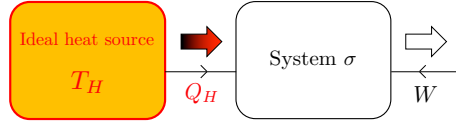


Figure 4.8: Kelvin stated that no engine can continuously convert heat into work from a single heat source. Calculation of ΔS_{cre} confirms this statement.

As the system is performing a cycle, $\Delta S_{\sigma} = 0$. Moreover, the exchanged entropy is given by:

$$\Delta S_{exc} = \frac{Q_H}{T_H}$$

The first principle applied to the system gives: $Q_H + W = 0$. The created entropy is then given by:

$$\Delta S_{cre} = \Delta S_{\sigma} - \Delta S_{exc} = \frac{W}{T_H}$$

The created entropy is positive if $W > 0$, meaning that the system receives work. Work can be transferred into heat but heat cannot be transformed into work, proving thus Kelvin statement.

4.3 Fundamental property relationships of state functions in close systems

After having introduced the new state function S , let's see how it is related to the other two state functions U and H and the state variables P , V , T . In other words, let's found the relationships linking together these thermodynamic properties in closed system. In the previous chapter, we have seen that in close systems the first law applied to reversible processes states that:

$$dU = \delta Q_{rev} + \delta W_{pf_{rev}}$$

with the shaft work is considered nil. The reversible heat and work can be expressed using the second law and the definition of work of pressure forces:

$$\delta Q_{rev} = T dS$$

$$\delta W_{pf_{rev}} = -P dV$$

By replacing in the first equation we obtain:

$$dU = T dS - P dV \quad (\text{for any **close** system})$$

This is a fundamental property relationship valid for any close system. Indeed, even if it has been obtained in the case of reversible processes, this equation relates only variables characterizing the initial and final state of a system (not the process). It is therefore valid for any process.

A similar relationship can be obtained also for enthalpy by deriving its definition and replacing the relationship of the internal energy:

$$H = U + PV$$

$$dH = dU + d(PV) = dU + P dV + V dP$$

$$dH = T dS - P dV + P dV + V dP = T dS + V dP$$

$$dH = T dS + V dP \quad (\text{for any **close** system})$$

Note: the careful student will notice that the property relationship of H becomes $H = \int V dP$ for adiabatic reversible processes. This corresponds to the equation used in section 3.10.4 to calculate the shaft work of a reversible pump (steady-state adiabatic flow processes).

From these two fundamental property relationships we can obtain the variation of entropy as function of the state variables only:

$$dS = \frac{dU}{T} + \frac{PdV}{T} = C_V \frac{dT}{T} + \frac{PdV}{T}$$

$$dS = \frac{dH}{T} - \frac{VdP}{T} = C_P \frac{dT}{T} - \frac{VdP}{T}$$

These two equations are valid for any close system. We will see in the next sections how they are developed for the specific case of ideal gases and incompressible liquids and solids.

4.4 Application of the second law to ideal gases

As seen in chapter 2, ideal gases are characterized by the state equation $PV = nRT$. By replacing this equation and explicating the total moles in the two entropy equations found in the previous section we obtain:

$$dS = n\bar{C}_{V_m} \frac{dT}{T} + nR \frac{dV}{V}$$

$$dS = n\bar{C}_{P_m} \frac{dT}{T} - nR \frac{dP}{P}$$

These differential forms can be integrated between an initial state i and a final state f to obtain:

$$\Delta_i S_\sigma = n\bar{C}_{V_m} \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right) \quad (\text{for ideal gases in close systems})$$

$$\Delta_i S_\sigma = n\bar{C}_{P_m} \ln \left(\frac{T_f}{T_i} \right) - nR \ln \left(\frac{P_f}{P_i} \right) \quad (\text{for ideal gases in close systems})$$

Both equations can be used to calculate the system entropy variation during **any type of process**. The choice of which one should be used depends on the state variables available for the calculations.

Note: we remind the reader that these equations developed for the ideal gas are not the only way to calculate the variation of entropy of an ideal gas. You can always use the general definition $\Delta_i S = \int_i^f \frac{\delta Q_{rev}}{T}$ and develop by knowing how to express the reversible heat exchanged depending on the process considered. The two methods will lead to the same numerical result.

4.5 Application of the second law to incompressible phases

For incompressible phases (both liquids and solids), we can consider that changes of pressure has no impact on the change of liquid volume ($dV \approx 0$) and the ratio V/T is very small that can be neglected. With these assumptions we obtain:

$$dS = n\bar{C}_m \frac{dT}{T}$$

which after integration between the initial and final state gives:

$$\Delta_t S_\sigma = n\bar{C}_m \ln\left(\frac{T_f}{T_i}\right) \quad (\text{for incompressible phases in close systems})$$

4.6 Application of the second law to phase transformations

We have seen in chapter 3 that changes of phase are isothermal and isobaric processes. We can therefore calculate the reversible heat exchanged during this process in order to calculate the associated entropy variation of the system. Starting from entropy definition and remembering that the heat exchanged during an isobaric process is equal to the system enthalpy variation we obtain:

$$\Delta_t S_\sigma = \int_i^f \frac{\delta Q_{rev}}{T} = \int_i^f \frac{dH}{T} = \frac{\Delta_t H}{T} = \frac{mL_{\text{phase change}}}{T} = \frac{n\Delta_{\text{phase change}}H}{T}$$

with both the molar and mass version are shown. The development of the integral is greatly simplified in this case by the fact that the process is isothermal.

4.7 Application of the second law to chemical reactions

Systems characterized by the presence of chemical reactions show as well a variation of the system entropy of course. The calculation of this entropy variation will be detailed in the next chapter 5 dedicated to reacting systems and how to calculate all state functions in this case.

4.8 Second law in open systems

In open systems, we have seen in chapter 3 that energy exchanges take place also through mass flows entering and leaving the control volume (see Figure 4.9). In a similar way as done in chapter 3, we can apply the second law to an open system by considering that entropy of the control volume (our system σ) vary not only because of the exchanged and created entropy over time but also because it is given by all inlet streams and removed by the outlet streams:

$$d_t S = \sum_i \dot{S}_i - \sum_j \dot{S}_j + \delta \dot{S}_{exc} + \delta \dot{S}_{cre}$$

with the $\dot{}$ indicating the rate of entropy. By naming $d_s \dot{S} = \sum_j \dot{S}_j - \sum_i \dot{S}_i$ we obtain:

$$d_t S + d_s \dot{S} = \delta \dot{S}_{exc} + \delta \dot{S}_{cre}$$

This is the differential form of the general equation of entropy balance. It can be integrated between an initial and final state to obtain:

$$\Delta_t S + \Delta_s \dot{S} = \dot{S}_{exc} + \dot{S}_{cre}$$

In this equation we remind the reader to pay attention to the different Δ terms:

- Δ_t is a variation of the quantity respect to the time (between final and initial states);
- Δ_s is a variation of the quantity respect to the space (between outlets and inlets streams);

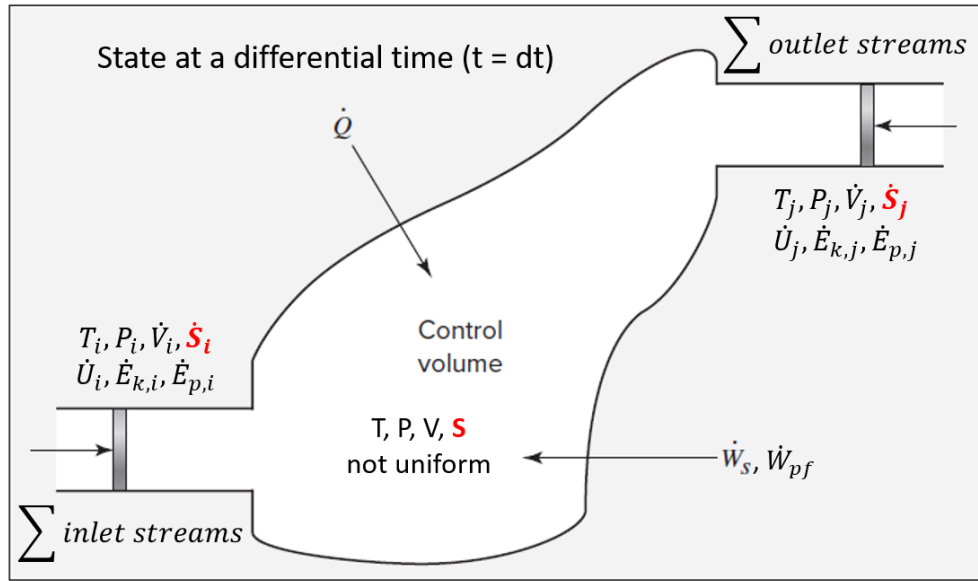


Figure 4.9: Example of control volume of an open system with all energy exchanges

4.8.1 Second law in steady-state flow processes

For a steady-state flow process the mass and entropy in the control volume are constant. This implies that the general equation of entropy balance for open systems becomes:

$$\Delta_s \dot{S} = \dot{S}_{exc} + \dot{S}_{cre} \quad (\text{for steady-state processes})$$

The calculation of the entropy variation in the space is done by using the same relationships found for entropy variation in the time by replacing initial and final state with inlet and outlet respectively. In this way we can calculate entropy variations for ideal gases and incompressible phases as well as during changes of phase.

4.9 Application of the second law to heat pumps and heat engines

Heat pumps and heat engines, sometimes called “thermal machines” are machines based on energy transfers from work to heat or from heat to work. Heat engines aim at producing work from heat (we saw in the previous section that one heat source is not enough: two are necessary). Heat pumps aim at producing heat, or cold (case of air conditioner or refrigerator) from work.

4.9.1 Generalisation - Application of the second principle

Let us now apply the second principle to a thermal machine operating according to any ideal cycles, *i.e.* the various transformations undergone by the transformation agent (system σ) are reversible and follow a thermodynamic cycle.

Application of the second law

To study the functioning of a thermal machine, we will consider the entropy created in the Universe made up of the system σ and j sources with which it exchanges heat and one can write:

$$S_{cre} = \Delta S_{\sigma} - \sum_j S_{ex,j}$$

The entropy variation of the system over a cycle is zero (S state function) and, *if the operation of the machine is reversible*, also the entropy created is zero giving:

$$\sum_j S_{ex,j} = 0$$

Note: $\Delta S_\sigma = 0$ because the system is cyclic; on the other hand, the variation in entropy of each heat source in the thermal machine depends on the mode of operation of each source.

As previously introduced in chapter 3 a bithermal machine integrates a transformation agent (system σ), which exchanges heat with a hot source (system σ_1) and a cold source (system σ_2). Whatever the signs of W , Q_1 and Q_2 , the writing can always be written for cyclic and reversible operation:

- **1st principle:** $W + Q_1 + Q_2 = 0$
- **2nd principle:** $S_{cre} = \Delta S_\sigma - S_{ex,1} - S_{ex,2} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$ because $\Delta S_\sigma = 0$ and Q_1 and Q_2 are defined in relation to the system σ (see Figure 4.10).

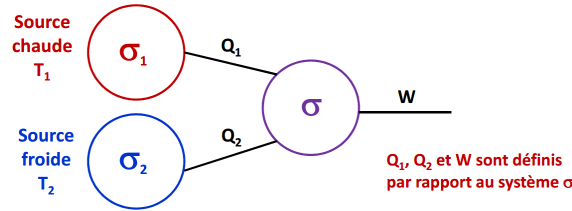


Figure 4.10: Diagram of a bithermal machine.

4.9.2 Characterisation of the performance of a thermal machine

Driving bithermal machines: engines

A representative diagram of the operation of an internal combustion engine is given in Figure 4.11. For an engine, its performance is given by the efficiency:

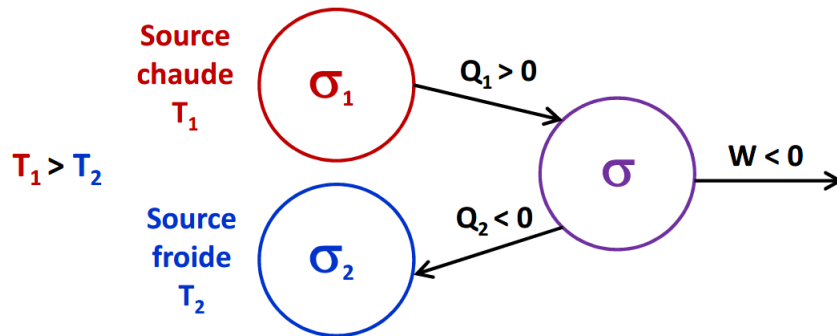


Figure 4.11: Representative diagram of an internal combustion engine operation.

$$\eta_{\text{engine}} = \frac{-W}{Q_1}$$

The 1st law allows one to write $-W = Q_1 + Q_2$ from where:

$$\eta_{\text{engine}} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1}$$

In the case of reversible operations, the 2nd law allows one to write:

$$S_{\text{cre}} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \rightarrow \frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

and the efficiency of a reversible driving machine can be expressed as function of the temperatures of the two heat sources:

$$\eta_{\text{engine,rev}} = 1 - \frac{T_2}{T_1}$$

We therefore find exactly the efficiency of the Carnot engine (see S5). Knowing that $T_1 > T_2$, the efficiency of an engine is always less than 1. This shows that an engine always supplies less mechanical energy than the heat received from the hot source, even when the operation is thermodynamically "perfect", *i.e.* reversible (or ideal).

Receiving bithermal machines

The representative diagram of the operation of a receiving machine is shown in Figure 4.12. For

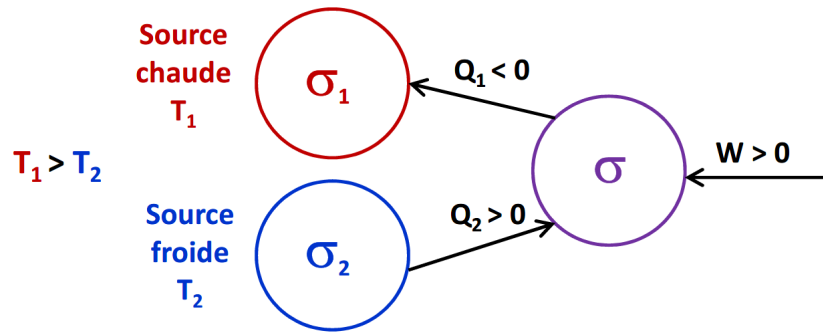


Figure 4.12: Representative diagram of the operation of a receiving machine.

refrigerating machines and heat pumps, the mechanical energy is always positive but the useful energy is exchanged at the cold source (refrigerator, air conditioner) or the hot source (heat pump) respectively. According to the 1st principle the CoP is:

- Refrigeration machine: $CoP_{\text{fridge}} = \frac{Q_2}{W}$
- Heat pump: $CoP_{\text{HP}} = \frac{-Q_1}{W}$

In the same way as for the driving machines, it is possible to express the CoP as function of only the temperatures of the cold and hot springs by using the 2nd principle. The **CoP of a reversible refrigerating machine** is:

$$CoP_{\text{fridge,rev}} = \frac{T_2}{T_2 - T_1}$$

whereas the **CoP of a reversible heat pump** is:

$$CoP_{\text{HP,rev}} = \frac{T_1}{T_2 - T_1}$$

Exercise 4.1 Based on the calculations made for the engine, find the expressions above. ■

Here again we find the CoP of the Carnot refrigeration machine or heat pump. For a refrigerating machine or heat pump, the CoP is greater than 1: there is an amplifying effect. In fact, in addition to the mechanical energy supplied, the system receives heat from a "free source" which does not appear in the denominator of the mathematical expression.

Case of irreversible operation

When the operation is irreversible, it is no longer possible to write:

$$S_{cre} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

This expression becomes:

$$S_{cre} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} > 0$$

because the created entropy of the universe can only increase in the irreversible case.

Taking the example of a driving machine, we know that $Q_{1,irrev} > 0$ so that:

$$\frac{Q_{2,irrev}}{Q_{1,irrev}} < -\frac{T_2}{T_1}$$

Using the definition of efficiency, it appears that:

$$\eta_{\text{engine,irrev}} < 1 - \frac{T_2}{T_1} \rightarrow \eta_{\text{engine,irrev}} < \eta_{\text{engine,rev}}$$

This is also verified for receiving machines.

Exercise 4.2 Based on the above demonstration, establish that $CoP_{irrev} < CoP_{rev}$ for receiving machines, both fridges and heat pumps. ■

For all thermal machines, the maximum performance is obtained during reversible operation of the machine (Carnot's Theorem).

Chapter 5

Thermochemistry

This chapter tackles the case of thermodynamic systems in which chemical reactions occur. The notion of advancement of a chemical reaction is introduced. Enthalpy, internal energy and entropy associated to the reaction are defined and their calculation for any chemical reaction at any temperature is shown. The notion of standard state is introduced. Finally, some applications of the first and second law of thermodynamics to chemical reactions are shown.

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The **learning Objectives** of this chapter are:

- Write the balanced equation of a combustion reaction with gaseous oxygen for a given fuel, draw up the associated RICE table and calculate the maximum advancement of the reaction by identification of the limiting reactant
- Handle the quantities of reaction ($\Delta_r H_T^\circ$, $\Delta_r U_T^\circ$ and $\Delta_r S_T^\circ$) when a chemical reaction occurs in the system.
- Define the standard state of a compound or element.
- Know the Hess' law to calculate $\Delta_r H_{298}^\circ$ and $\Delta_r S_{298}^\circ$.
- Know the Kirchhoff's law to calculate $\Delta_r \bar{H}_T^\circ$ and $\Delta_r \bar{S}_T^\circ$ at any temperature.
- Calculate the heat exchanged by a chemical reaction occurring at constant P and T .
- Calculate the heat exchanged by a chemical reaction occurring at constant V and T .
- Calculate the temperature variation due to chemical reactions occurring in adiabatic systems.
- Evaluate the possibility of a chemical reaction by calculation of the created entropy.

5.1 Advancement of a chemical reaction

A thermodynamic system in which a chemical reaction can take place will be called a **chemical system**. The chemical reaction will induce a change in the composition of the system. Indeed, following the modification of the inter-atomic bonds, certain constituents (*the reactants*) will disappear while new ones (*the products*) will appear.

The evolution of a chemical system from an initial state to a final state of equilibrium can be followed by the evolution of an adapted quantity, characteristic of the reactants and products: number of moles, molar concentration, mass concentration, partial pressure, molar or mass fraction. The **progress chart** is a valuable tool for characterising the composition of the chemical system at different points in the process: at the initial state, at an intermediate point in time t in any form and in the final state.

5.1.1 Notion of chemical reaction

Conditions under which a chemical reaction takes place

The chemical reaction reflects the macroscopic changes in the chemical system from the initial state (where nothing has reacted) to the final state (where its composition no longer varies on a macroscopic scale). Two cases will then be possible:

- **either the chemical reaction will take place at constant pressure** (or monobaric process, *i.e.* the pressure of the reactants will be equal to the pressure of the products at the end of the reaction, or once equilibrium has been reached, but may have varied during the reaction), often at atmospheric pressure, but not exclusively;
- **or the chemical reaction will take place at constant volume**, in an incompressible chamber or a bomb calorimeter (in which case, the final pressure after reaction may be different from the initial pressure of the reactants).

Chemical equation or balanced reaction equation

A chemical equation or a balanced reaction equation is the writing of the chemical reaction. The reactants and products are represented by their formulas (usually unrefined). By convention, the reactants are placed on the left and the products on the right either with a simple arrow (\rightarrow) in the case of a total reaction, or a double arrow (\rightleftharpoons) in the case of a balanced reaction.

Dimensionless coefficients, called stoichiometric coefficients, are placed in the formula before each species involved, to fulfil the mass and charge conservation.

Writing a chemical equation must satisfy:

- the conservation of elements: each side of the equation must contain the same number of the same element whether these are present in ions, molecules or crystals;

- charge conservation: the algebraic sum of the positive and negative charges on each side of the equation must be the same.

Stoichiometric coefficients indicate the proportions in which the quantities of reactant materials react regardless of the quantities of reactant materials present.

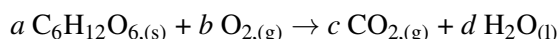
Finally, because of the energy aspect is linked to changes in physical state, ***it will be essential to specify the physical state of the reactants and products involved in the reaction being studied.***

How to establish a balanced reaction equation? Example of a combustion reaction

Reminder: the term ***combustion expresses the complete oxidation of an organic substance called fuel in the presence of an oxidant (gaseous oxygen in the majority of cases).*** A combustion reaction leads to the ***release of significant energy in the form of heat (exothermic reaction).***

The reactants of a combustion reaction will therefore be: the organic species whose combustion is carried out and the gaseous oxygen (unless otherwise specified). As organic substances contain carbon (C) and hydrogen (H), the reaction products are the oxides CO₂ and H₂O. If the fuels also contain nitrogen N (amines) or sulphur S, oxides NO_x and SO_x will also be found at the end of the reaction (x integer). The physical state must be specified according to the conditions under which combustion is carried out.

For the combustion of solid glucose C₆H₁₂O₆ carried out at 298 K under pressure $P = 1$ bar :



the symbols (s), (l) and (g) indicating that the substance is in a solid, liquid or gaseous state respectively.

Since Lavoisier's work, we know that "*nothing is lost, nothing is created, everything is transformed*", so there must be perfect equality between the atoms on either side of the reaction arrow, *i.e.* the same number of carbon atoms on the right and on the left, *i.e.* $6a = c$ (the stoichiometric coefficient (a) is multiplied by the number of atoms in the molecule, in this case 6). The same with the other atoms:

$$\text{C} : 6a = c$$

$$\text{H} : 12a = 2d$$

$$\text{O} : 6a + 2b = 2c + d$$

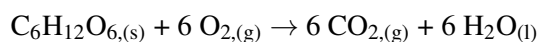
Having 3 equations for 4 unknowns, we put: $a = 1$. We deduce from this:

$$b = 6$$

$$c = 6$$

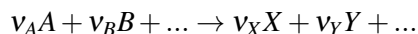
$$d = 6$$

Hence:



5.1.2 Advancement of reaction

Let's consider a chemical reaction transforming reactants A, B,... into products X, Y,... with stoichiometric coefficients v_i :



Definition 5.1.1 The advancement of reaction, noted ξ (pronounced ksi) is defined by:

$$\xi = \frac{n_A(t) - n_A(0)}{\nu_A} = \frac{n_B(t) - n_B(0)}{\nu_B} = \frac{n_X(t) - n_X(0)}{\nu_X} = \frac{n_Y(t) - n_Y(0)}{\nu_Y} = \frac{n_i(t) - n_i(0)}{\nu_i}$$

where:

- $n_i(0)$ is the amount of initial material of the substance;
- $n_i(t)$ is the quantity of material in the considered state of progress (instant t);
- ν_i is a stoichiometric coefficient of substance i .

Thus, the amount of material of a reactant i at the moment t is expressed as follows:

$$\begin{aligned} n_i^{\text{reactant}}(t) &= n_i^{\text{reactant}}(0) - \nu_i^{\text{reactant}} \xi \\ \Delta n_i^{\text{reactant}} &= -\xi \nu_i^{\text{reactant}} \end{aligned}$$

Similarly, the quantity of material in a product j at the moment t will express itself as follows:

$$\begin{aligned} n_j^{\text{product}}(t) &= n_j^{\text{product}}(0) + \nu_j^{\text{product}} \xi \\ \Delta n_j^{\text{product}} &= +\xi \nu_j^{\text{product}} \end{aligned}$$

■ **The advancement of reaction is independent of the substance i (or j) chosen to calculate it.**

5.1.3 RICE chart

RICE charts (or ICE table) are used in order keep track of changes in a chemical reaction. RICE stands for Reaction, Initial, Change and Equilibrium. It is used to keep track of the amount of reactants and product during the course of the chemical reaction.

■ **Example 5.1** Here is an example of RICE chart describing the reaction of 0.5 mol of H_2 reacting with 0.5 mol of O_2 :

Reaction	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$		
Initial (mol)	0.5	0.5	0
Change (mol)	$-\xi$	$-\xi/2$	ξ
Equilibrium (mol)	0	0.25	0.5

Assuming a complete reaction, it is important to identify the limiting reactant by calculating the maximum value of ξ for each reactant and selecting the smallest one. In the previous example $\xi_{\max} = 0.5$ for H_2 and $\xi_{\max} = 1$ for O_2 , therefore the limiting reactant is H_2 and $\xi_{\max} = 0.5$ for the reaction.

Exercise 5.1 The combustion reaction of 9.00 g of solid glucose (of the empirical formula $\text{C}_6\text{H}_{12}\text{O}_6$) is carried out in 2.50 mol of air under pressure $P = 1$ bar and at a temperature $T = 298$ K. Specify the molar composition of the system in the initial state and in the final state, the reaction being total.

1) Evaluation in the initial state (under the simplifying hypothesis that the air is composed of 20% oxygen and 80% nitrogen):

Substance	Initial number of moles
$\text{C}_6\text{H}_{12}\text{O}_{6(s)}$	$n_0 = \frac{m(\text{C}_6\text{H}_{12}\text{O}_6)}{M(\text{C}_6\text{H}_{12}\text{O}_6)} = 0.05 \text{ mol}$
$\text{O}_{2(g)}$	$n'_0 = 0.2 \times 2.50 = 0.50 \text{ mol}$
$\text{N}_{2(g)}$	$n''_0 = 0.8 \times 2.50 = 2.00 \text{ mol}$

2) Writing of the balanced reaction equation and of the RICE chart in mol (we note ξ the molar advancement of the reaction):

Reaction	$\text{C}_6\text{H}_{12}\text{O}_{6(s)} + 6 \text{O}_{2(g)} \rightarrow 6 \text{CO}_{2(g)} \rightarrow 6 \text{H}_2\text{O}_{(l)}$			
Initial state	0.05	0.50	0	0
Change	$-\xi$	-6ξ	6ξ	ξ
Equilibrium	$0.05 - \xi_{\max}$	$0.50 - 6\xi_{\max}$	$6\xi_{\max}$	ξ_{\max}

3) Identification of the limiting reactant:

- Hyp 1: $\text{C}_6\text{H}_{12}\text{O}_{6(s)}$ is the limiting reactant. Then $0.05 - \xi_{\max} = 0 \Rightarrow \xi_{\max} = 0.05 \text{ mol}$
- Hyp 2: $\text{O}_{2(g)}$ is the limiting reactant. Then $0.50 - 6\xi_{\max} = 0 \Rightarrow \xi_{\max} = 0.08 \text{ mol}$

The limiting reactant is the one whose consumption leads to progress ξ_{\max} the lowest: in this case it is the glucose $\text{C}_6\text{H}_{12}\text{O}_{6(s)}$.

4) Conclusion: composition of the system in its final state:

Molecule	$\text{C}_6\text{H}_{12}\text{O}_{6(s)}$	$\text{O}_{2(g)}$	$\text{N}_{2(g)}$	$\text{CO}_{2(g)}$	$\text{H}_2\text{O}_{(l)}$
Nb of final moles	0	0.20	2.00	0.30	0.30

Stoichiometric proportions

Reactants are introduced in stoichiometric proportions *when their initial material quantities are proportional to their stoichiometric coefficients*. Under these conditions, if the reaction is total, all the reactants will be completely consumed at the end of the reaction.

- R** In the example of combustion of glucose treated above, this would correspond to:
 $n'_0(\text{O}_{2(g)}) = 0.30 \text{ mol}$ for $n_0(\text{C}_6\text{H}_{12}\text{O}_{6(s)}) = 0.05 \text{ mol}$.

5.2 Heat (or enthalpy) of reaction

Heat effects of chemical processes are just as important as those of physical processes. Chemical reactions are accompanied by the transfer of heat, by temperature changes or by both. The ultimate cause lies in the difference between the chemical bonds in the products and reactants. For example, for a combustion reaction, the change in chemical bonding from reactants (fuel and oxygen) to products (water and CO_2) releases heat (called heat of combustion, $\Delta_{\text{comb}}H$). Then, this heat can be entirely transferred to the surroundings without modifying the system temperature (case of isothermal reactions) or it can be entirely used to increase the system temperature (case of adiabatic reactions). These two cases are the two extremes of the infinite combination of possible effects that a system can experience due to chemical reactions. Indeed, each reaction carried out in a particular way is accompanied by particular heat effects (called *heats of reaction*) and their complete tabulation is impossible. In order to reduce the required data to a minimum, our object is therefore to devise methods of calculating heat effects for reactions carried out in diverse ways from data

of reactions carried out in an arbitrarily defined *standard way* thus leading to *standard heats of reaction*.

Heats of reaction are based on experimental measurements. Most easily measured are *heats of combustion*, because of the nature of such reactions. A simple procedure is provided by a flow calorimeter (open system) made by a combustion chamber followed by a heat exchanger (see schematic in Figure 5.1). Fuel is mixed with air at an initial temperature T_i and the mixture flows

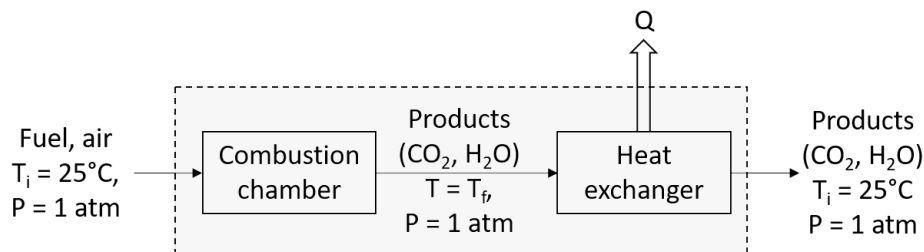


Figure 5.1: Schematic of a flow calorimeter (grey dashed outer box).

into the combustion chamber where the reaction occurs forming the combustion products and increasing the temperature to T_f . Then the combustion products are cooled down to the initial temperature T_i . Because no shaft work is produced, potential- and kinetic-energy changes are negligible and we are in steady-state conditions, the overall energy balance reduces to

$$\Delta_s \dot{H} = \dot{Q} \quad (\text{for chemical reactions in **isothermal steady-state** processes})$$

Thus the enthalpy change caused by the combustion reaction is equal in magnitude to the heat released by the combustion products (that is known). The enthalpy change of reaction is called **heat of reaction**. We point out that a similar relation can be obtained also for chemical reactions occurring in closed systems at constant pressure (*e.g.* in an isothermal reaction calorimeter where the heat released is removed). In this case the overall energy balance reduces to

$$\Delta_r H = Q \quad (\text{for chemical reactions in a **closed constant-pressure isothermal** system})$$

obtaining again that the enthalpy change caused by the combustion reaction is equal in magnitude to the heat released by the combustion products. The corresponding molar quantity of the heat of reaction, noted $\Delta_r H$ and expressed in $\text{J} \cdot \text{mol}^{-1}$, is defined as:

$$\Delta_r H \equiv \left(\frac{\partial H}{\partial \xi} \right)_{T,P}$$

and it allows us to add the contribution of the chemical reaction to the differential variation of the enthalpy of a system beyond its dependence on T and P :

$$dH = \left(\frac{\partial H}{\partial T} \right)_{P,\xi} dT + \left(\frac{\partial H}{\partial P} \right)_{T,\xi} dP + \Delta_r H d\xi$$

This equation shows us that for **isothermal and isobaric processes** (*i.e.* almost all chemical reactions considered in this course) we obtain the integrated relation:

$$\Delta H = \Delta_r H \cdot \xi_{max}$$

with ΔH showing the subscript t or s depending if the reaction is carried on in a closed ($\Delta_t H$) or open ($\Delta_s \dot{H}$) system respectively.

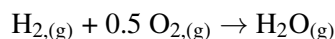
The sign of the molar heat of reaction, which corresponds to the sign of the heat Q generated during a chemical reaction, allows us to distinguish between three types of chemical reactions:

If $\Delta_r H > 0$ (heat absorbed by the system), the reaction is called **endothermic**.

If $\Delta_r H < 0$ (heat released by the system), the reaction is called **exothermic**.

If $\Delta_r H = 0$ (no heat exchange), the reaction is called **athermal**.

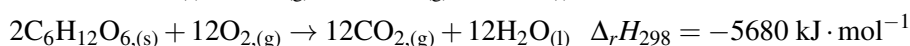
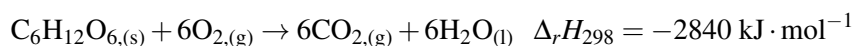
■ **Example 5.2** As an example, let's consider the water synthesis reaction carried out in a reaction calorimeter:



characterised by a molar enthalpy of reaction $\Delta_r H = -241.82 \text{ kJ} \cdot \text{mol}^{-1}$ (exothermic reaction). The reaction of 1 mol of H_2 with 0.5 mol of O_2 leads to an enthalpy variation of the system of $\Delta_t H = \Delta_r H \cdot \xi = -241.82 \text{ kJ}$ being the advancement of the reaction equal to one ($\xi = 1 \text{ mol}$). Conversely, the reaction of 0.5 mol of H_2 with 0.25 mol of O_2 leads to an system enthalpy variation of $\Delta H = \Delta_r H \cdot \xi = -120.91 \text{ kJ}$ because $\xi = 0.5 \text{ mol}$ in this case. ■

Note: the writing Δ_r implicitly indicate that the reaction quantity is a molar quantity. It is therefore unnecessary (and redundant) to put a bar on the letter representing the quantity.

When a molar heat of reaction is given for a particular reaction, it applies for the stoichiometric coefficients as written. If each stoichiometric coefficient is doubled, the heat of reaction is doubled. For example, for the two following versions of the glucose combustion carried on at 298 K we have:



5.3 Internal energy of reaction

If a chemical reaction (*e.g.* a combustion) is carried on a closed constant-volume vessel which is also kept at constant temperature by removing the heat released, the overall energy balance between the becomes:

$$\Delta_t U = Q \quad (\text{for chemical reactions in a **closed constant-volume isothermal** system})$$

In these conditions, and in a similar way to what observed in the previous section with enthalpy, the change of the internal energy of the system caused by the combustion reaction is equal in magnitude to the heat released by the combustion products (that is known). The corresponding molar quantity of the internal energy of reaction, noted $\Delta_r U$ and expressed in $\text{J} \cdot \text{mol}^{-1}$, is defined as:

$$\Delta_r U \equiv \left(\frac{\partial U}{\partial \xi} \right)_{T,V}$$

and it allows us to add the contribution of the chemical reaction to the differential variation of the internal energy of a system beyond its dependence on T and V :

$$dU = \left(\frac{\partial U}{\partial T} \right)_{V,\xi} dT + \left(\frac{\partial U}{\partial V} \right)_{T,\xi} dV + \Delta_r U d\xi$$

This equation shows us that for **isothermal and isochoric processes** (*i.e.* the few chemical reactions that are not carried on in isobaric conditions in this course) we obtain the integrated relation:

$$\Delta_t U = \Delta_r U \cdot \xi_{\text{max}}$$

All properties previously described for $\Delta_r H$ in the case of constant-pressure chemical reactions can be translated to $\Delta_r U$ in the case of constant-volume chemical reactions.

5.3.1 Relationship between enthalpy and internal energy of reaction

We have seen that for chemical reactions occurring in closed systems, the final temperature T_f of products must be considered equal to the initial temperature of the reactants (isothermal or monothermal conditions, $T_i = T_f = T$), in order to be able to calculate the thermodynamic reaction quantities. Moreover we suppose that:

- the gases (reactants or products) present in the system are ideal gases;
- the volume of the condensed phases (liquid or solid) present in the system is negligible compared to that of the gases meaning that the volume of the system can therefore be assimilated to that of the gases, as well as its pressure.

Under these hypothesis we can say that any volume and pressure variation of the closed system is due to the gas phase. From $H = U + PV$:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P_f V_f - P_i V_i = \Delta U + n_{gas}^{prod} RT_f - n_{gas}^{reac} RT_i = \Delta U + RT \Delta n_{gas}$$

with Δn_{gas} representing the variation ($n_{gas}^{prod} - n_{gas}^{reac}$) of the number of moles in the gas phase during the chemical reaction.

Important note: we have seen that the internal energy variation of a substance (ideal gas or condensed phase) undergoing a monothermal process is zero. This result is only true if the substance in question does not undergo chemical modifications (or changes of phase) which, by their nature, induce variations in the microscopic potential energy. For the chemical reaction considered above, ΔU is therefore not null although the reaction takes place in monothermal conditions. The same applies to ΔH .

It is deduced that:

$$\xi \Delta_r H = \xi \Delta_r U + RT \Delta n_{gas}$$

and therefore:

$$\Delta_r H = \Delta_r U + RT \frac{\Delta n_{gas}}{\xi}$$

Let's make explicit the term Δn_{gas} . For any chemical reaction, potentially taking place under non-stoichiometric conditions (*i.e.* excess reactants may remain at the end of the reaction and/or products were present before the start of the reaction):

$$\Delta n_{gas} = n_{gas}^{prod} - n_{gas}^{reac}$$

In addition we know that: $n_{gas}^{reac} = \xi \sum_{\text{reactants, gas}} \nu_i$ with ν_i being the stoichiometric coefficients of the reactants.

At the same way $n_{gas}^{prod} = \xi \sum_{\text{products, gas}} \nu'_i$ with ν'_i the stoichiometric coefficients of the products. So, by replacing Δn_{gas} of the products and the reactants:

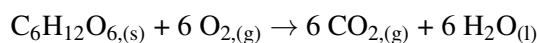
$$\Delta n_{gas} = \xi \left(\sum_{\text{products, gas}} \nu'_i - \sum_{\text{reactants, gas}} \nu_i \right)$$

which gives us:

$$\Delta_r H = \Delta_r U + RT \left(\sum_{\text{products, gas}} \nu'_i - \sum_{\text{reactants, gas}} \nu_i \right)$$

with v_i and v'_i corresponding respectively to the stoichiometric coefficients of the reactants and of the products in the gaseous state. This equation is valid only under the assumption that the volume of the condensed phases is negligible compared to the volume of the gases considered as ideal (this conditions will always be true for our applications).

■ **Example 5.3** The glucose combustion



we have that:

$$\Delta_r H = \Delta_r U + RT(v_{\text{CO}_2} - v_{\text{O}_2}) = \Delta_r U + RT(6 - 6) = \Delta_r U$$

In this particular case, we have found that $\Delta_r H = \Delta_r U$. ■

5.4 Entropy of reaction

As previously done for the enthalpy and the internal energy of reaction, we can calculate also the variation of entropy of a system undergoing a chemical reaction. If the reaction is carried on in a **closed constant-pressure isothermal** system, the entropy variation calculated according to the second law is:

$$\Delta S_\sigma = S_{ex} + S_{cr} = \frac{Q}{T} + S_{cr} = \frac{H}{T} + S_{cr}$$

which for a reversible ($S_{cr} = 0$) chemical reaction gives:

$$\Delta S_\sigma = \frac{H}{T} \quad (\text{for reversible reactions in a closed constant-pressure isothermal system})$$

As already done for the enthalpy of reaction, we can define the corresponding molar entropy of reaction (expressed in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$):

$$\Delta_r S \equiv \left(\frac{\partial S}{\partial \xi} \right)_{T,P} \quad (\text{for reactions in a closed constant-pressure isothermal system})$$

that, again, allows us to add the contribution of the chemical reaction to the differential variation of the system entropy beyond its dependence on T and P (specifically chosen for isobaric and isothermal processes):

$$dS = \left(\frac{\partial S}{\partial T} \right)_{P,\xi} dT + \left(\frac{\partial S}{\partial P} \right)_{T,\xi} dP + \Delta_r S d\xi$$

This equation shows us that for **isothermal and isobaric processes** we obtain the integrated relation:

$$\Delta S_\sigma = \Delta_r S \cdot \xi_{max}$$

Conversely, if the reaction is carried on in a **closed constant-volume isothermal** system, the entropy variation calculated according to the second law is:

$$\Delta S_\sigma = S_{ex} + S_{cr} = \frac{Q}{T} + S_{cr} = \frac{U}{T} + S_{cr}$$

which for a reversible ($S_{cr} = 0$) chemical reaction gives:

$$\Delta S_{\sigma} = \frac{U}{T} \quad (\text{for reversible chemical reactions in a closed constant-volume isothermal system})$$

Then we can define the corresponding molar entropy of reaction (expressed in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$):

$$\Delta_r S \equiv \left(\frac{\partial S}{\partial \xi} \right)_{T,V} \quad (\text{for chemical reactions in a closed constant-volume isothermal system})$$

that, again, allows us to add the contribution of the chemical reaction to the differential variation of the system entropy beyond its dependence on T and V (specifically chosen for isochoric and isothermal processes):

$$dS = \left(\frac{\partial S}{\partial T} \right)_{V,\xi} dT + \left(\frac{\partial S}{\partial V} \right)_{T,\xi} dV + \Delta_r S d\xi$$

This equation shows us that for **isothermal and isochoric processes** we obtain the integrated relation:

$$\Delta S_{\sigma} = \Delta_r S \cdot \xi_{max}$$

The attentive reader would have noticed that the last equation is the same written for isobaric and isothermal processes although it has been obtained in a different way. This is an abuse of notation due to the fact that chemical reactions are carried on under isobaric conditions most of the time. It is left to the reader to distinguish between the two cases depending on the process conditions. All properties previously described for $\Delta_r H$ and $\Delta_r U$ can be translated to $\Delta_r S$.

5.5 Standard state

If the reactants and products of a reaction are in their *standard states*, then the heat effect is the heat of reaction in *standard state* (or *standard conditions*).

The definition of a standard state is straightforward. For a given temperature,

Definition 5.5.1 A standard state is defined as the state of a substance at specified pressure, composition and physical conditions as, *e.g.*, gas, liquid, or solid.

The standard state in use throughout the world have been established by general agreement. They are based on *standard-state pressure* of 1 bar (10^5 Pa). With respect to composition, the standard states used in this course are states of pure species (the situation is different in case of solutions as you will see in the Chemistry course of the 2nd year). For liquids and solids it is the actual real state of the pure species at the standard-state pressure. Conversely, for gases the chosen physical state is the ideal gas state. The standard state chosen for gases is hypothetical or fictitious because at 1 bar real gases deviate from the ideal-gas state. However they seldom deviate much, and for most purposes enthalpies for the real-gas state at 1 bar and the ideal-gas state are negligibly different. In summary, the standard states that we will use are:

- *Pure gases*: the pure substance in the ideal gas state at 1 bar.
- *Pure liquids and solids*: the real pure liquid or solid at 1 bar.

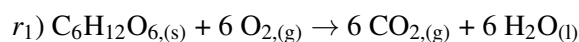
Be careful: one must understand that standard states apply at **any temperature**. There is no specification of temperature for any standard state. *Reference temperatures*, also in use with heats of reaction, are entirely independent of standard states.

With respect to a general chemical reaction, $aA + bB \rightarrow cC + dD$, the standard heat of reaction at temperature T is defined as the enthalpy change when a moles of A and b moles of B in their *standard states at temperature T* react to form c moles of C and d moles of D in their *standard states at temperature T* . The mechanism of this change does not depend on the calculation of the enthalpy change. One may view the process as occurring in a "box of tricks". If the properties of reactants and products in their standard states are not significantly different (*i.e.* they are at the same temperature) the standard heat of reaction is the actual heat of reaction. If this is not the case, additional steps must be incorporated into the calculation scheme.

Properties values in the standard state are denoted by the degree symbol ($^\circ$). For example, ΔH_T° is the heat (or enthalpy) of reaction in the standard state (or in standard conditions).

All conditions for a standard state are fixed except temperature, which is always the temperature of the system. Standard state properties are functions of temperature only.

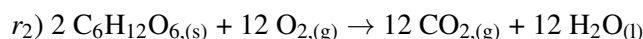
■ **Example 5.4** Example: to cement the ideas, let's take the example of the glucose combustion reaction to show the influence of temperature on one hand and the writing of the reaction on the other. If the equation of the reaction is written as:



At 25°C $\Delta_{r1}H_{298}^\circ = -2816 \text{ kJ}\cdot\text{mol}^{-1}$

At 37°C $\Delta_{r1}H_{310}^\circ = -2776 \text{ kJ}\cdot\text{mol}^{-1}$

Conversely, if the equation of the reaction is written as:



At 37°C $\Delta_{r2}H_{310}^\circ = -5552 \text{ kJ}\cdot\text{mol}^{-1} = 2\Delta_{r1}H_{310}^\circ$ being all the stoichiometric coefficients multiplied by two (as also seen previously). ■

5.5.1 Standard reference condition of a chemical element

Elements and simple substances are constituents from which all chemical buildings can be formed. One element can correspond to several forms of the simple substance (O_2 and O_3 for oxygen, $\text{C}_{(\text{graphite})}$ and $\text{C}_{(\text{diamond})}$ for carbon ...).

■ **Example 5.5** Example: tin is in the form α cubic from 0 K to 291 K, β quadratic from 291 to 495 K, γ orthorhombic from 495 K to 505 K, liquid from 505 to 2533 K, in the gaseous state (monoatomic gas) above 2533 K. ■

It is therefore necessary to further clarify the notion of the standard reference state of an element.

The standard reference state of an element, at temperature T is the state of the most stable single associated substance, of the lowest atomicity, in the most stable physical state at this temperature T and at below $P^\circ = 1 \text{ bar}$.

Cases of interest for our course:

- **carbon** exists in two stable allotropic varieties: graphite carbon and diamond carbon. Whatever the T is, the standard reference state of carbon is the **graphite carbon** $\text{C}_{(\text{graphite})}$ at T under P° .
- elements other than noble gases whose associated simple substances have a boiling temperature below 25°C at 1 bar (O, N, Cl...): the standard reference state is, whatever the temperature, the **perfect diatomic gas** associated with this temperature T under P° .

We will therefore remember:

Element	C	H	O	N	Cl
Standard state of reference	C _(graphite)	H _{2(gas)}	O _{2(gas)}	N _{2(gas)}	Cl _{2(gas)}

5.6 Standard heat (or enthalpy) of formation

Tabulating data even for just one temperature and for just the *standard* heats of reaction for all of the vast number of possible reactions would still be impractical. Fortunately, the standard heat of any reaction at temperature T can be calculated if the **standard heats of formation** at the same temperature are known for the compounds taking part in the reaction.

Definition 5.6.1 A *formation reaction* is defined as a reaction that produces a single compound from its constituent elements.

For example the reaction $\text{C} + 0.5 \text{O}_2 + 2 \text{H}_2 \rightarrow \text{CH}_3\text{OH}$ is a formation reaction for methanol. The reaction $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ is **not** a formation reaction, because it does not form sulphuric acid from its constituent elements (C, O₂, H₂) but from other compounds. Formation reactions are understood to produce 1 mol of product; the heat of formation is therefore based on *1 mol of the compound formed*.

Exercise 5.2 Something very important is the ability to recognise a chemical equation corresponding to a standard reaction of formation and, also, the ability to write down the equation of the reaction of formation of a given compound to obtain its standard reaction of formation.

Questions:

1. Is the following reaction: $\text{CO}_{(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$ a standard reaction of formation?
2. Write down the standard reaction of formation for $\text{CO}_{2(\text{g})}$.
3. write the standard reaction of formation of $\text{NH}_{3(\text{g})}$.

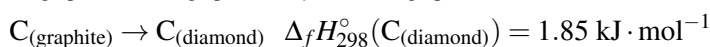
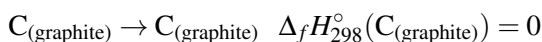
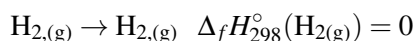
Answers:

1. No because $\text{CO}_{(\text{g})}$ does not correspond to an element in its standard reference state.
2. $\text{C}_{(\text{graphite})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$
3. $\frac{1}{2} \text{N}_{2(\text{g})} + \frac{3}{2} \text{H}_{2(\text{g})} \rightarrow \text{NH}_{3(\text{g})}$.

Heats of reaction at any temperature can be calculated from heat-capacity data if the value for one temperature is known; the tabulation of data can therefore be reduced to the compilation of *standard heats of formation at a single temperature*. The usual choice for this reference temperature is 298 K or 25 °C. The standard heat of formation of compound at 298 K is represented by the symbol $\Delta_f H^\circ_{298}$. The degree symbol denotes the standard-state value, subscript f identifies a heat of formation, and the 298 is the absolute temperature in kelvins. Tables of these values for common substances can be usually found in standard handbooks (some of these values are reported at the end your tutorial booklet). To summarise:

- a standard enthalpy of formation $\Delta_f H^\circ_T$ is only dependent on temperature T ;
- in the thermodynamic tables, **the standard enthalpies of formation at 298 K** (i.e. 25 °C) of a large number of compounds are found, as follows $\Delta_f H^\circ_{298}$. These tables constitute thermodynamic databases even if the writing of these reactions of formation does not imply that the reaction is feasible in practice;
- **the standard enthalpy of formation of a substance in its standard reference state is zero.**

■ Example 5.6



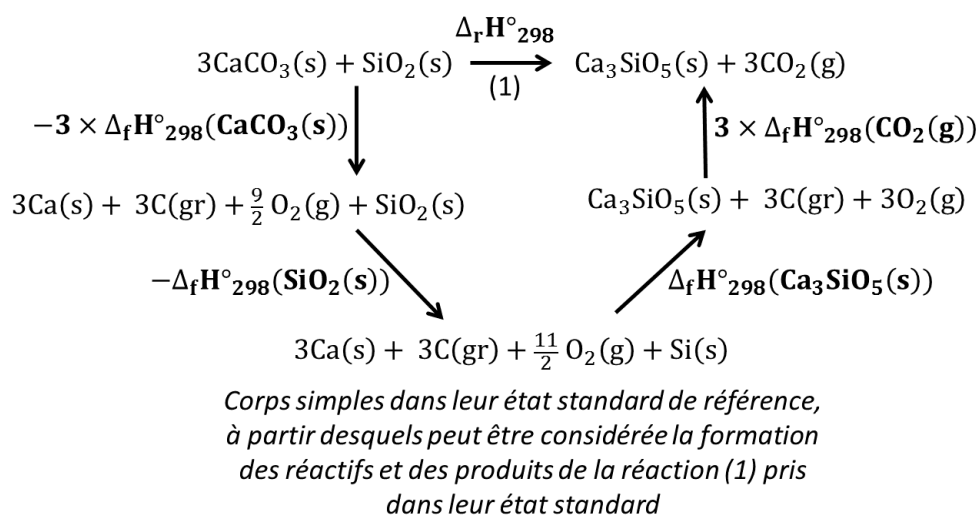
Unlike graphite, carbon in the diamond state does not corresponds to the reference standard state of carbon at 298 K at a pressure of 1 bar and so its standard enthalpy of formation is not zero. ■

When chemical reactions are combined by addition, the standard heats of reaction are simply added to give the standard heat of the resulting reaction. This is possible because enthalpy is a state function, and its changes for given initial and final states are independent of path. In particular, formation reactions and standard heats of formation may be combined to produce any desired reaction (not itself a formation reaction) and its accompanying standard heat of reaction. One can imagine accomplishing any overall reaction by converting the reactants to the elements in their standard states, by the reverse of their formation reactions, then converting those elements to the products, by their formation reactions. Summing the heats of reaction of these steps gives the heat of reaction for the overall reaction. Reactions written for this purpose often include an indication of the physical state of each reactant and product, *i.e.* the letter *g*, *l* or *s* is placed in parentheses after the chemical formula to show whether it is a gas, a liquid, or a solid. This might seem unnecessary because a pure chemical species at a particular temperature and 1 bar can usually exist only in one physical state. However, fictitious states (*e.g.* the ideal-gas state) are often employed for convenience in such calculations. Let's now see an example of calculation of the standard enthalpy of reaction using tabulated values of the standard enthalpies of formation.

5.6.1 Calculation of the standard enthalpy of reaction at 298 K (Hess' law)

Being the enthalpy a state function, its variations during any process, as for example a chemical reaction, is independent of the path followed, *i.e.* the number and nature of the intermediate steps. It is thus possible to express the standard enthalpy of any reaction as a function of the standard enthalpies of formation of the reagents and products. It is sufficient to decompose the chemical reaction studied into the reactions of formation of reagents and products.

Let's see an application on the reaction of formation (1) of a cement (Portland cement):



In this example, one can finally write:

$$\Delta_r H_{298(1)}^\circ = 3 \times \Delta_f H_{298}^\circ(\text{CO}_{2(\text{g})}) + \Delta_f H_{298}^\circ(\text{Ca}_3\text{SiO}_{5(\text{s})}) - \Delta_f H_{298}^\circ(\text{SiO}_{2(\text{s})}) - 3 \times \Delta_f H_{298}^\circ(\text{CaCO}_{3(\text{s})})$$

and calculate the value of the enthalpy variation of the reaction (1) from the values provided by the thermodynamic tables.

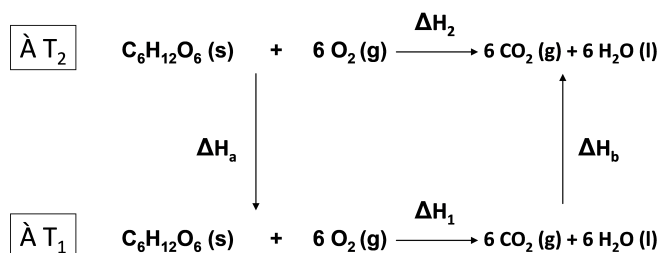
By generalising to any isothermal and isobaric reaction at 298 K, we obtain the **Hess' law**:

$$\Delta_r H_{298}^\circ = \sum_{\text{products}} \nu_j \times \Delta_f H_{298,(j)}^\circ - \sum_{\text{reactants}} \nu_i \times \Delta_f H_{298,(i)}^\circ$$

with ν_i ($\Delta_f H_{298,(i)}^\circ$) and ν_j ($\Delta_f H_{298,(j)}^\circ$) corresponding to the stoichiometric coefficients (standard enthalpies of formation) of reactants and products respectively.

5.6.2 Calculation of standard enthalpy of reaction at any T (Kirchhoff's law)

We have seen that the standard enthalpy of formation depends on the temperature. It is also possible to calculate $\Delta_r H_T^\circ$ at any temperature from the knowledge of $\Delta_r H_{298}^\circ$ (or, more in general, at any temperature). Indeed, being enthalpy H a state function, its variation between the initial and final state does not depend on the path followed. If we know the enthalpy variation associated with this reaction $\Delta_r H_{T_1}^\circ$ at a given temperature T_1 , it will be possible to calculate $\Delta_r H_{T_2}^\circ$ at a temperature T_2 different from T_1 by using the path in the following figure:



From this figure, it is easy to deduce that: $\Delta H_2 = \Delta H_a + \Delta H_1 + \Delta H_b$.

ΔH_a represents the heat received by the reagents to pass from the temperature T_2 to the temperature T_1 and ΔH_b represents the heat received by the products to pass from the temperature T_1 to the temperature T_2 at constant pressure, *i.e.*:

$$\Delta H_a = (n_0 \times \bar{C}_{p,(C_6H_{12}O_6)} + 6 \times n_0 \times \bar{C}_{p,(O_2)}) \times (T_1 - T_2)$$

$$\Delta H_b = (6 \times n_0 \times \bar{C}_{p,(CO_2)} + 6 \times n_0 \times \bar{C}_{p,(H_2O)}) \times (T_2 - T_1)$$

with $\bar{C}_{p,(i)}$ the molar heat capacities at constant pressure, assumed here to be independent of temperature.

Similarly: $\Delta H_1 = n_0 \times \Delta_r H_1^\circ$ and $\Delta H_2 = n_0 \times \Delta_r H_2^\circ$.

Thus, after simplifying n_0 it becomes:

$$\Delta_r H_2^\circ = \Delta_r H_1^\circ + (6 \times \bar{C}_{p,(CO_2)} + 6 \times \bar{C}_{p,(H_2O)} - \bar{C}_{p,(C_6H_{12}O_6)} - 6 \times \bar{C}_{p,(O_2)}) \times (T_2 - T_1)$$

By generalising to any chemical reaction, for which **no change in the physical or allotropic state** of the reagents and products occurs in the temperature range $(298 - T)$, we obtain the general expression of the **Kirchhoff's law**:

$$\Delta_r H_T^\circ = \Delta_r H_{298}^\circ + \int_{298}^T \left[\sum_{\text{products}} \nu_j' \bar{C}_{p,(j)}' - \sum_{\text{reactants}} \nu_i \bar{C}_{p,(i)} \right] \cdot dT$$

with ν_i (ν_j') representing the stoichiometric coefficients and $\bar{C}_{p,(i)}$ ($\bar{C}_{p,(j)}'$) the molar heat capacities at constant pressure of the reagents (products).

Note: be careful to integrate this equation in the case where the molar calorific capacities vary according to the temperature.

In the simple case where the heat capacities do not depend on T , this equation becomes:

$$\Delta_r H_T^\circ = \Delta_r H_{298}^\circ + \left(\sum_{\text{products}} \nu_i' \bar{C}_{p,(i)}' - \sum_{\text{reactants}} \nu_i \bar{C}_{p,(i)} \right) \cdot (T - 298)$$

Note 1: if the temperature range is limited and no change of state takes place, one can neglect the influence of T on $\Delta_r H^\circ$ so $\Delta_r H_T^\circ \approx \Delta_r H_{298}^\circ$. This is called the **Ellingham approximation**.

Note 2: if reagents and/or products are in a solid or liquid state, the molar heat capacity \bar{C} is used. This capacity does not depend on how the reaction is carried out (at constant pressure or volume).

Note 3: Kirchhoff's law has been established here in the standard state in order to be able to use the thermodynamic data tables to access the value of $\Delta_r H_T^\circ$. The approach can be transpose to a different pressure P other than P° if we know $\Delta_r H_T^\circ$ and the values of the thermal capacities at the considered pressure.

5.7 Standard internal energy of reaction

In the same way as done for the standard enthalpy of reaction, we can calculate the standard internal energy of reaction ($\Delta_r U_T^\circ$) of any reaction at any temperature by using the Hess' law and the Kirchhoff's law. Indeed, being U a state function as H the same calculations are possible starting from the values of the standard internal energy of formation. Therefore, we obtain the general expression of the Hess' law for any isothermal and isochoric reaction at 298 K:

$$\Delta_r U_{298}^\circ = \sum_{\text{products}} \nu_j \times \Delta_f U_{298,(j)}^\circ - \sum_{\text{reactants}} \nu_i \times \Delta_f U_{298,(i)}^\circ$$

with ν_i ($\Delta_f U_{298,(i)}^\circ$) and ν_j ($\Delta_f U_{298,(j)}^\circ$) corresponding to the stoichiometric coefficients (standard internal energies of formation) of reactants and products respectively. This equation allows us to know the standard internal energy of any reaction at 298 K. If we need the standard internal energy of reaction at a different temperature T we can use the general expression of the Kirchhoff's law for any isothermal and isochoric reaction:

$$\Delta_r U_T^\circ = \Delta_r U_{298}^\circ + \int_{298}^T \left[\sum_{\text{products}} \nu_j' \bar{C}_{V,(j)}' - \sum_{\text{reactants}} \nu_i \bar{C}_{V,(i)} \right] \cdot dT$$

with ν_i (ν_j') representing the stoichiometric coefficients and $\bar{C}_{V,(i)}$ ($\bar{C}_{V,(j)}'$) the molar heat capacities at constant volume of the reagents (products). However, as previously seen the internal energy of reaction and the enthalpy of reaction are related by the following equation valid for any temperature:

$$\Delta_r H = \Delta_r U + RT \left(\sum_{\text{products, gas}} \nu_i' - \sum_{\text{reactants, gas}} \nu_i \right)$$

It is therefore possible to calculate the standard internal energy of reaction at any temperature directly from the standard enthalpy of the same reaction at the same temperature.

5.8 Standard entropy of reaction

The Hess' law and the Kirchhoff's law previously introduced allow us to calculate also the standard entropy of reaction ($\Delta_r S_T^\circ$) of any reaction at any temperature in the same way as shown for the standard enthalpy of reaction. Indeed, in the same thermodynamic tables reporting tabulated values of the standard enthalpy of formation we can also find the values of the standard entropy of formation represented by the symbol S° or \bar{S}° (both notations are accepted) and expressed in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Note: Why is it not defined $\Delta_f S^\circ$? Contrary to enthalpy, there is a reference for entropy: the entropy of a perfectly crystallised pure body is zero at 0 K. This law is the third principle of thermodynamics. It is then possible to define the standard molar entropy S° of each species, which is zero at 0 K.

Therefore, as previously shown for the standard enthalpy and internal energy of reaction we can use the Hess' law to calculate the standard entropy of any reaction at 298 K:

$$\Delta_r S_{298}^\circ = \sum_{\text{products}} \nu_j \times S_{298,(j)}^\circ - \sum_{\text{reactants}} \nu_i \times S_{298,(i)}^\circ$$

with ν_i ($S_{298,(i)}^\circ$) and ν_j ($S_{298,(j)}^\circ$) corresponding to the stoichiometric coefficients (standard entropies of formation) of reactants and products respectively.

Then, the Kirchhoff's law allows us to find the standard entropy of formation at any temperature T from the one at 298 K. However, we must first distinguish between an isobaric and an isochoric process in order to apply correctly the Kirchhoff's law.

For an **isobaric process** we have the general expression:

$$\Delta_r S_T^\circ = \Delta_r S_{298}^\circ + \int_{298}^T \left[\frac{\sum_{\text{products}} \nu_j' \bar{C}_{P,(j)}' - \sum_{\text{reactants}} \nu_i \bar{C}_{P,(i)}}{T} \right] \cdot dT$$

with ν_i (ν_j') representing the stoichiometric coefficients and $\bar{C}_{P,(i)}$ ($\bar{C}_{P,(j)}'$) the molar heat capacities at constant pressure of the reagents (products).

If the heat capacities do not depend on T this equation becomes:

$$\Delta_r S_T^\circ = \Delta_r S_{298}^\circ + \left(\sum_{\text{products}} \nu_j' \bar{C}_{P,(j)}' - \sum_{\text{reactants}} \nu_i \bar{C}_{P,(i)} \right) \cdot \ln \left(\frac{T}{298} \right)$$

For an **isochoric process** we obtain:

$$\Delta_r S_T^\circ = \Delta_r S_{298}^\circ + \int_{298}^T \left[\frac{\sum_{\text{products}} \nu_j' \bar{C}_{V,(j)}' - \sum_{\text{reactants}} \nu_i \bar{C}_{V,(i)}}{T} \right] \cdot dT$$

with ν_i (ν_j') representing the stoichiometric coefficients and $\bar{C}_{V,(i)}$ ($\bar{C}_{V,(j)}'$) the molar heat capacities at constant volume of the reagents (products).

As before, if the heat capacities do not depend on T this equation becomes:

$$\Delta_r S_T^\circ = \Delta_r S_{298}^\circ + \left(\sum_{\text{products}} \nu_i' \bar{C}_{V,(i)}' - \sum_{\text{reactants}} \nu_i \bar{C}_{V,(i)} \right) \cdot \ln \left(\frac{T}{298} \right)$$

As for $\Delta_r H^\circ$ and $\Delta_r U^\circ$, if the temperature range $(298 - T)$ is limited and no change of physical state takes place, one can neglect the influence of T thus obtaining $\Delta_r S_T^\circ \approx \Delta_r S_{298}^\circ$ (**Ellingham's approximation**).

Note: be careful to integrate these more delicate expressions in the case where the molar calorific capacities vary according to the temperature.

5.9 Applications of the first law to chemical reactions: examples

Chemical reactions lead to a change in the nature of the constituents, involving breaks in interatomic bonds followed by the formation of new bonds. While the rupture of a bond is endothermic (which requires energy), the formation of a bond is exothermic (which releases energy) and the overall energy balance of the chemical reaction leads to an exchange of energy with the surrounding.

We are interested in the application of the 1st law of thermodynamics to chemical reactions. The 1st principle is concerned with establishing energy balances for the envisaged processes without taking into account the real possibility of these processes (which will be discussed in the next sections). The chemical reaction will most often involve an exchange of only heat (unless differently specified in the exercise) with the surrounding, which is assumed to be at constant pressure and temperature (*e.g.* in a laboratory for practical experiments). Let's see the two different cases representing the extreme cases that we can find.

5.9.1 Case 1: isothermal reactions in closed systems

We carry on an isothermal and isobaric process in a closed reactor that allows the heat exchange through the reactor walls (case of an organic synthesis tank for example).

Note: if the chemical system is in thermal and mechanical equilibrium with its external medium in the initial state and in the final state of the process ($T_i = T_f = T_{ext}$ and $P_i = P_f = P_{ext}$) but not during the intermediate states, the process is irreversible and considered **monothermal** and **monobaric**. However, being the enthalpy a state function, the same results that will be shown for the reversible isothermal and isobaric case can be applied also for irreversible monothermal and monobaric processes.

Exercise 5.3 Determine the heat exchanged with the surroundings during the combustion of solid glucose ($C_6H_{12}O_{6,(s)}$) with air forming liquid water. The reaction is carried out at $P = 1$ bar in a closed constant-pressure vessel in isothermal ($T_i = T_f = 100^\circ\text{C}$) conditions. Some data are shown in the following figure whereas the needed thermodynamic quantities are reported here:

- for $C_6H_{12}O_{6,(s)}$: $\Delta_f H_{298}^\circ = -1268 \text{ kJ}\cdot\text{mol}^{-1}$, $\bar{C}_m = 115 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $O_{2,(g)}$: $\Delta_f H_{298}^\circ = 0$, $\bar{C}_{P_m} = 29.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $CO_{2,(g)}$: $\Delta_f H_{298}^\circ = -393.5 \text{ kJ}\cdot\text{mol}^{-1}$, $\bar{C}_{P_m} = 37.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $H_2O_{(l)}$: $\Delta_f H_{298}^\circ = -285.8 \text{ kJ}\cdot\text{mol}^{-1}$, $\bar{C}_m = 75.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

We have seen in section 5.2 that the energy balance in this case is:

$$Q = \Delta_r H = \Delta_r H_{373}^\circ \xi_{max}$$

<p><i>Etat initial</i></p> <p>Température initiale : $T_i = T_{\text{ext}}$ Pression initiale : $P_i = P_{\text{ext}}$</p> <p>0,05 mol de $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ 0,50 mol de $\text{O}_2(\text{g})$ 2,00 mol de $\text{N}_2(\text{g})$</p>	<p>$Q_p = \Delta H < 0$</p> <p>Car réaction de combustion exothermique</p>	<p><i>Etat final</i></p> <p>Température finale : $T_f = T_{\text{ext}}$ Pression finale : $P_f = P_{\text{ext}}$</p> <p>0,20 mol de $\text{O}_2(\text{g})$ 2,00 mol de $\text{N}_2(\text{g})$ 0,30 mol de $\text{CO}_2(\text{g})$ 0,30 mol de $\text{H}_2\text{O}(\text{l})$</p>
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In order to know the heat exchanged by the reaction, we need to know just the standard enthalpy of reaction of the glucose combustion at the desired temperature and the maximum advancement of the reaction. The latter is obtained by drawing the RICE table:

Reaction	$\text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}$	$+ 6 \text{O}_{2(\text{g})}$	$\rightarrow 6 \text{CO}_{2(\text{g})} + 6 \text{H}_2\text{O}_{(\text{l})}$
Initial state	0.05	0.50	0
Change	$-\xi$	-6ξ	6ξ
Equilibrium	0	0.20	0.30

Here $\xi_{\text{max}} = 0.05 \text{ mol}$.

The standard enthalpy of reaction at 100° is obtained using first the Hess' law to find $\Delta_r H_{298}^\circ$:

$$\begin{aligned}\Delta_r H_{298}^\circ &= \nu_{\text{CO}_2(\text{g})} \cdot \Delta_f H_{298,(\text{CO}_2(\text{g}))}^\circ + \nu_{\text{H}_2\text{O}(\text{l})} \cdot \Delta_f H_{298,(\text{H}_2\text{O}(\text{l}))}^\circ + \\ &\quad - \nu_{\text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}} \cdot \Delta_f H_{298,(\text{C}_6\text{H}_{12}\text{O}_{6(\text{s}))}}^\circ - \nu_{\text{O}_2(\text{g})} \cdot \Delta_f H_{298,(\text{O}_2(\text{g}))}^\circ = \\ &= 6 \cdot (-393.5 \text{ kJ} \cdot \text{mol}^{-1}) + 6 \cdot (-285.8 \text{ kJ} \cdot \text{mol}^{-1}) - (-1300 \text{ kJ} \cdot \text{mol}^{-1}) - 6 \cdot (0) = \\ \Delta_r H_{298}^\circ &= -2775.8 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

and then the Kirchhoff's law (case of molar heat capacities independent of the temperature) to have $\Delta_r H_{373}^\circ$:

$$\begin{aligned}\Delta_r H_{373}^\circ &= \Delta_r H_{298}^\circ + (6\bar{C}_{P_m,(\text{CO}_2(\text{g}))} + 6\bar{C}_{m,(\text{H}_2\text{O}(\text{l}))} - \bar{C}_{m,(\text{C}_6\text{H}_{12}\text{O}_{6(\text{s}))}} - 6\bar{C}_{P_m,(\text{O}_2(\text{g}))}) \cdot (373 \text{ K} - 298 \text{ K}) = \\ &= -2775.8 \text{ kJ} \cdot \text{mol}^{-1} + (6 \cdot 37.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 6 \cdot 75.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + \\ &\quad - 115 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - 6 \cdot 29.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \cdot (373 \text{ K} - 298 \text{ K}) = \\ \Delta_r H_{373}^\circ &= -2747.1 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

We can see that $\Delta_r H_{373}^\circ \approx \Delta_r H_{298}^\circ$ (difference of around 1%), thus suggesting that the Ellingham's approximation ($\Delta_r H_T^\circ \approx \Delta_r H_{298}^\circ$) is valid in our temperature range. At this point we can calculate the heat exchanged by the system undergoing the chemical reaction:

$$Q = \Delta_r H_{373}^\circ \xi_{\text{max}} = -2747.1 \text{ kJ} \cdot \text{mol}^{-1} \cdot 0.05 \text{ mol} = -137.4 \text{ kJ}$$

We found a negative heat meaning that the reaction releases heat as expected for an exothermic reaction ($\Delta_r H_T^\circ < 0$).

Note: if the reaction was carried on in a constant-volume vessel always in isothermal conditions, we should have used $Q = \Delta_r U = \Delta_r U_{373}^\circ \xi_{\text{max}}$. In this case, we can proceed in exactly the same way calculating ξ_{max} and $\Delta_r H_{373}^\circ$. Then we can obtain $\Delta_r U_{373}^\circ$ by:

$$\begin{aligned}\Delta_r U_{373}^\circ &= \Delta_r H_{373}^\circ - RT(\nu_{\text{CO}_2} - \nu_{\text{O}_2}) = \Delta_r H_{373}^\circ - 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot 373 \text{ K} \cdot (6 - 6) = \\ \Delta_r U_{373}^\circ &= \Delta_r H_{373}^\circ\end{aligned}$$

At this point we can calculate the heat $Q = \Delta_r U_{373}^\circ \xi_{max}$. Be careful: consider only the stoichiometric coefficients of compounds in the **gaseous phase** to pass from $\Delta_r H_T^\circ$ to $\Delta_r U_T^\circ$. Moreover, the fact that for this specific case we found $\Delta_r U_T^\circ = \Delta_r H_T^\circ$ does not mean that it is always true.

5.9.2 General methodology to calculate the standard enthalpy of reaction

In thermochemistry, one will very frequently look for the heat released by a given chemical reaction involving a given quantity of matter. According to the relations previously established, we can see that this requires knowledge of:

- the conditions in which the chemical reaction is carried out: isothermal, isobaric and/or isochoric conditions;
- the maximum molar advancement of the reaction ξ_{max} : this quantity is easily known in the case of a total reaction because it corresponds to the quantity of the limiting reagent initially introduced;
- the enthalpy of reaction $\Delta_r H$ (or internal energy of reaction $\Delta_r U$) if working in isobaric (isochoric) conditions.

If we place ourselves (which will be usually the case) in isothermal and isobaric conditions:

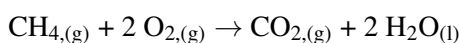
- the maximum molar advancement of the reaction ξ_{max} is known by drawing up the advancement table of the reaction and assuming in most cases that the reaction is total;
- the standard state is used to fix the pressure $P = P^\circ = 1$ bar (to be able to use the thermodynamic tables);
- the calculation of Q requires knowledge of the standard enthalpy of reaction $\Delta_r H_T^\circ$ which can be calculated or from the standard enthalpies of formation $\Delta_f H^\circ$ applying the Hess law, or from the standard reaction enthalpies measured experimentally.

Exercise 5.4 Determination of the higher (HCV) and lower (LCV) calorific value

The calorific value of a fuel is the heat released by the combustion of a unit mass of fuel ($\frac{\Delta_r H_T^\circ}{M_{fuel}}$). Combustion may take place at constant volume (as in a calorimeter bomb) or at constant pressure (combustion at atmospheric pressure) forming water either in the gaseous phase (lower calorific value) or in the liquid phase (higher calorific value). The difference between HCV and LCV is due to the water formed in the gas phase that carries away its heat of vaporization from the system.

Let's calculate the HCV and LCV of the combustion of one moles of methane in the gas phase at 298 K and 1 bar.

To calculate the HCV we write the combustion equation with formation of liquid water:



We start calculating the standard heat of reaction using the Hess law:

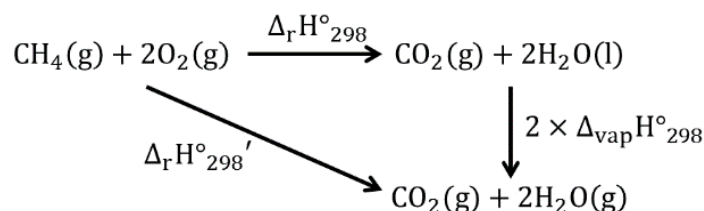
$$\begin{aligned}\Delta_r H_{298}^\circ &= \Delta_f H_{298}^\circ(\text{CO}_{2(g)}) + 2 \times \Delta_f H_{298}^\circ(\text{H}_2\text{O}_{(l)}) - \Delta_f H_{298}^\circ(\text{CH}_{4(g)}) - 2 \times \Delta_f H_{298}^\circ(\text{O}_{2(g)}) \\ \Delta_r H_{298}^\circ &= -890.3 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

and then we obtain the HCV:

$$\text{HCV} = \frac{\Delta_r H_{298}^\circ}{M_{\text{CH}_4}} = -55.64 \text{ kJ} \cdot \text{g}^{-1}$$

If the water is formed in a gaseous state we can either calculate the PCV by using the same method of the HCV (with the difference that water will be considered in the gas phase now) or we can start from the previous result and we can follow the path shown in the next image obtaining:

$$\Delta_r H_{298}^{\circ l} = \Delta_r H_{298}^\circ + 2 \times \Delta_{vap} H_{298}^\circ$$



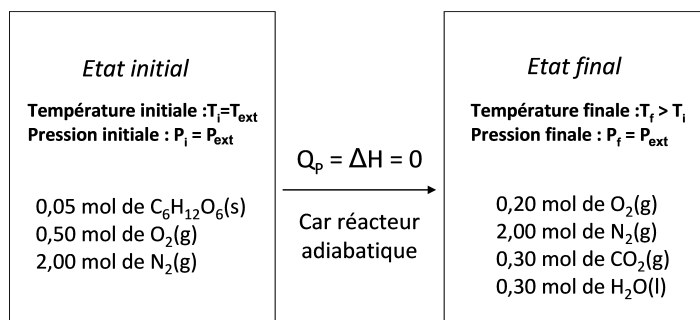
Knowing that $\Delta_{\text{vap}} H^\circ_{298} = 44 \text{ kJ}\cdot\text{mol}^{-1}$ we then obtain $\Delta_r H^\circ_{298}' = -802.3 \text{ kJ}\cdot\text{mol}^{-1}$. Less heat will be released, resulting in the lower calorific value $\text{LCV} = -50.14 \text{ kJ}\cdot\text{g}^{-1}$. It is essential to specify the physical state of the reagents and products involved in a chemical reaction and to identify the temperatures at which the physical state of the reagents and products changes within the temperature range under consideration.

5.9.3 Case 2: adiabatic reactions in closed systems

We realize an isobaric process (as before, the same results apply for a monobaric process) in an **adiabatic reactor** (no heat exchange possible through the walls of the reactor). In this case, due to the impossibility of heat exchange, we will have a final temperature of the system different from the initial one ($T_f > T_i$ if exothermic reaction or $T_f < T_i$ if endothermic reaction).

Exercise 5.5 Determine the final temperature T_f of the system obtained from the combustion of solid glucose ($\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$) with air forming liquid water. The reaction is carried out at $P = 1$ bar in a closed adiabatic constant-pressure vessel. Some data are shown in the following figure whereas the needed thermodynamic quantities are reported here:

- for $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$: $\Delta_f H^\circ_{298} = -1268 \text{ kJ}\cdot\text{mol}^{-1}$, $\bar{C}_m = 115 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $\text{O}_2(\text{g})$: $\Delta_f H^\circ_{298} = 0$, $\bar{C}_{P_m} = 29.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $\text{N}_2(\text{g})$: $\Delta_f H^\circ_{298} = 0$, $\bar{C}_{P_m} = 29.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $\text{CO}_2(\text{g})$: $\Delta_f H^\circ_{298} = -393.5 \text{ kJ}\cdot\text{mol}^{-1}$, $\bar{C}_{P_m} = 37.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $\text{H}_2\text{O}(\text{l})$: $\Delta_f H^\circ_{298} = -285.8 \text{ kJ}\cdot\text{mol}^{-1}$, $\bar{C}_m = 75.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- for $\text{H}_2\text{O}(\text{g})$: $\Delta_{\text{vap}} H^\circ_{373} = 44 \text{ kJ}\cdot\text{mol}^{-1}$, $\bar{C}_{P_m} = 33.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$



In this case, the final temperature T_f is called adiabatic flame temperature. The difficulty of this case is that the temperature is not constant and, therefore, we must split the entire process in two hypothetical steps to decouple the heat effect due to the chemical reaction from the heat effect due to the heating of the system. The two steps are:

- the first where the chemical reaction takes place at a given constant temperature (typically the initial temperature T_i) in which we consider that only the system composition changes;
- the second where we consider that only the system temperature changes. The system

composition is the one obtained at the end of the reaction calculated in the previous step. This decomposition is made possible by the fact that enthalpy is a state function. The reason why we proceed in this way is that we can only calculate the standard heat of reaction at a constant temperature. A particular attention must be put during the second step (change of T) if a change in the physical state of one or more components of the system occurs in the temperature range between T_i and T_f (e.g. water). In this case we cannot simply consider the heat effect due to the temperature change but, we must consider also the heat effect due to phase transition. Let's now solve the exercise. The initial and final state of the system are indicated in the previous figure where we also see that ΔH is the enthalpy variation of the system between the initial and final state. We then introduce an intermediate state characterized by $T = T_i$, $P = 1$ bar and the system composition equal to the one of the final state. This means that, going from the initial to the intermediate state the reaction has occurred at constant $T = T_i$. Let's call ΔH_1 the system enthalpy variation between the initial and intermediate state and ΔH_2 the system enthalpy variation between the intermediate and final state in which there is only the change of T . We can see that:

$$\Delta H = \Delta H_1 + \Delta H_2 = Q = 0$$

because the system is adiabatic and the process isobaric. At this point, in order to calculate T_f , we need to calculate ΔH_1 and also to express ΔH_2 as function of T_f . The calculations of the system enthalpy variation during the first step are the same shown in the case n°. Indeed:

$$\Delta H_1 = \Delta_r H_{298}^\circ \xi_{max} = -2775.8 \text{ kJ} \cdot \text{mol}^{-1} \cdot 0.05 \text{ mol} = -138.8 \text{ kJ}$$

The numerical values of $\Delta_r H_{298}^\circ$ and ξ_{max} can be obtained using the Hess' law and drawing the RICE table as already shown in the previous case.

We now explicitate ΔH_2 as function of T_f knowing that during the second step no reaction occurs and we have only the variation of T (case with heat capacities independent of T):

$$\begin{aligned} \Delta H_2 &= \int_{T_i}^{T_f} \sum_j (n_j \times \bar{C}_{P,j}) dT = \\ &= \int_{T_i}^{T_f} (n_{\text{O}_2} \cdot \bar{C}_{P_m,(\text{O}_{2,(\text{g})})} + n_{\text{N}_2} \cdot \bar{C}_{P_m,(\text{N}_{2,(\text{g})})} + n_{\text{CO}_2} \cdot \bar{C}_{P_m,(\text{CO}_{2,(\text{g})})} + n_{\text{H}_2\text{O}} \cdot \bar{C}_{m,(\text{H}_2\text{O}_{(\text{l})})}) dT = \\ &= (n_{\text{O}_2} \cdot \bar{C}_{P_m,(\text{O}_{2,(\text{g})})} + n_{\text{N}_2} \cdot \bar{C}_{P_m,(\text{N}_{2,(\text{g})})} + n_{\text{CO}_2} \cdot \bar{C}_{P_m,(\text{CO}_{2,(\text{g})})} + n_{\text{H}_2\text{O}} \cdot \bar{C}_{m,(\text{H}_2\text{O}_{(\text{l})})}) \int_{T_i}^{T_f} dT = \\ &= (0.20 \text{ mol} \cdot 29.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 2.00 \text{ mol} \cdot 29.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + \\ &\quad + 0.30 \text{ mol} \cdot 37.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 0.30 \text{ mol} \cdot 75.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(T_f - T_i) = \\ \Delta H_2 &= 97.8 \text{ J} \cdot \text{K}^{-1}(T_f - T_i) \end{aligned}$$

We point out that in the integral we have put **all compounds and elements present in the final state**, so not only the products of the reaction (i.e. CO_2 and H_2O) but also the reactant in excess (i.e. O_2) left at the end and the element not participating at the reaction (i.e. N_2) that are heated together with the products of the reaction. We can now calculate T_f :

$$\begin{aligned} \Delta H_1 + \Delta H_2 &= 0 \\ \Delta_r H_{298}^\circ \xi_{max} + (n_{\text{O}_2} \cdot \bar{C}_{P_m,(\text{O}_{2,(\text{g})})} + n_{\text{N}_2} \cdot \bar{C}_{P_m,(\text{N}_{2,(\text{g})})} + n_{\text{CO}_2} \cdot \bar{C}_{P_m,(\text{CO}_{2,(\text{g})})} + n_{\text{H}_2\text{O}} \cdot \bar{C}_{m,(\text{H}_2\text{O}_{(\text{l})})})(T_f - T_i) &= 0 \\ T_f = T_i - \frac{\Delta_r H_{298}^\circ \xi_{max}}{n_{\text{O}_2} \cdot \bar{C}_{P_m,(\text{O}_{2,(\text{g})})} + n_{\text{N}_2} \cdot \bar{C}_{P_m,(\text{N}_{2,(\text{g})})} + n_{\text{CO}_2} \cdot \bar{C}_{P_m,(\text{CO}_{2,(\text{g})})} + n_{\text{H}_2\text{O}} \cdot \bar{C}_{m,(\text{H}_2\text{O}_{(\text{l})})}} \\ T_f = 298 \text{ K} - \frac{-138.8 \cdot 10^3 \text{ J}}{97.8 \text{ J} \cdot \text{K}^{-1}} \\ T_f &= 1717 \text{ K} \end{aligned}$$

This result have been obtained considering that the water remains in the liquid state in the final state (as stated by the exercise). Let's see now the case where we obtain **water in the gaseous phase** in the final state (as it is in reality). The only part that changes concerns the calculation of ΔH_2 :

$$\begin{aligned}
 \Delta H_2 &= \int_{T_i}^{T_f} \sum_j (n_j \times \bar{C}_{P,j}) dT = \\
 &= \int_{T_i}^{T_f} (n_{\text{O}_2} \cdot \bar{C}_{P_m,(\text{O}_2,(\text{g}))} + n_{\text{N}_2} \cdot \bar{C}_{P_m,(\text{N}_2,(\text{g}))} + n_{\text{CO}_2} \cdot \bar{C}_{P_m,(\text{CO}_2,(\text{g}))}) dT + \\
 &+ \int_{T_i}^{T_b} n_{\text{H}_2\text{O}} \cdot \bar{C}_{m,(\text{H}_2\text{O},(\text{l}))} dT + n_{\text{H}_2\text{O}} \cdot \Delta_{\text{vap}} H_{373}^\circ \int_{T_b}^{T_f} n_{\text{H}_2\text{O}} \cdot \bar{C}_{P_m,(\text{H}_2\text{O},(\text{g}))} dT = \\
 &= (n_{\text{O}_2} \cdot \bar{C}_{P_m,(\text{O}_2,(\text{g}))} + n_{\text{N}_2} \cdot \bar{C}_{P_m,(\text{N}_2,(\text{g}))} + n_{\text{CO}_2} \cdot \bar{C}_{P_m,(\text{CO}_2,(\text{g}))})(T_f - T_i) + \\
 &+ n_{\text{H}_2\text{O}} \cdot \bar{C}_{m,(\text{H}_2\text{O},(\text{l}))}(T_b - T_i) + n_{\text{H}_2\text{O}} \cdot \Delta_{\text{vap}} H_{373}^\circ + n_{\text{H}_2\text{O}} \cdot \bar{C}_{P_m,(\text{H}_2\text{O},(\text{g}))}(T_f - T_b) = \\
 &= (0.20 \text{ mol} \cdot 29.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 2.00 \text{ mol} \cdot 29.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 0.30 \text{ mol} \cdot 37.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \cdot \\
 &\cdot (T_f - 298 \text{ K}) + 0.30 \text{ mol} \cdot 75.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} (373 \text{ K} - 298 \text{ K}) + 0.30 \text{ mol} \cdot 44 \cdot 10^3 \text{ J} \cdot \text{mol}^{-1} + \\
 &+ 0.30 \text{ mol} \cdot 33.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} (T_f - 373 \text{ K}) = \\
 \Delta H_2 &= 75.21 \text{ J} \cdot \text{K}^{-1} (T_f - 298 \text{ K}) + 1694.25 \text{ J} + 13.2 \cdot 10^3 \text{ J} + 10.08 \text{ J} \cdot \text{K}^{-1} (T_f - 373 \text{ K})
 \end{aligned}$$

where $T_b = 373 \text{ K}$ is the water boiling temperature at 1 bar and $\Delta_{\text{vap}} H_{373}^\circ$ is the water enthalpy of vaporisation at 373 K and 1 bar. In this case we have considered the change of phase of the water molecules during the heating of the second step and we decided to let it happens at 100°C because we know the enthalpy of vaporisation at that temperature and pressure. Then, we proceed as before to find T_f :

$$\begin{aligned}
 \Delta H_1 + \Delta H_2 &= 0 \\
 \Delta_r H_{298}^\circ \xi_{\text{max}} + (n_{\text{O}_2} \cdot \bar{C}_{P_m,(\text{O}_2,(\text{g}))} + n_{\text{N}_2} \cdot \bar{C}_{P_m,(\text{N}_2,(\text{g}))} + n_{\text{CO}_2} \cdot \bar{C}_{P_m,(\text{CO}_2,(\text{g}))})(T_f - T_i) + \\
 &+ n_{\text{H}_2\text{O}} \cdot \bar{C}_{m,(\text{H}_2\text{O},(\text{l}))}(T_b - T_i) + n_{\text{H}_2\text{O}} \cdot \Delta_{\text{vap}} H_{373}^\circ + n_{\text{H}_2\text{O}} \cdot \bar{C}_{P_m,(\text{H}_2\text{O},(\text{g}))}(T_f - T_b) = 0 \\
 T_f &= 1760 \text{ K}
 \end{aligned}$$

Note: if the chemical reaction was carried on in a closed adiabatic constant-volume vessel, the entire process would have been adiabatic and isochoric instead of isobaric. In this case, we proceed in the same way replacing the enthalpy with the internal energy because we have $\Delta U = Q = 0$ in the system.

5.9.4 General methodology to calculate the adiabatic flame temperature

The adiabatic flame temperature is defined as the maximum temperature reached during a monobaric adiabatic process (even if no flame is produced by the reaction!). To calculate the final temperature of a system subjected to a chemical reaction under adiabatic isobaric (or monobaric) conditions (calorimeter or reaction so fast that heat exchanges with the surrounding during the reaction are neglected), it is necessary to:

1. Write the balanced equation of the reaction.
2. Draw up a progress table to find out the (mass or molar) quantities of **all species** present in the initial and final states (including inert gases that are not involved in the reaction).
3. Establish a cycle to separate in two steps:
 - the enthalpy change due to the chemical reaction at constant temperature (T_i):

$$\Delta H_1 = \Delta_r H_{298}^\circ \xi_{\text{max}}$$

- the enthalpy change due to the temperature variation from T_i to T_f of **all species** n_j present at the end of the reaction, including inert gases and/or excess reagents:

$$\Delta H_2 = \int_{T_i}^{T_f} \sum_j (n_j \cdot \bar{C}_{P,j}) dT$$

- Exploit the "state function" character of the enthalpy:

$$\Delta H = \Delta H_1 + \Delta H_2 = Q = 0$$

- Isolate T_f in the literal expression.
- Carry out the numerical application paying attention to the consistency of the units.

Exercise 5.6 One mole of methane is burnt with 20 moles of air (considered made of 80% nitrogen and 20% oxygen) in an adiabatic calorimeter. The reagents are initially at a pressure of 1.0 bar and a temperature of 25°C. Reagents and products are considered in the gaseous state. Calculate the final temperature of the system.

Data at 25°C:

LCV ($\text{CH}_{4,\text{(g)}}$) = -802.3 kJ·mol⁻¹ (see the previous exercise for the definition of LCV).

Substance	$\text{CH}_{4,\text{(g)}}$	$\text{O}_{2,\text{(g)}}$	$\text{H}_2\text{O}_{\text{(g)}}$	$\text{CO}_{2,\text{(g)}}$	$\text{N}_{2,\text{(g)}}$
\bar{C}_p (J·mol ⁻¹ ·K ⁻¹)	30	30	30	45	30

Numeric answer: $T_f = 1.3 \times 10^3$ °C. ■

Note: the *adiabatic explosion temperature* is the maximum temperature reached during an isochoric adiabatic process (even if it does not result in an explosion!). The reasoning will be identical when using the internal energy variation to calculate the heat of reaction and the heat exchanged during the temperature variation.

5.10 Application of the second law to chemical reactions: examples

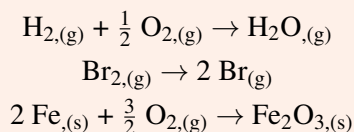
We have seen in chapter 4 that the entropy is associated with the molecular disorder of the system. For example, in the change of state $\text{H}_2\text{O}_{\text{(s)}} \rightarrow \text{H}_2\text{O}_{\text{(l)}}$ the associated entropy variation is positive and equal to 22.0 J·K⁻¹·mol⁻¹. This means that the molecular disorder (or disorder degree more in general) has increased going from the solid to the liquid phase. Indeed, in the solid state the water molecules vibrate around a perfectly defined fixed mean position of the crystal whereas, in the liquid state the water molecules are animated by a disordered and incessant movement. The disorder is therefore much greater in the liquid state than in the solid state. In the same way the disorder in the gas phase is greater than in the liquid phase.

We can therefore consider that for any chemical compound:

$$S_{\text{gas}} \gg S_{\text{liquid}} \gg S_{\text{solid}}$$

This consideration allows us to provide a qualitative justification for entropy variations associated with a chemical reaction (which can be positive or negative). In particular, if the chemical reaction determines an increase (reduction) of the number of moles in the gaseous phase going from the reactants to the products, we can affirm that the entropy of the system increases (reduces) due to the occurring reaction.

Exercise 5.7 Without using the thermodynamic tables, can you predict the sign of the system entropy variation due to the chemical reactions in the following cases?



Spontaneous evolution of a chemical reaction

In this chapter we have seen so far how to perform energy balances on chemical reactions under different conditions in order to calculate, for example, the heat exchanged by the system. We will focus now on how to determine if a chemical reaction is an irreversible, reversible or impossible process under the imposed conditions.

Note: be careful because, as for any type of process, chemical reactions that are impossible in some conditions may become possible, *i.e.* reversible or irreversible, if we change the system conditions, *i.e.* temperature and pressure.

In chapter 4 we have established that for any process:

- $S_{cr} > 0$: process possible (or spontaneous) and irreversible
- $S_{cr} = 0$: process possible (or spontaneous) and reversible
- $S_{cr} < 0$: process impossible

with S_{cr} being the created entropy of the Univers during the process. Let's see now how to calculate the created entropy associated to a chemical reaction.

$$S_{cr} = \Delta S_{\sigma} - S_{ex}$$

In order to calculate ΔS_{σ} and S_{ex} , we need to know the conditions under which the reaction is carried on. We consider the case of isothermal and isobaric conditions (those encountered most of the time). In this case we have already seen in this chapter (section 5.4) that:

$$\Delta S_{\sigma} = \Delta_r S_T^{\circ} \cdot \xi_{max}$$

with $\Delta_r S_T^{\circ}$ the standard entropy of reaction calculated with the Hess's law and also the Kirchhoff's law if needed (see section 5.8), and ξ_{max} the maximum advancement of the reaction (see section 5.1). The exchanged entropy is equal to (see section 5.4):

$$S_{ex} = \frac{Q}{T} = \frac{\Delta H}{T} = \frac{\Delta_r H_T^{\circ} \cdot \xi_{max}}{T}$$

We can then calculate the created entropy:

$$S_{cr} = \Delta_r S_T^{\circ} \cdot \xi_{max} - \frac{\Delta_r H_T^{\circ} \cdot \xi_{max}}{T}$$

and depending on its sign we can know if the process is possible (or spontaneous) or not.

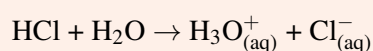
Note: if the reaction is carried on under **isothermal and isochoric** conditions we calculate ΔS_{σ} in the same way whereas we use the internal energy instead of the enthalpy to calculate S_{ex} :

$$S_{ex} = \frac{Q}{T} = \frac{\Delta U}{T} = \frac{\Delta_r U_T^{\circ} \cdot \xi_{max}}{T}$$

Exercise 5.8 Consider the preparation of a solution of hydrochloric acid HCl at $1 \text{ mol} \cdot \text{L}^{-1}$. The pressure in the laboratory is $P^\circ = 1 \text{ bar}$ and the temperature is $T_{\text{laboratory}} = 25^\circ\text{C}$. Thermodynamic data at 298 K:

Substance	HCl	H ₂ O	H ₃ O ⁺	Cl ⁻
$\Delta_f H_{298}^\circ$ (kJ·mol ⁻¹)	-40.020	-285.83	-343.93	-40.023
S_{298}° (J·mol ⁻¹ ·K ⁻¹)	13.17	69.95	13.95	13.17

The equation for the reaction of dissolution of one mole of hydrochloric acid HCl in one litre of aqueous solution is complete ($\xi_{\text{max}} = 1$) because HCl is a strong acid that will dissociate totally in water:



We can calculate the created entropy as:

$$\begin{aligned} S_{\text{cr}} &= \Delta S_\sigma - S_{\text{ex}} \\ \Delta S_\sigma &= \Delta_r S_{298}^\circ \cdot \xi_{\text{max}} = -56.00 \text{ J} \cdot \text{K}^{-1} \\ S_{\text{ex}} &= \frac{Q}{T_{\text{ext}}} = \frac{\Delta H_\sigma}{T_{\text{ext}}} = \frac{\Delta_r H_{298}^\circ \cdot \xi_{\text{max}}}{T_{\text{laboratory}}} = 194.98 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

Thus, $S_{\text{cr}} = 138.98 \text{ J} \cdot \text{K}^{-1} > 0$.

The dissolution reaction of hydrochloric acid in water is therefore possible (or spontaneous) and irreversible under these conditions, *i.e.* $T = 25^\circ\text{C}$ and $P = 1 \text{ bar}$. ■

Introduction of a new state function

We conclude this chapter by introducing a new state function (that will be treated extensively in the next chapter) called Gibbs energy, noted G , that is defined as:

$$G \equiv H - TS$$

The interest of this function is that it allows a quicker evaluation of the possibility of an **isothermal and isobaric process**, as chemical reactions for example. Indeed, for chemical reactions we can simply evaluate the sign of the variation of the standard Gibbs energy, ΔG_T° , to know if it is possible or not as previously done with S_{cr} . We can see that:

$$\begin{aligned} S_{\text{cr}} &= \Delta_r S_T^\circ \cdot \xi_{\text{max}} - \frac{\Delta_r H_T^\circ \cdot \xi_{\text{max}}}{T} \\ S_{\text{cr}} &= \Delta S_T^\circ - \frac{\Delta H_T^\circ}{T} \\ TS_{\text{cr}} &= T\Delta S_T^\circ - \Delta H_T^\circ \\ -TS_{\text{cr}} &= -T\Delta S_T^\circ + \Delta H_T^\circ \\ -TS_{\text{cr}} &= \Delta H_T^\circ - T\Delta S_T^\circ = \Delta G_T^\circ \\ \Delta G_T^\circ &= -TS_{\text{cr}} \end{aligned}$$

Being the variation of standard Gibbs energy equal to minus the created entropy (without considering the absolute temperature that does not affect the sign being always positive), we can say that for chemical reactions carried on in standard conditions:

- $\Delta G_T^\circ < 0$: process possible (or spontaneous) and irreversible
- $\Delta G_T^\circ = 0$: process possible (or spontaneous) and reversible
- $\Delta G_T^\circ > 0$: process impossible

The advantage of using the Gibbs energy instead of the created entropy is that the calculation of ΔG_T° requires only the knowledge of the parameters of the system and is more straightforward than the calculation of S_{cr} . Indeed, although the good student of thermodynamics would find easy the calculation of S_{cr} for chemical reactions, and so the calculation of ΔG_T° redundant, the latter can be done more easily without the precise knowledge of the surroundings that is not always straightforward as the system.

Note: keep in mind that $\Delta G_T^\circ = -TS_{cr}$ only for **isothermal** (or monothermal) and **isobaric** (or monobaric) processes. For any other type of process, the calculation of ΔG_T° will give you just a number without any information on the fact if the process is possible or not. The **only** parameter telling us if any process is possible or not remains always the created entropy.

Chapter 6

Physical and chemical equilibria

This chapter presents the fundamental thermodynamic concepts used to study the physical and chemical equilibria. The notion of thermodynamic potential is introduced. The state function Gibbs energy is introduced and its use to processes occurring at constant T and P is shown. The thermodynamic fundamental property relations are introduced and expressed for closed and open systems. The notion of chemical potential is introduced. Applications of the Gibbs energy and chemical potential are shown for chemical-reaction equilibrium and for phase equilibrium (*e.g.* Clapeyron equation).

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The **learning Objectives** of this chapter are to:

- Define and use thermodynamic potentials
- Define the Gibbs energy
- Identify the equilibrium state of a closed system at constant T and P
- Know the fundamental property relation of the Gibbs energy for a closed and open system
- Define the chemical potential of a substance
- Apply the fundamental property relation of the Gibbs energy for a chemical-reaction equilibrium
- Apply the fundamental property relation of the Gibbs energy for a phase equilibrium
- Obtain the Clapeyron equation
- Integrate of the Clapeyron equation for the cases of vaporisation, sublimation and melting

6.1 Thermodynamic potentials

Thermodynamic potentials are scalar quantities used to represent the thermodynamic state of a system. More accurately, they are state functions that describe the equilibrium behaviour of a system as a function of so-called "natural variables", *i.e.* P , T , V and S . Four common thermodynamic potentials are (see section 6.3):

- Internal energy $U = f(S, V)$;
- Enthalpy $H = f(S, P)$;
- Gibbs energy $G = f(T, P)$;
- Helmholtz energy $F = f(T, V)$.

Just as in mechanics, where potential energy is defined as capacity to do work, the four thermodynamic potentials have different meanings for a closed system:

- Internal energy is the capacity to do work (both of pressure forces and other types) plus the capacity to release heat.
- Enthalpy is the capacity to do works other than pressure forces plus the capacity to release heat.
- Gibbs energy ($G = H - TS$) is the capacity to do works other than pressure forces.
- Helmholtz energy ($F = U - TS$) is the capacity to do both work of pressure forces and other types of work.

Thermodynamic potentials are very useful when calculating the equilibrium results of a chemical reaction (chemical equilibrium) or of change of phase (physical equilibrium). Indeed, chemical reactions and changes of phase usually take place under some constraints such as constant pressure and temperature, or constant entropy and volume. Under these conditions there is a corresponding thermodynamic potential that comes into play. Just as in mechanics, the system will tend towards lower values of potential and at equilibrium, under these constraints, the potential will take on an unchanging minimum value. The thermodynamic potentials can also be used to estimate the total amount of energy available from a thermodynamic system under the appropriate constraint.

In particular, when the entropy S and the volume V of a closed system are held constant, the internal energy U decreases and reaches a minimum value at equilibrium (see section 6.2.1). This follows from the first and second laws of thermodynamics and is called the principle of minimum energy. The following three statements are directly derivable from this principle (see section 6.2.1):

- When the pressure P and the entropy S of a closed system are held constant, the enthalpy H decreases and reaches a minimum value at equilibrium.
- When the temperature T and the pressure P of a closed system are held constant, the Gibbs energy G decreases and reaches a minimum value at equilibrium.
- When the temperature T and the volume V of a closed system are held constant, the Helmholtz energy F decreases and reaches a minimum value at equilibrium.

The interest of using thermodynamic potentials is that, based only on the knowledge of system variables, they allow one to know immediately the direction in which a system will evolve under certain conditions. This means that we can say if a process affecting our system is possible (irreversible or reversible) or not without calculating the created entropy S_{cr} associated to the process which requires the knowledge of the surrounding variables and conditions (to calculate the exchanged entropy S_{ex}). We have seen a practical example at the end of chapter 5, where the thermodynamic potential G allowed us to state if a chemical reaction (an isobaric and isothermal process) is possible (or spontaneous) or not.

While we introduced and used extensively U and H in chapter 3 to do energy balances, their use as potential thermodynamics will not be treated in this course. The same is true also for the Helmholtz energy that has been introduced here only for the sake of knowledge. In the following part of the chapter we will focus only on the Gibbs energy because, in this course and also in Chemistry of the 2nd year, you will deal only with chemical reactions and changes of phase that are processes

carried on in isobaric (or monobaric) and isothermal (or monothermal) conditions.

6.2 The Gibbs energy (or Gibbs free energy)

Definition 6.2.1 The mathematical (and only) definition of Gibbs energy G is

$$G \equiv H - TS$$

It represents the difference between the state function H and the product of the state variable T and the state function S . Therefore, also G is a state function. This implies that the Gibbs energy depends only on the initial and the final state of a system, and not on the path followed between these two states (*i.e.* type of process).

6.2.1 Physical interpretation of the Gibbs energy

Consider a closed system σ containing an arbitrary number of species and composed of an arbitrary number of phases in which the temperature and pressure are spatially uniform. The system is initially in a non-equilibrium state with respect to mass transfer between phases and chemical reaction (all of them **within** the system). Irreversible processes take the system ever close to an equilibrium state. We imagine that the system and its surroundings are always in thermal ($T = T_{ext}$) and mechanical ($P = P_{ext}$) equilibrium. Heat exchanges and expansion work (*i.e.* work of pressure forces) between the system and the surroundings are then accomplished reversibly. No other types of work (*i.e.* shaft work and non-mechanical work) are considered. Under these circumstances the exchanged entropy between the system and the surroundings is:

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

The second law of thermodynamics states that a process is reversible if:

$$\Delta S_{\sigma} - S_{ex} = S_{cr} \geq 0$$

with ΔS_{σ} being the total variation of entropy of the system. Combining these expressions yields, upon rearrangement:

$$Q \leq T \Delta S_{\sigma}$$

Application of the first law of thermodynamics with the assumption of reversible mechanical interactions with the surroundings provides:

$$\Delta_t U_{\sigma} = Q + W_{pf} \rightarrow Q = \Delta_t U_{\sigma} - W_{pf}$$

Combining the two last equations and rearranging gives:

$$\Delta_t U_{\sigma} - W_{pf} - T \Delta S_{\sigma} \leq 0$$

Because this equation relates only state variables, it must be satisfied for changes in the state of any closed system of spatially uniform T and P , without restriction to the conditions of reversibility assumed in its derivation. The inequality applies to every change of the system between non-equilibrium states, and it dictates the direction of change that leads toward equilibrium. The equality holds for changes between equilibrium states (*i.e.* reversible processes).

The last equation is very general and its application to practical problems is difficult; restricted

versions are much more useful. For example, if a process is restricted to occur at constant T and P , we obtain:

$$\Delta_i U_\sigma + P\Delta_i V - T\Delta_i S_\sigma \leq 0$$

and from the definition of enthalpy and Gibbs energy we obtain:

$$\Delta_i H_\sigma - T\Delta_i S_\sigma \leq 0$$

$$\Delta_i G_\sigma \leq 0 \quad \text{for processes at constant } P \text{ and } T$$

where the equality ($\Delta_i G_\sigma = 0$) applies to isobaric and isothermal reversible processes (equilibrium conditions) whereas the inequality ($\Delta_i G_\sigma < 0$) applies to monobaric and monothermal irreversible processes (out of equilibrium conditions).

The last equation is very useful because T and P , which are easily measured and controlled, are more conveniently held constant than other variables, such as U and V . This equation indicates that all irreversible processes occurring without change of T and P between the initial and final state (monothermal and monobaric processes) must decrease the Gibbs energy of the system.

The equilibrium state of a closed system is that state for which the total Gibbs energy of the system is a minimum with respect to all possible changes at the given T and P .



Although T and P are most easily held constant in experimental work, in molecular simulation studies, other variables are often more easily held constant.

Note: from the inequality $\Delta_i U_\sigma - W_{pf} - T\Delta_i S_\sigma \leq 0$ the following statements introduced in the previous section on the use of the thermodynamic potential can be easily demonstrated:

$$\Delta_i U_\sigma \leq 0 \quad \text{for } \mathbf{isochoric} \text{ and } \mathbf{isoentropic} \text{ processes}$$

$$\Delta_i H_\sigma \leq 0 \quad \text{for } \mathbf{isobaric} \text{ and } \mathbf{isoentropic} \text{ processes}$$

$$\Delta_i F_\sigma \leq 0 \quad \text{for } \mathbf{isochoric} \text{ and } \mathbf{isothermal} \text{ processes}$$

Similarly, for processes occurring at constant internal energy and volume ($\Delta_i V = 0$ and $\Delta_i U = 0$):

$$\Delta_i S_\sigma \leq 0 \quad \text{for } \mathbf{isochoric} \text{ and at constant } U \text{ processes}$$

An isolated system is necessarily constrained to constant internal energy and volume, and validity of the last equation follows directly from the second law.

Caution: the variation of Gibbs energy $\Delta_i G_\sigma$ can be calculated for any type of process, but it can only be used as a thermodynamic potential to predict the evolution of a system under the restrictive conditions above (no change of T and P between the initial and final state and only work of pressure forces exchanged by the system during the process). We have already seen that if other state variables are held constant there are other state functions to be used as thermodynamic potential of the system. Let's see here the case when also other types of work can be exchanged by the system with the surroundings. In this case we obtain:

$$\Delta_i U_\sigma - W_{pf} - W_s - W_{\text{non-mech}} - T\Delta_i S_\sigma \leq 0$$

which at constant T and P leads, for a closed system, to:

$$\Delta_i G_\sigma \leq W_s + W_{\text{non-mech}}$$

where the equality applies for reversible processes. The last equation shows us that the variation of Gibbs energy of a closed system represents its capacity to do all types of work other than the work of pressure forces (as stated in section 6.1). In addition, the equation shows us that, for the same $\Delta_r G_\sigma$, the work not of pressure forces received (given) by the system during the process will be higher (lower) for the irreversible case because part of it will be lost to create entropy ($S_{cr} > 0$).

■ **Example 6.1** Batteries are closed thermodynamic systems capable of providing electrical work (W_e) thanks to two chemical reactions (a reduction and an oxidation) occurring within the system. In this case, the variation of Gibbs energy of the system is equal to the electrical work provided in a reversible way by the system to the surroundings ($\Delta_r G_\sigma = W_e$). We will see this case more in details in the course of Chemistry of the 2nd year. ■

6.3 Fundamental property relations

6.3.1 Case of closed systems

Considering closed systems with n moles of a pure substance, the first law in its differential form can be written for reversible processes:

$$d(n\bar{U}) = \delta Q_{rev} + \delta W_{rev}$$

By knowing that $\delta Q_{rev} = Td(n\bar{S})$ and $\delta W_{rev} = -Pd(n\bar{V})$ we obtain:

$$d(n\bar{U}) = Td(n\bar{S}) - Pd(n\bar{V})$$

where \bar{U} , \bar{S} and \bar{V} are the molar values of the internal energy, entropy and volume that need to be multiplied by the total number of moles n . All of the *primitive* thermodynamic properties, *i.e.* P , T , V , S and U , are included in this equation. It is a **fundamental property relation** connecting these properties for closed systems. All other equations relating properties of such systems derive from it. Additional thermodynamic properties are defined as a matter of convenience, in relation to the primary properties. We can therefore obtain for closed systems made of n moles equivalent fundamental property relations involving the enthalpy and the Gibbs energy:

$$d(n\bar{H}) = Td(n\bar{S}) + n\bar{V}dP$$

$$d(n\bar{G}) = -n\bar{S}dT + n\bar{V}dP$$

The three equations of U , H and G are derived for a reversible process. However they contain only *properties* of the system, which depend only on the state of the system, and not on the path followed to reach that state. These equations are therefore valid for a closed system undergoing reversible or irreversible processes. The system may consist of a single phase (homogeneous system) or of several phases (heterogeneous system); it may undergo chemical reactions or not.

The choice of which equation to use in a particular application is dictated by convenience. However the Gibbs energy G is special because of its unique functional relation to T and P . Temperature and pressure are unique among thermodynamic quantities in that they are intensive variables with no extensive counterpart. They can be defined and measured locally, at a single point, which makes their measurement and control much more straightforward than for other thermodynamic variables.

6.3.2 Case of open systems (chemical potential)

The differential equations previously established show that the quantities U , H and G are respectively a function of the variables S and V , S and P , T and P for a closed system. For the more general case of a homogeneous open system, material can enter and leave the system and U , H and G will be also function of the number of moles n of the chemical species present in the system. Therefore, in addition to the two thermodynamic variables identified above, we must add the number of moles n of the pure substance.

For example, the Gibbs energy of a system with n moles of a substance will be $G = f(T, P, n)$ and its property relation is:

$$d(n\bar{G}) = \left(\frac{\partial(n\bar{G})}{\partial T} \right)_{P,n} dT + \left(\frac{\partial(n\bar{G})}{\partial P} \right)_{T,n} dP + \left(\frac{\partial(n\bar{G})}{\partial n} \right)_{T,P} dn$$

Such an expression should obviously lead, at n constant, to the expression $d(n\bar{G}) = -n\bar{S}dT + n\bar{V}dP$ which makes it possible to write in this case:

$$d(n\bar{G}) = -n\bar{S}dT + n\bar{V}dP + \left(\frac{\partial(n\bar{G})}{\partial n} \right)_{T,P} dn$$

The term $\left(\frac{\partial(n\bar{G})}{\partial n} \right)_{T,P}$ represents the variation in the Gibbs energy of the system respect to the moles of the substance at constant temperature and pressure. This term is given its own symbol and name.

Definition 6.3.1 It is, by definition, the **chemical potential** of the substance forming the system:

$$\mu \equiv \left(\frac{\partial(n\bar{G})}{\partial n} \right)_{T,P}$$

With this definition we can write:

$$d(n\bar{G}) = -n\bar{S}dT + n\bar{V}dP + \mu dn$$

which is the **fundamental property relation** for single phase fluid systems of variable mass. A more general equation allowing one to consider also the case of variable composition of the system (made of more substances i) is:

$$d(n\bar{G}) = -n\bar{S}dT + n\bar{V}dP + \sum_i \mu_i dn_i$$

with μ_i the chemical potential of each substance i (or species) forming the system.

This last equation is the foundation upon which the study of equilibrium in chemical reactions and between different phases is built and is more commonly found in the following form where all term are divided by the number of total moles n of the system:

$$d\bar{G} = -\bar{S}dT + \bar{V}dP + \sum_i \mu_i dx_i$$

with x_i the molar fraction of each substance i of the system.

Finally, having introduced the chemical potential, we can see that, at constant T , P and molar ratio composition of a system, we can express the total Gibbs energy of the system as the sum of the chemical potential of all species:

$$n\bar{G} = \int d(n\bar{G}) = \int \sum_i \mu_i dn_i = \sum_i \mu_i n_i$$

The differential of the last expression is:

$$d(n\bar{G}) = d\left(\sum_i \mu_i n_i\right) = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

that combined with the fundamental property relation gives:

$$\sum_i \mu_i dn_i + \sum_i n_i d\mu_i = -n\bar{S}dT + n\bar{V}dP + \sum_i \mu_i dn_i$$

$$\sum_i n_i d\mu_i = -n\bar{S}dT + n\bar{V}dP$$

The last equation is called **Gibbs–Duhem relation** and relates the differential of the chemical potential to the differential of T and P .

6.4 Application of the Gibbs energy

Practical applications of the Gibbs energy and the chemical potential are found when treating chemical and phase equilibria at constant T and P .

6.4.1 Chemical equilibria

For a closed single phase system containing n_i chemically reactive species the following equation previously introduced must both be valid:

$$\begin{aligned} d(n\bar{G}) &= -n\bar{S}dT + n\bar{V}dP \\ d(n\bar{G}) &= -n\bar{S}dT + n\bar{V}dP + \sum_i \mu_i dn_i \end{aligned}$$

Indeed, the former was specifically obtained for closed systems whereas the latter must be valid because is more general (and so it includes also the case of closed systems). Moreover, for a closed system, all differentials dn_i must result only from chemical reaction (no mass exchange between the system and the surroundings). Comparison of these two equations shows that they can both be valid only if:

$$\sum_i \mu_i dn_i = 0$$

This last equation represents a general criterion for chemical-reaction equilibrium in a single phase closed system, and provides the basis for developing working equations for the solution of reaction-equilibrium problems. Indeed, at constant T and P the integration of the last equation over the total number of moles allows one to calculate the total Gibbs energy of the system before and after the chemical reaction takes place:

$$n\bar{G} = \int \sum_i \mu_i dn_i = \sum_i \mu_i n_i$$

and after we can calculate the variation of total Gibbs energy due to the chemical reaction:

$$\Delta_r G_\sigma = (n\bar{G})_{\text{after reaction}} - (n\bar{G})_{\text{before reaction}}$$

According to the value of $\Delta_r G_\sigma$, we can immediately evaluate if the chemical reaction is:

- possible and irreversible ($\Delta_r G_\sigma < 0$);
- possible and reversible ($\Delta_r G_\sigma = 0$);

- impossible $\Delta_r G_\sigma > 0$.

We have found a similar result at the end of chapter 5 using a different approach. However, there we found the value of the standard Gibbs energy ΔG_T° which tells us if a chemical reaction is possible or not in standard conditions (*i.e.*, $P = 1$ bar). Here, the approach is more general because based on the use of the Gibbs energy as thermodynamic potential for any process at constant T and P (with chemical reactions as specific case). It tells us if a chemical reaction is possible or not in its processing conditions (and not only in the standard state). You will see in the course of Chemistry of the 2nd year that the $\Delta_r G_\sigma$ and ΔG_T° are related and the knowledge of the latter is necessary to the study of chemical reaction equilibria.

6.4.2 Physical equilibria

With respect to phase equilibrium, we note that for a closed non-reacting system consisting of two phases α and β in equilibrium, each individual phase is open to the other, and species can move between phases. We can therefore write the fundamental property relation of the Gibbs energy for an open system to each phase separately:

$$d(n\bar{G})^\alpha = -(n\bar{S})^\alpha dT + (n\bar{V})^\alpha dP + \sum_i \mu_i^\alpha dn_i^\alpha$$

$$d(n\bar{G})^\beta = -(n\bar{S})^\beta dT + (n\bar{V})^\beta dP + \sum_i \mu_i^\beta dn_i^\beta$$

where superscripts α and β identify the phases. For the system to be in thermal and mechanical equilibrium, T and P must be uniform.

The change in total Gibbs energy of the two-phase system is the sum of the equations for the separate phases (assuming that surface effects are negligible):

$$d(n\bar{G})^\alpha + d(n\bar{G})^\beta = -[(n\bar{S})^\alpha + (n\bar{S})^\beta]dT + [(n\bar{V})^\alpha + (n\bar{V})^\beta]dP + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$$

$$d(n\bar{G}) = -n\bar{S}dT + n\bar{V}dP + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$$

with the total Gibbs energy ($n\bar{G}$), entropy ($n\bar{S}$) and volume ($n\bar{V}$) of the system are given by the sum of the contributions coming from both phases.

Because the two-phase system is closed, the fundamental property relation of the Gibbs energy for a closed system is also valid:

$$d(n\bar{G}) = -n\bar{S}dT + n\bar{V}dP$$

Comparing the two equations shows that at equilibrium:

$$\sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta = 0$$

The changes dn_i^α and dn_i^β result from mass transfer between the phases; mass conservation therefore requires:

$$dn_i^\alpha = -dn_i^\beta \rightarrow \sum_i (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha = 0$$

Quantities dn_i^α are independent and arbitrary; the only way the left side of the last equation can, in general, be zero is for each term in parenthesis separately to be zero. Hence:

$$\mu_i^\alpha = \mu_i^\beta \quad (i = 1, 2, \dots, N)$$

where N is the number of species present in the system.

Two phases (and by extension multiple phases) at the same T and P are in equilibrium when the chemical potential of each species is the same in all phases.

The application of the last equation to specific phase-equilibrium problems requires the expression of G and μ_i as function of temperature, pressure and composition. The simplest of these, the ideal-gas state mixture and the ideal liquid solution are treated more in details in the course of Chemistry of the 2nd year.

6.4.3 Clapeyron equation

The equality of the chemical potentials when two phases α and β are at equilibrium at the same T and P , allows us to obtain a relation between the temperature and the pressure of the system at equilibrium. Let's consider a closed system made of one mole of a pure substance with two phases at thermal and mechanical equilibrium. We have previously seen that at equilibrium we must have:

$$\mu_\alpha = \mu_\beta$$

If we move the system towards a new equilibrium position by slightly modifying both μ_α and μ_β , we obtain:

$$\mu_\alpha + d\mu_\alpha = \mu_\beta + d\mu_\beta \rightarrow d\mu_\alpha = d\mu_\beta$$

meaning that, at equilibrium, any differential variation of the chemical potential of one phase is compensated by an equal variation of the chemical potential of the other phase. Using now the Gibbs-Duhem relation (see section 6.3.2) we can obtain:

$$-\bar{S}_\alpha dT + \bar{V}_\alpha dP = -\bar{S}_\beta dT + \bar{V}_\beta dP$$

$$\frac{dP}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha}$$

with $(\bar{S}_\beta - \bar{S}_\alpha)$ and $(\bar{V}_\beta - \bar{V}_\alpha)$ representing respectively the entropy and volume variation when a mole passes from the phase α to β at the temperature T under pressure P .

Since the phase change (transition $\alpha \rightarrow \beta$) takes place in a reversible way, we have:

$$\Delta_{\text{phase change}} G_T = \Delta_{\text{phase change}} H_T - T \Delta_{\text{phase change}} S_T = 0 \rightarrow$$

$$\Delta_{\text{phase change}} S_T = \bar{S}_\beta - \bar{S}_\alpha = \frac{\Delta_{\text{phase change}} H_T}{T}$$

with $\Delta_{\text{phase change}} H_T$ representing the enthalpy variation during the change of state.

Hence :

$$\frac{dP}{dT} = \frac{\Delta_{\text{phase change}} H_T}{T(\bar{V}_\beta - \bar{V}_\alpha)}$$

The last equation is called the **Clapeyron equation**. In the $P - T$ diagram, this ratio represents the slope at all points of the boundaries between the physical states of the pure substance.

Clapeyron equation in the cases of vaporisation

In the case of vaporisation the phase change $\alpha \rightarrow \beta$ corresponds to liquid \rightarrow gas (or vapour). In this case the Clapeyron equation is written:

$$\frac{dP}{dT} = \frac{\Delta_{\text{vap}} H_T}{T(\bar{V}_{\text{gas}} - \bar{V}_{\text{liq}})}$$

This differential form can be integrated by applying three following hypothesis:

- Hyp 1: the molar volume of the gas phase is very large compared to the molar volume of the liquid phase ($\bar{V}_{gas} \gg \bar{V}_{liq}$) which implies that: $(\bar{V}_{gas} - \bar{V}_{liq}) \approx \bar{V}_{gas}$
- Hyp 2: the gas phase is considered as an ideal gas which implies: $\bar{V}_{gas} = \frac{V}{n} = \frac{RT}{P}$
- Hyp 3: the enthalpy of vaporisation is independent of T (true only in a restricted temperature range).

We therefore obtain:

$$\frac{dP}{dT} = \frac{\Delta_{vap}H_T}{T(\bar{V}_{gas} - \bar{V}_{liq})} \approx \frac{\Delta_{vap}H_T}{T\bar{V}_{gas}} = \frac{P\Delta_{vap}H_T}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta_{vap}H_T}{R} \frac{dT}{T^2}$$

and integrating the last equation in the temperature range $T_1 - T_2$:

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta_{vap}H_T}{R} \frac{dT}{T^2}$$

$$\ln \frac{P_2^*}{P_1^*} = -\frac{\Delta_{vap}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

The last equation is the **integrated form** of the Clapeyron equation for the case of the vaporisation. It relates the variation as a function of T of the pressure of a system made of a pure substance and showing a liquid and gas phase at equilibrium. We remind the reader that in this case the system pressure corresponds to the vapour pressure (P^*) of the substance. This equation has been already introduced in Chapter 2, although without demonstrating its origin, by putting $\Delta_{vap}H_T = Q$ because in isobaric processes the heat exchanged by the system is equal to the variation of enthalpy of the system itself (see Chapter 3).

Note: this equation can be found in the more general form $\ln P^* = \frac{A}{T} + B$ with $A = -\frac{\Delta_{vap}H}{R}$ and B an integration constant.

Clapeyron equation in the cases of sublimation

In the case of sublimation the phase change $\alpha \rightarrow \beta$ corresponds to solid \rightarrow gas (or vapour). In this case the Clapeyron equation is written:

$$\frac{dP}{dT} = \frac{\Delta_{sub}H_T}{T(\bar{V}_{gas} - \bar{V}_{sol})}$$

By applying the same three hypothesis introduced in the case of the vaporisation, we obtain in the same way the integrated form of the Clapeyron equation for the case of the sublimation:

$$\ln \frac{P_2^*}{P_1^*} = -\frac{\Delta_{sub}H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Here we have obtained the mathematical form of the vaporisation and sublimation curves in the $P - T$ diagram. The pressure P^* in this expression is the vapour pressure of the gas above the liquid or solid phase of the pure substance under study. By taking experimental measurement of P^* and T during vaporisation or sublimation, and by plotting of $\ln P^*$ as a function of $\frac{1}{T}$ you can determine $\Delta_{vap}H_T$ or $\Delta_{sub}H_T$.

From the previous equations, we can deduce the relative positions of the sublimation curves and

the vaporisation in the $P - T$ diagram. We have indeed:

$$\begin{aligned}\Delta_{melt}H + \Delta_{vap}H &= \Delta_{sub}H \\ \left(\frac{dP}{dT}\right)_{vap} &= P \frac{\Delta_{vap}H}{RT^2} \\ \left(\frac{dP}{dT}\right)_{sub} &= P \frac{\Delta_{sub}H}{RT^2}\end{aligned}$$

Being $\Delta_{vap}H_{melt} > 0$ we have $\Delta_{sub}H > \Delta_{vap}H$ and then we can deduce that:

$$\left(\frac{dP}{dT}\right)_{sub} > \left(\frac{dP}{dT}\right)_{vap}$$

At the triple point the slope of the sublimation curve is therefore greater than the slope of the vaporisation curve.

Clapeyron equation in the cases of melting

In the case of melting the phase change $\alpha \rightarrow \beta$ corresponds to solid \rightarrow liquid. In this case the Clapeyron equation is written:

$$\frac{dP}{dT} = \frac{\Delta_{melt}H_T}{T(\bar{V}_{liquid} - \bar{V}_{solid})}$$

In this case, the integrated form of the Clapeyron equation is obtained in a different way than the previous cases of vaporisation and sublimation. We start affirming that for both solid and liquid phases (*i.e.* condensed phases) the molar volume can be expressed in terms of density:

$$\bar{V}_{\text{condensed phase}} = \frac{V_{\text{condensed phase}}}{n} = \frac{V_{\text{condensed phase}}M}{nM} = \frac{M}{\rho_{\text{condensed phase}}}$$

with M the molar mass of the considered substance. Hence:

$$\begin{aligned}\frac{dP}{dT} &= \frac{\Delta_{melt}H_T}{T\left(\frac{M}{\rho_{liquid}} - \frac{M}{\rho_{solid}}\right)} = \frac{\Delta_{melt}H_T}{TM\left(\frac{1}{\rho_{liquid}} - \frac{1}{\rho_{solid}}\right)} \\ dP &= \frac{\Delta_{melt}H_T}{M\left(\frac{1}{\rho_{liquid}} - \frac{1}{\rho_{solid}}\right)} \frac{dT}{T}\end{aligned}$$

and integrating the last equation in the temperature range $T_1 - T_2$:

$$\int_{P_1}^{P_2} dP = \int_{T_1}^{T_2} \frac{\Delta_{melt}H_T}{M\left(\frac{1}{\rho_{liquid}} - \frac{1}{\rho_{solid}}\right)} \frac{dT}{T}$$

$$P_2 - P_1 = \frac{\Delta_{melt}H_T}{M\left(\frac{1}{\rho_{liquid}} - \frac{1}{\rho_{solid}}\right)} \ln \frac{T_2}{T_1}$$

The last equation is the **integrated form** of the Clapeyron equation for the case of the melting. Here we have obtained the mathematical form of the melting curve in the $P - T$ diagram. We can see that, being typically $\rho_{solid} > \rho_{liquid}$, the slope $\frac{dP}{dT}$ of the melting curve is **positive** for any substance with only one notable exception consisting in the water.

Note: special case of water

It is known that the density of ice (0.92 g/cm^3) is lower than the density of liquid water (1 g/cm^3). Therefore, the molar volume \bar{V}_{ice} of the ice is greater than the molar volume $\bar{V}_{liquid \text{ water}}$ of the liquid water meaning that the slope $\frac{dP}{dT}$ of the melting curve is **negative for water**.

Knowing that the melting temperature under atmospheric pressure is equal to 273.15 K (0°C), the temperature of the triple point of water will be higher than 0°C (Figure 6.1), and at temperatures slightly below 0°C ice can be melted by simply increasing the pressure (this is what allows the skier to glide over the snow, which melts superficially under his weight).

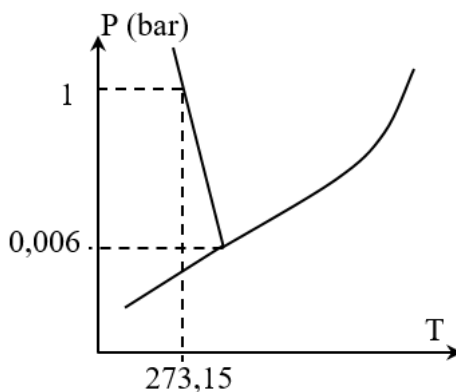


Figure 6.1: Water melting curve in the vicinity of the triple point.

Chapter 7

Stakes

7.1 Stake 1 “Transforming energy” (\$1)

7.1.1 Notion of energy losses

Performance concept

The law of conservation of energy tells us that energy is not created but it is transformed from a stock of primary energy to enable its final use in the form of work and heat transfers (cf. O1 and MB1). However, it undergoes several types of transformation (heat to work, work to heat, kinetic energy to potential energy, potential energy to kinetic energy, mechanical work to electricity... (Figure 7.1)) characterised by energy losses that make part of the initial primary energy unusable by the final consumer. We speak, therefore, of **conversion efficiency** (η_c). The energy is also transported from its place of extraction, processing or storage to the end user. Each stage of transport is also accompanied by losses: this is known as **transport efficiency** (η_t). These yields are cumulative:

$$E_{final} = E_{primary} \times \eta_c \times \eta_t$$

Primary energy extraction vs. final consumption

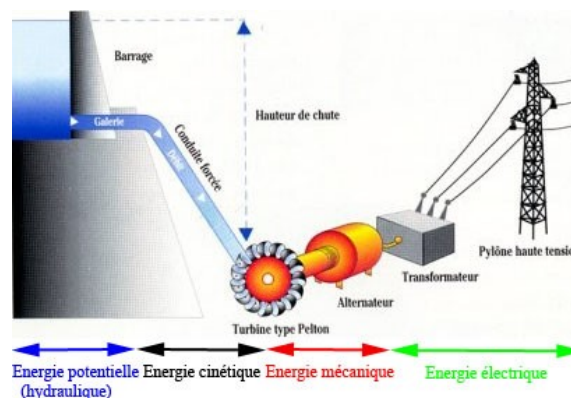


Figure 7.1: Capturing the driving force of water to generate electricity. Water accumulated in dams or diverted through water intakes is potential energy available to drive the turbine of a generator. Hydraulic energy is then transformed into kinetic energy and then into mechanical energy. This turbine is mechanically coupled to a generator and drives it in rotation in order to convert the mechanical energy into electrical energy. For installations of a certain power, the voltage has to be raised by a transformer.

Global primary energy extraction in 2017 is distributed as shown in Figure 7.2. It represents 13,972 Mtep, or 5.85×10^{20} J. It has been multiplied by a factor of 2.3 since 1973 and continues to increase. If we evaluate the total energy consumed worldwide, we can see that it represents only 70% of the primary energy extracted: the accumulation of conversion, production and transport efficiencies leads to 30% of energy losses.

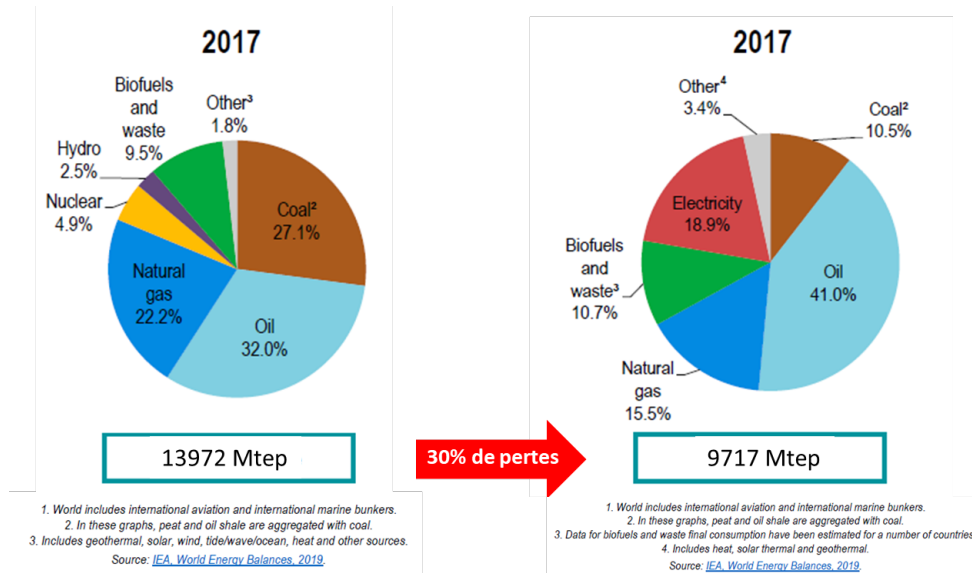


Figure 7.2: World primary energy extracted, right, and energy consumed (world), left, in 2017 (source: Key Word Energy Statistics, International Energy Agency, 2019).

The case of electricity

Electricity accounted for 18.5% of the world's final energy consumption in 2015 (18.9% in 2017, see Figure 7.2). The global electricity production mix is still largely dominated by coal (39.3% of global production in 2015), which is a major emitter of greenhouse gases (Figure 7.3). Decarbonised energies remain for the time being a minority in this mix (33.7% of world production). Hydropower in particular produced 3,978 TWh in the world in 2015 (16% of the mix), *i.e.* more than nuclear (2,571 TWh), wind (838 TWh) and photovoltaic (247 TWh) production combined.

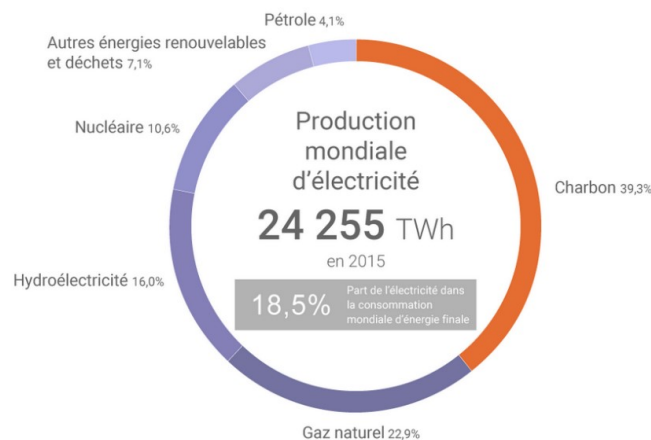


Figure 7.3: Primary sources used for global electricity generation in 2015 (source: <https://www.connaissancedesenergies.org/les-chiffres-cles-de-lenergie-dans-le-monde-170926>).

In France, for electricity, 1 kWh of final energy (used at the meter) is equivalent to 2.6 kWh of primary energy. This conversion rate, normalised, has been calculated taking into account the average efficiency of electricity production in power stations in France, which is 43.5%, as well as distribution losses, which are 5%. This gives an electricity production efficiency of 38.5%, hence the coefficient of 2.6.

7.1.2 Power quality

The conversion of energy degrades its quality, which reduces the quantity of usable energy (*cf.* O12 and O13), particularly due to the existence of irreversibilities in the processes (*cf.* O14). Experience shows that any spontaneous evolution of a system tends to give increasingly disordered states (which is quantified by an increase in the entropy of the universe (*cf.* O13)). Heat is an energy transfer leading to disordered movements of the atoms or molecules constituting the system (linked to the thermal agitation of the particles), whereas work, qualified as noble energy, corresponds to an energy transfer leading to a coherent movement of the particles (Figure 7.4). Work therefore tends to be transformed into heat, which appears as a degraded form of energy. The losses identified throughout an energy chain (*cf.* MB1) thus correspond to heat lost by the system during its process, which cannot be fully reconverted into noble energy; the stakes in recovering this fatal heat are therefore of the first order.

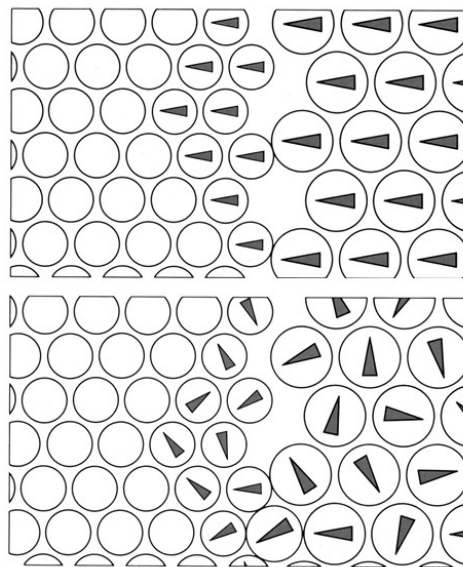


Figure 7.4: Diagram of the movement of particles associated with energy transfer in the form of work on the top (coherent movement) and in the form of heat on the bottom (incoherent movement).

7.2 Stake 2 “Energy mix” (S2)

7.2.1 Definition

The *energy mix*, or *energy bouquet*, represents the distribution of the different sources of primary energy consumed in a given geographical area. The energy mix therefore includes the different forms of primary energy detailed in section S1, nuclear, chemical, thermal and mechanical energy, but is often presented with this breakdown:

- fossil fuels,
- renewable energies,
- nuclear energy.

At the global level, the energy mix is more than 80% dominated by fossil fuels.

The composition of the energy mix is different for each region, country or company. It varies according to the availability of resources, the energy needs to be covered and the political choices made by different leaders. The energy mix is a first step in the energy transition. It ensures that energy production is not based on a single type of primary energy.

Diversification of energy sources reduces dependence on certain types of energy. It can also make it possible to gradually abandon the most polluting energies.

The share of primary energies in the world consumption, of a country, a community, an industry is generally expressed in percentages. All primary energy sources are accounted for, including those consumed for transport, heating of buildings, *etc.* The energy mix should not be confused with final energy consumption (*cf.* O1), which defines actual energy consumption, nor with the electricity mix, which only takes into account energy sources contributing to the production of electricity; yet electricity accounts for only 18.5% of final energy consumption at world level.

7.2.2 Current issues

Global awareness of environmental and societal issues, changing production and consumption patterns and the development of new technologies are a real challenge for the energy sector, a revolution that calls into question the functioning of the current energy system and implies a different approach in the way we must think about the energy system of 2050, in terms of choice and complementarity of energies.

The challenges posed by climate change imply a significant change in our modes of production, distribution and consumption.

In France, the Energy Transition Law for Green Growth (LTECV), published in the “Journal Officiel” on 18 August 2015, sets a number of ambitious objectives aimed at changing the national energy mix by sharply reducing consumption while increasing the share of renewable and recuperative energies (RE&R). It is therefore expected that there will be a significant reduction in end uses (of the order of 20% in 2030 and 50% in 2050) and a significant increase in the share of R&R in the national energy mix (32% in 2030, of which 40% in the electricity mix and 10% in the gas network). This inclusion of the energy transition as a major political challenge is accompanied by the strengthening of territories as a privileged framework for public policies. Local authorities are at the heart of this process of development and transformation through their decisions on planning, development, urbanism, transport, investment and support for local players. The national objectives of optimising the energy mix cannot be achieved without a strong mobilisation of local authorities, which must act on the following three main components:

- the reduction of final energy requirements;
- the mobilisation of renewable and recuperative energy sources;
- the coordination of energy transport and distribution infrastructures.

The evolution of the energy mix will therefore require a change in the choices made for regional and local urban planning. The success of this transition depends in particular on the ability of all the players to better think about land use and planning in order to reduce energy needs and encourage

the evolution of networks towards an optimised use of renewable energies available on the territory, or nearby.

7.2.3 The French energy mix and comparisons in Europe

A country's energy mix depends on several factors, which change over time: availability of primary resources, geopolitical situation, industrial fabric, political choices, *etc.* Thus, between the 1970s and the end of the 20th century, energy consumption in France changed profoundly. The 1973 oil shock led France to a major energy transition, prompting it to turn to nuclear power, since the country could not take advantage of oil or gas resources that were easily exploitable in its subsoil. Between 1970 and 2012, the share of oil in the French energy mix thus changed from 64% to 31%, while the share of coal fell from 21% to 4% over the same period. For its part, nuclear power, which only accounted for 1.5% of the total energy mix in 1970, finally represented 41% of energy choices forty years later. Conversely, since then, the share of renewable energies has grown steadily, from 6.7% in 1970 to 9.4% in 2015.

At present (see Figure 7.5), the French energy mix consists of 42.5% nuclear, 30.6% oil, 14.2% gas, 3.3% coal and 9.4% renewable energies and waste. Among the renewable energies, wood energy is the leading source of energy consumed on the territory and represents 3.8% of the total energy mix. Hydroelectricity represents 2% of the overall mix, wind power 0.7% and solar power 0.3%.

Figure 7.5 also illustrates the impact of public policies on the local energy mix, for countries that are relatively comparable from a social and economic point of view. In 2011, shortly after the Fukushima disaster, Germany decided to shut down its reactors by 2022 at the latest. Today, 35% of electricity comes from coal-fired power plants, which has profoundly changed the energy mix in this country. The situation in Belgium illustrates a third classic situation in Europe, with a very strong dependence on hydrocarbons (about three quarters of primary energies). In detail, the Belgian energy mix is composed of 46% oil products, 27% natural gas, 13% nuclear and 14% renewable energies and waste.

7.2.4 Conclusion

Faced with this assessment, what future can be drawn up for the ***French energy mix***?

France, like many countries around the world, is engaged in a process of energy transition that should lead to a profound change in its energy mix. Renewable energies are destined to become much more important in the future. Indeed, France aims to increase the share of renewable energies in its overall energy consumption to 32% by 2030. Prior to this deadline, France has set itself a voluntary target of producing 23% of its gross final energy consumption from renewable energy sources by 2020. In practice, this should translate into 33% for heat production, 27% for electricity production and 10.5% for transport. The same applies to the share of fossil fuels, whose consumption is expected to fall by 30% by 2030.

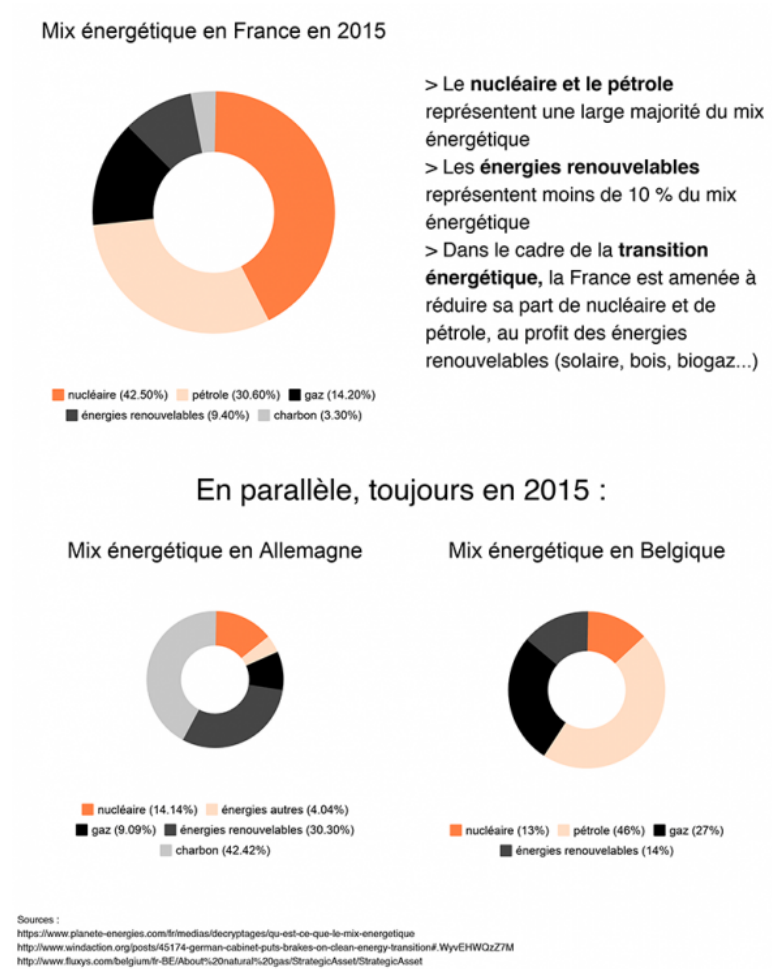


Figure 7.5: Representation of primary energies in 2015 in the French energy mix, and comparison with other European countries.

7.3 Stake 3 “Storing energy” (S3)

This item is largely inspired by the website: <http://www.smartgrids-cre.fr/index.php?p=stockage> consulted on 9 January 2020, and on the publication: "Le stockage d'énergie - Enjeux, solutions techniques et opportunités de valorisation", ENEA, March 2012.

7.3.1 Storage issues

While most primary energy (gas, oil or coal) is easily stored, it is very difficult to store electricity in large quantities. It is, however, possible to convert it into other intermediate and storable forms of energy (potential, kinetic, chemical or thermal), which is done with efficiencies that can be relatively low (*cf.* S1). Furthermore, global electricity consumption is expected to double by 2050, from 24,000 TWh/year today (*cf.* S1) to around 40,000 TWh/year (source: International Energy Agency - IEA), with intensive deployment of wind and solar power, which are intermittent and therefore require the implementation of efficient storage facilities. The development of energy storage means will contribute to:

- an environmental gain linked to the large-scale deployment of decarbonated energies;
- provide centralised or decentralised responses to local or global constraints;
- independence from fossil resources, which is an economic advantage in the long term, as an increase in the price of these resources and in the price of CO₂ is foreseeable.

In addition, storage has many other advantages, especially for network management:

- smoothing out peaks and reducing the consumption of fossil fuels;
- avoid investment in new peak or extreme peak power plants;
- limit the stopping/starting of thermal units and improve the efficiency of thermal power stations;
- to compensate for fatal energy production interruptions (*e.g.* windless periods) by transferring energy over several days;
- smoothing intermittent production (photovoltaic and wind power);
- to be free from power cuts (backup); *etc...*

7.3.2 The different stationary electricity storage technologies

Energy storage solutions are divided into four categories.

Mechanical storage

Pumping stations

Pumping stations are gravitational storage technologies. They consist of two water reservoirs at different heights connected by a pipe system. They are equipped with a pumping system that transfers water from the lower basin to the upper basin during off-peak hours. During peak hours, the station operates like a conventional hydroelectric power station. We can distinguish:

1. inflow pumping stations, which enable a volume of water to be pumped up between its own reservoir and the upper reservoir of a turbine chute. The turbined water thus comes from the gravity and pumping station inputs;
2. pumped energy transfer stations (WWTPs, Figure 7.6): these are characterised by pump-turbine cycles between a lower reservoir and an upper reservoir, thanks to reversible pump-turbines. The pumping can be "mixed" (the turbined water comes from gravity and pumping station inputs) or "pure" (the natural inputs to the upper reservoir are negligible). Due to the lack of availability of natural sites and the environmental and societal impacts of hydropower projects, WWTPs are also installed on the seafloor, with the sea as the lower reservoir and an upstream reservoir at the top of a cliff or constituted by a dam.

Compressed air energy storage

High-power Compressed Air Energy Storage (CAES) facilities consist of storing air in underground

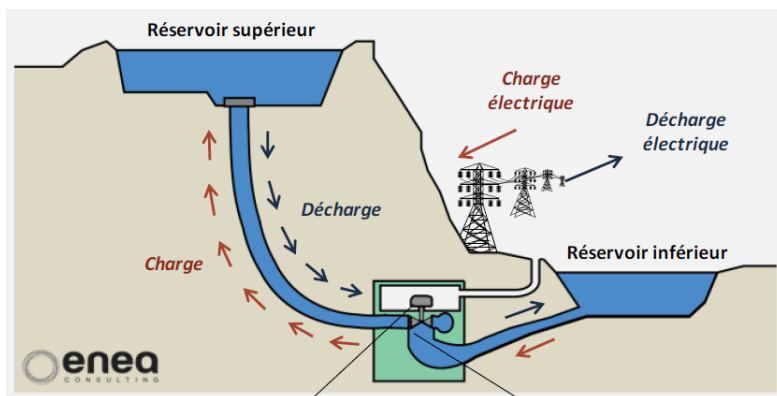


Figure 7.6: Schematic diagram of an underground piped WWTP (based on "Le stockage d'énergie - Enjeux, solutions techniques et opportunités de valorisation, ENEA, March 2012).

caverns (former salt mine or natural gas storage caverns) using a compressor, using the electricity available at low cost during periods of low consumption. At the time of peak consumption, this compressed air is released to turn turbines that produce electricity. Unfortunately, the efficiency of the CAES is reduced because the compression of the air is accompanied by heating. In order to improve their performance, thermal storage systems are being developed to recover heat (adiabatic storage).

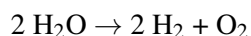
Inertial storage

The flywheel principle, used for a long time in the control of steam engines, nowadays makes it possible to temporarily store energy in the form of mechanical rotation. A flywheel consists of a carbon fibre mass (ring or tube) driven by an electric motor. The electrical energy input enables the mass to rotate at very high speeds (between 8,000 and 16,000 rpm) in a few minutes. Once started, the mass continues to rotate, even if there is no power left. Electricity is therefore stored in the flywheel as kinetic energy. It can be restored by using a motor as an electric generator, causing the flywheel to gradually decrease in speed.

Electrochemical storage

Storage via hydrogen

During periods of low electricity consumption, an intermittent electrolyser uses electricity to decompose water into oxygen and hydrogen, depending on the reaction:



Exercise 7.1 Show that this reaction is a redox reaction and determine the two half equations. ■

The hydrogen formed in this way is compressed, liquefied or transformed into a metal hydride for storage.

Secondly, we can feed electricity back into the grid from stored hydrogen in three different ways:

1. the first consists of powering a fuel cell: the reverse oxidation reaction of hydrogen $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$ then takes place and produces electricity, which can be injected into the grid or power the electric motor of a vehicle if the fuel cell is on board;
2. the second consists of synthesising natural gas using the methanation process: $\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$. Methane (a powerful greenhouse gas, but with a good calorific value) can be injected directly into the existing gas network or above all be used to power a "conventional" gas power plant, producing electricity from the release of energy produced by the reaction: $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$;

3. the third is to use hydrogen directly in a specially designed gas power plant to produce electricity from the combustion of hydrogen: $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$.

Exercise 7.2 Calculate the heat of reaction for each of the above reactions using Hess’s law. ■

During their use, electrolyzers and fuel cells give off heat (between 20 and 50% of the system’s energy, depending on the technology), the recovery of which improves the economic efficiency of the system.

Electrochemical batteries

Electrochemical batteries are designed by stacking discs composed of different types of chemical elements. There are lead-acid, nickel-cadmium, nickel-metal hydride, lithium-ion, lithium-polymer, lithium-air, sodium-sulphur, sodium chloride, *etc.* batteries. The stack is then connected to a power electronics system which, during discharge, converts the direct current of the batteries into alternating current at the desired voltage, frequency and power. This system is also used in the opposite direction to recharge the batteries.

The main advantages of batteries are their flexible sizing and responsiveness. However, the production of an electric car battery requires a lot of resources and energy (*it can, for example, represent up to 40% of the carbon footprint of an electric vehicle*): metals and electronic circuits are rare materials. Lithium is a resource that is difficult to extract and whose production has a very strong impact on the environment. The recycling of materials used in batteries is also currently limited.

Circulation batteries

In circulating battery storage systems, two liquid electrolytes containing metal ions, separated by a proton exchange membrane, circulate through electrodes. The charge exchange produces or absorbs electricity.

Electromagnetic storage

For example, SMES (Superconducting Magnetic Energy Storage) technology stores energy in the form of a magnetic field created by the flow of direct current through a superconducting ring cooled below its “critical temperature”.

Thermal storage (heat and cold)

Thermal storage installations (heat and cold) mainly concern the industrial and tertiary markets with projects of the order of 1 to 10 MW, heating networks, and the residential market via domestic hot water tanks. These installations have significant potential in terms of competitiveness for tertiary and industrial activities and in terms of their impact on peak electricity demand. Indeed, by storing heat or cold during periods of low electricity demand, the potential for shifting power demand is significant. On heating networks, heat storage makes it possible to optimise the sizing of installations, particularly when extending existing networks. The storage of heat in domestic hot water tanks today mobilises a fleet of several million installations, which represents a power demand of several gigawatts at most. This power demand is predictable and controllable, which makes it possible to offset this power demand in a programmed manner. Thermal storage can also be used to regulate the production of certain renewable energy sources. Concentrating solar thermal power plants can be backed up with thermal storage to stabilise their electricity production. Improvements and innovations are of course expected, but mature, cost-effective solutions already exist. Whether for cold or heat, these solutions, based on the storage of ice, hot water, molten salts or phase-change materials (Figure 7.7), are available and are beginning to become widespread.

The use of the electric vehicle as a storage device

The arrival of electric vehicles is a key element in the management of the electrical network. A car is unused 95% of its life time and the average use of an electric vehicle will require less than 80% of battery capacity for daily journeys. It is therefore possible, during periods when the vehicle is connected to the electrical grid, to use the stored electricity to inject it into the network during

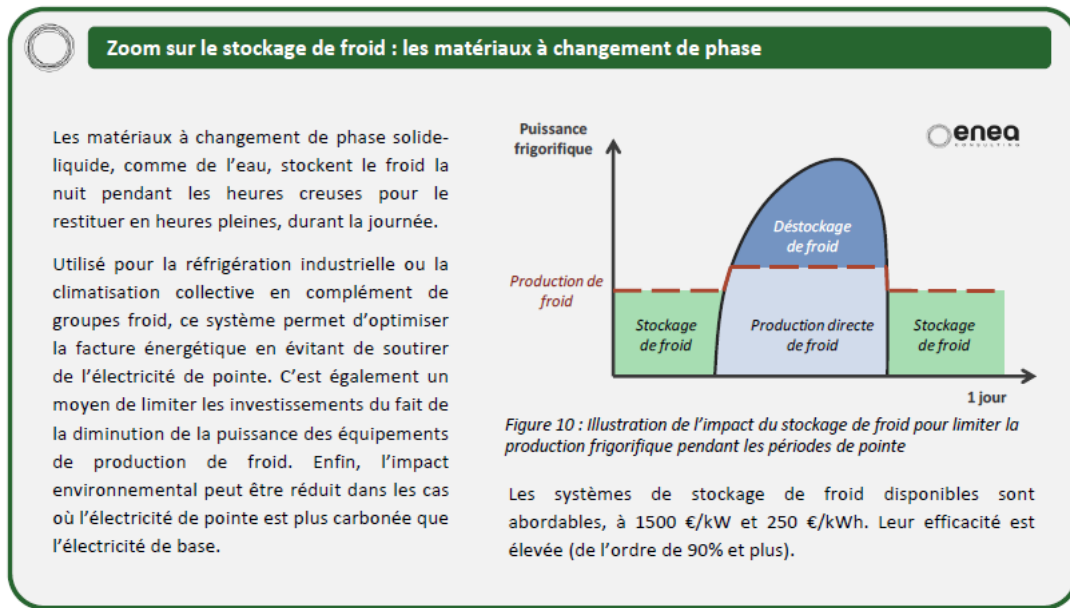


Figure 7.7: Cold storage through the use of phase change materials (based on "Le stockage d'énergie - Enjeux, solutions techniques et opportunités de valorisation, ENEA, March 2012).

periods of high demand or, conversely, to charge the vehicle's battery during off-peak hours. This is the "vehicle-to-grid" concept, which consists of using electric vehicle batteries as mobile storage capacity. For a fleet of one million connected electric cars, the storage capacity could reach 10 GWh. This storage capacity could prove valuable during peak periods.

7.3.3 Comparison and maturity of the different storage devices

The degree of maturity of various storage technologies is shown below in Figure 7.8. Many of them are still at the R&D stage. The STEPs stand out from the crowd, accounting for 99% of the world's installed storage capacity nowadays.

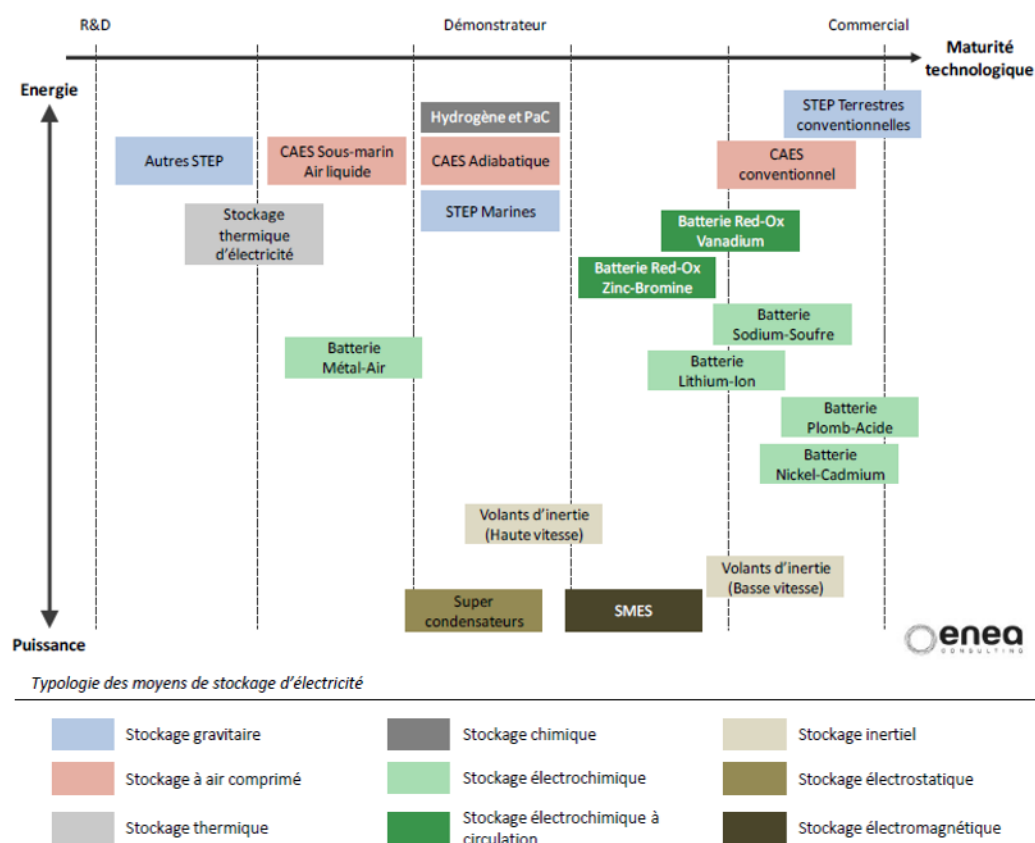


Figure 7.8: Level of technological maturity of the different electricity storage devices (based on "Le stockage d'énergie - Enjeux, solutions techniques et opportunités de valorisation, ENEA, March 2012).

7.4 Stake 4 “Fatal heat, or waste heat” (S4)

7.4.1 Background

Faced with the current challenges related to energy, both in terms of resources and impacts on health and the environment, there are three main levers for action: energy sobriety, efficiency and energy recovery.

Energy sobriety covers all the approaches that aim to limit energy consumption by changing our behaviour and, more broadly, our lifestyle. The energy competition organised this year between INSA residences A and B is a good illustration of this!

Improving energy efficiency consists of increasing the useful energy recovered at the output of a device (engine, oven, refrigerating machine) for the same amount of energy introduced into it. This notion is widely covered in your Thermodynamics course this year, and refers you to the concepts of irreversibility, conversion efficiency, coefficient of performance, which are defined and studied in the O10, O13, O14, MB6-1, MB6-2 and S1 sections. This is the path that has concentrated most of the research and development efforts since the first oil shock.

The third way results from a simple observation: all processes involving energy are associated with larger or smaller heat losses, linked to heat transfers in materials, mechanical friction or the Joule effect. All of these losses constitute what is known as *fatal heat*.

7.4.2 Definition and events

The French Environment and Energy Management Agency (ADEME) proposes the following definition for fatal heat: *“It is the heat generated by a process that does not constitute its primary purpose, and which is not recovered”*.

Where do the main sources of fatal heat come from? All activities generate fatal heat as for example:

- Individual and collective heating.
- Industrial sites and particularly refineries, metallurgy...
- Electricity production sites.
- Waste incineration plants and sewage treatment plants.
- Data centres.

The fatal heat therefore comes in different forms of rejection:

- Liquid discharges: cooling water in industry and washing water.
- Gaseous emissions: fumes, hot air for drying, water vapour.
- Diffuse emissions: natural cooling of hot materials, amplified by insulation defects.

7.4.3 Illustration of energy losses in an industrial furnace

Figure 7.9 below summarises the energy balance of an industrial furnace. It appears that 60 to 80% of the energy contained in the fuel is potentially lost, but the causes of these losses are multiple, which complicates their recovery.

7.4.4 The “deposits” of fatal heat

As a reminder of the importance of fatal heat recovery, we often speak of “deposits” to qualify what is still today an energy loss.

In 2017, ADEME published a study in which the main deposits in France are identified and quantified:

- 109.5 TWh in industry;
- 8.4 TWh in wastewater treatment plants, waste incineration plants and data centres;
- 16.7 TWh in heat distribution networks.

We encourage you to compare these figures with the orders of magnitude presented at the beginning of the year on energy. You will then have a better understanding of the issues related to

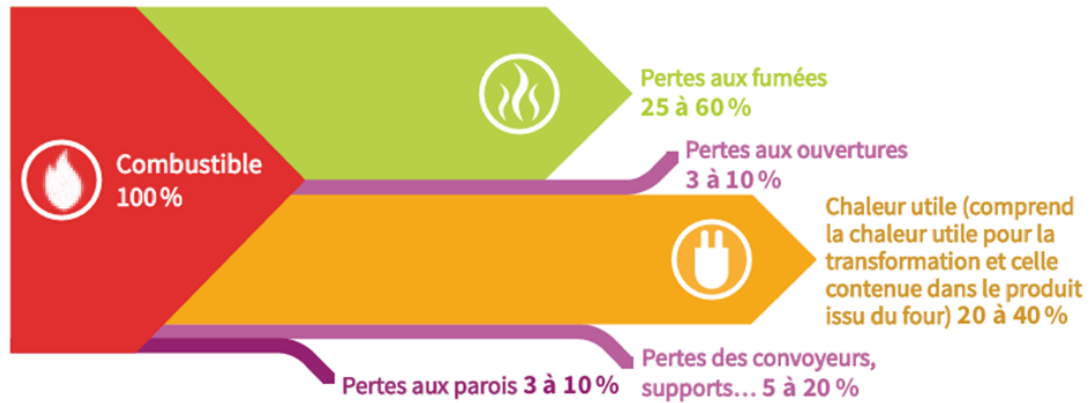


Figure 7.9: Representative steady-state energy balance for the operation of an industrial furnace (source: ADEME).

the recovery of fatal heat!

7.4.5 How to recover the fatal heat?

There are many ways to make the most of the fatal heat. The main one is a direct use of heat:

- by internal recovery, to meet the company’s heating needs in particular;
- by external recovery, for example by participating in the supply of a district heating network.

In some cases, it is also possible to consider using this heat for electricity generation, but the conversion efficiencies are then much lower. Probably the most promising technology for generating electricity from this recovered heat is the *Organic Rankine Cycle* (Figure 7.10).

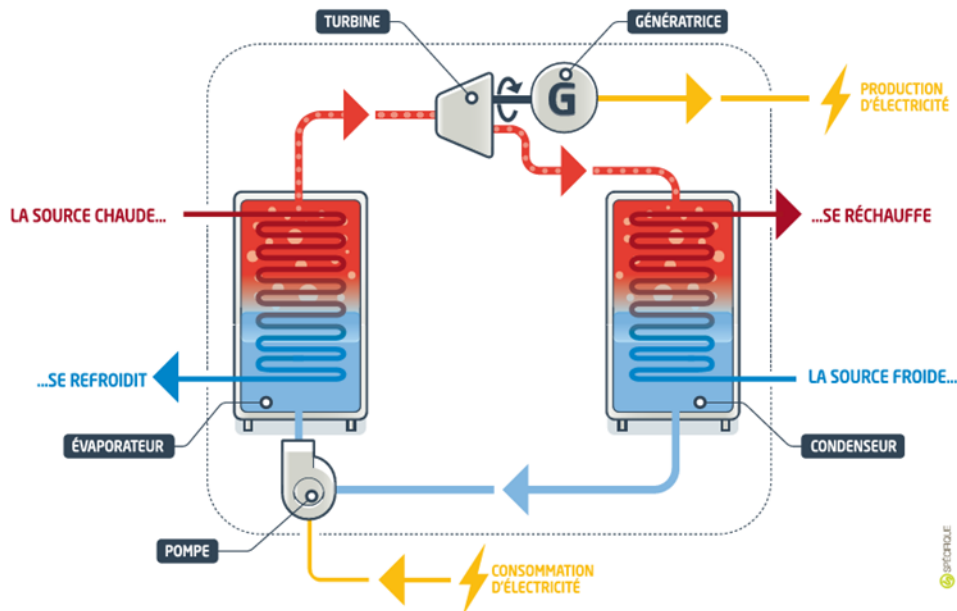


Figure 7.10: Functioning of an Organic Rankine Cycle (ORC).

For those who are interested, you can consult the Ecole des Mines ParisTech website for an explanation of the thermodynamic functioning of this cycle. It also contains information on other thermal machines (<https://direns.mines-paristech.fr/Sites/Thopt/fr/co/cycles-orc.html>).

Generally speaking, it should also be remembered that the higher the temperature of the waste, the

easier and the cheaper it is to recover the fatal heat from a technological point of view. Indeed, the law describing heat transfer shows that the heat flow is proportional to the temperature gradient. In short, it is easier to recover a small amount of energy at high temperatures than the reverse!

7.4.6 Conclusion

In conclusion, the recovery of fatal heat is still a relatively little-used route to meet today's energy challenges. At the same time, recovering this heat makes it possible to reduce our consumption of energy resources, most of which are fossil fuels, and to limit greenhouse gas emissions, mainly carbon dioxide. However, the practical implementation of recovery systems requires a significant investment, which further limits their large-scale use.

Main source: website of the French Environment and Energy Management Agency, ADEME (<https://www.ademe.fr/>)

7.5 Stake 5 “The Carnot cycle”

This section is largely inspired by the engineer’s book Thermodynamics, Olivier Cleynen, Framabook 2018.

A bit of context

At the beginning of the 19th century, a young Parisian polytechnic named Sadi Carnot became interested in the operation of heat engines, then in full expansion. Carnot was looking for the maximum amount of work that could be generated from a given quantity of coal. The interesting thing about Carnot’s approach is that he completely disregarded the technological aspect to look for the principles underlying the operation of engines. This is all the more difficult because at the time they functioned by using the boiling and condensation of steam, and the notion of cycle was not yet acquired, nor was the notion of energy conservation. Carnot died shortly after its publication and before his work could be recognised; his conception of heat was fundamentally wrong; and yet the theoretical engine he described serves as a reference in the design offices of all engine manufacturers today.

Ideal or reversible machine concept

Carnot was looking for the theoretical engine with maximum performance. He imagined a unique way of transforming heat into work and work into heat. His machine can work in both directions: as a driving (engine) or receiving (refrigerating) machine.

The maximum performance of a machine is achieved when its operation is reversible. Based on this observation, Carnot thought in the following way:

1. all thermal machines work with the expansion and contraction of a substance subjected alternately to two temperatures;
2. in order to be reversible, all heat transfers must be carried out with small temperature differences: these transformations will then be isothermal;
3. in order to be reversible, the stages where the substance changes temperature (to go from one heat reservoir to another) must take place without heat transfer with the surroundings: these transformations will then be adiabatic;
4. in order to allow a return to the previous configuration during each process, they must all be reversible (infinitely slow).

Carnot draws here a theoretical thermodynamic cycle, composed of two isothermal and two adiabatic processes. He did not need to quantify any heat transfer; and has not yet taken into account any technological detail. However, it is certain that the thermodynamic cycle he describes is the most efficient (or at least the less inefficient) that is possible to carry out.

The Carnot cycle is used as a reference cycle for thermal machines and therefore allows an ideal configuration for comparison with the other cycles, particularly in terms of performance.

The four stages of the Carnot driving machine (engine or motor)

We can describe the Carnot cycle with a constant mass of fluid trapped in a cylinder undergoing four transformations. The fluid passes between temperatures T_C (high-temperature heat source) and T_F (low-temperature cold source), to develop a net work (Figure 7.11):

1. Reversible adiabatic compression from 1 to 2: in this stage we wish to bring the fluid to a high temperature without heating it. The cycle starts in 1, when the fluid is in the cylinder at low temperature T_F . In order to bring it to a high temperature, the fluid is reversibly adiabatically compressed (cf O10). The temperature of the fluid increases from T_F to T_C . This phase is labour-intensive ($W_{1-2} > 0$).
2. Isothermal heating from 2 to 3: in this stage, we want to take a quantity of heat Q_C from the high-temperature source. Starting from 2 (fluid temperature is T_C), the cylinder is brought in contact with the hot source (also at temperature T_C) and heat is provided with an infinitesimal

temperature difference: this is an isothermal expansion. The temperature of the fluid remains constant at T_C . This phase is labour-producing ($W_{2-3} < 0$).

3. Reversible adiabatic expansion from 3 to 4: in this step, we want to cool down the fluid until its temperature is the T_C , the same of the cold source. Starting from 3 (the fluid is at temperature T_C), the fluid is expanded adiabatically (the cylinder is thermally insulated during this stage) in order to obtain work by avoiding any heat transfer; this is a reversible adiabatic expansion. The piston continues its slow recoil, and the fluid temperature drops down to T_F . This phase is labour-producing ($W_{3-4} < 0$).
4. Isothermal cooling from 4 to 1: in this last step, we wish to reject a quantity of heat Q_F to the external cold source at T_F . Starting from 4 (where the fluid is at the low temperature T_F), the fluid must be compressed at constant temperature T_F to bring it back to its initial volume. We proceed with an isothermal cooling: the piston is progressively compressed, and the temperature of the fluid is kept constant at T_F by removing heat with the low-temperature cold source. This phase is labour-intensive ($W_{4-1} > 0$).

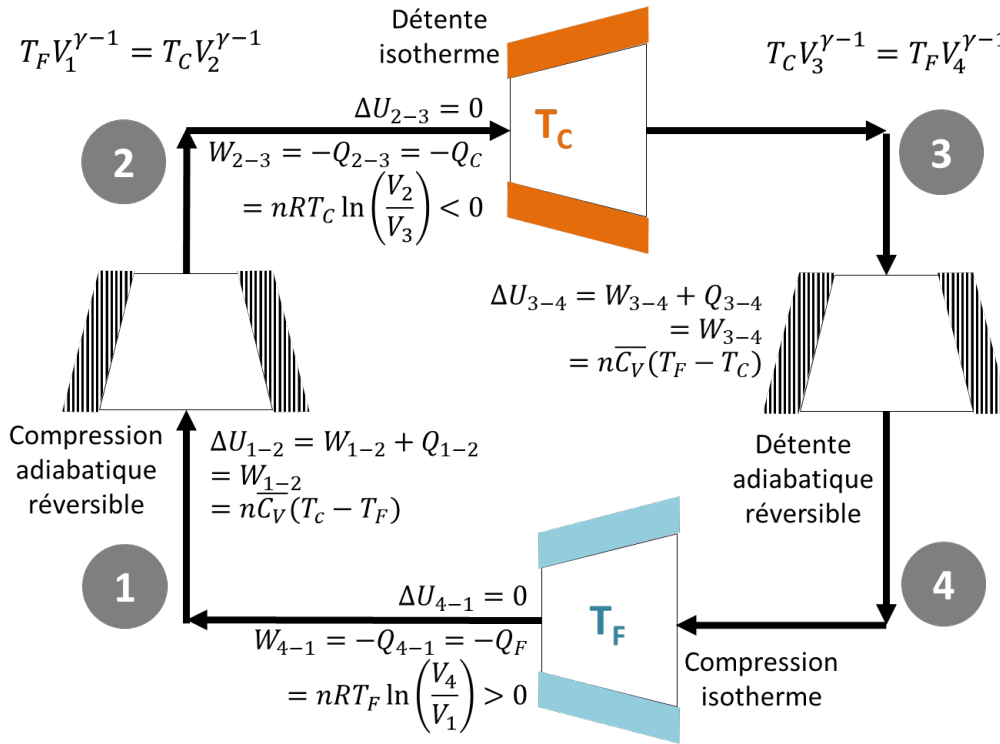


Figure 7.11: Transformations taking place in a Carnot driving machine (motor) between a cold source T_F and a hot source in T_C .

Exercise 7.3 Perform all the calculations in Figure 7.12 yourself, based on what is explained in chapter 3. ■

In the end, the engine receives an amount of heat $|Q_C|$ at high temperature and rejects a lower amount $|Q_F|$ at low temperature. The difference between these two quantities is the work produced:

$$W_{tot} = W_{1-2} + W_{2-3} + W_{3-4} + W_{4-1} = -(Q_C + Q_F)$$

This amount of work W_{tot} is the maximum that can be obtained from a quantity of heat Q_C between two given temperatures T_F and T_C .

The cycle of the Carnot engine can be plotted on a pressure-volume diagram (for example in Figure

7.12 with an ideal gas). In particular, it can be seen that the compression phases take place at a lower pressure and volume than the expansion phases: the cycle is work-producing. As all the processes are reversible, the area circumscribed in the path 1-2-3-4-1 represents the total amount of work W_{tot} produced (cf. O8).

Note: the fact that none of these steps is feasible in practice will not have escaped the perspicacious student. To allow all stages to be reversible, the movement of the piston must be infinitely slow, and thus the fluid must travel through the cycle in an infinite amount of time. Carnot's engine therefore achieves maximum performance with infinitely low power.

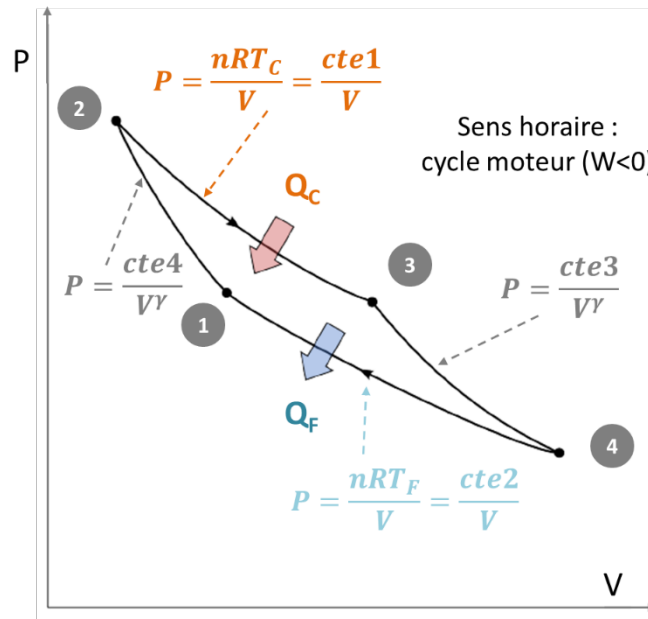


Figure 7.12: P-V diagram of the Carnot engine made with a perfect gas. The evolutions $2 \rightarrow 3$ and $4 \rightarrow 1$ are respectively made at T_C and T_F . For the cycle path, see O9 and MB4-1.

Carnot motor efficiency

The efficiency (**CoP**) of the Carnot engine is the ratio between the work produced (W_{tot}) and the heat received (Q_C). The application of the first principle tells us that:

$$\Delta_t U = W + Q_C + Q_F = 0$$

from where:

$$\eta = \frac{-W_{tot}}{Q_C} = \frac{Q_C + Q_F}{Q_C} = 1 + \frac{Q_F}{Q_C}$$

The efficiency of a Carnot engine will always be $0 < \text{CoP} < 1$ because $Q_F < 0$ and $Q_C > 0$. However, according to the calculations in Figure 7.11:

$$Q_C = -nRT_C \ln \left(\frac{V_2}{V_3} \right)$$

$$Q_F = -nRT_F \ln \left(\frac{V_4}{V_1} \right)$$

In addition:

$$\begin{aligned} T_F V_1^{\gamma-1} &= T_C V_2^{\gamma-1} \\ T_C V_3^{\gamma-1} &= T_F V_4^{\gamma-1} \end{aligned}$$

from where:

$$\frac{T_F V_1^{\gamma-1}}{T_F V_4^{\gamma-1}} = \frac{T_C V_2^{\gamma-1}}{T_C V_3^{\gamma-1}} \rightarrow \frac{V_1}{V_4} = \frac{V_2}{V_3}$$

It is deduced that:

$$\eta_{(\text{ideal})} = 1 + \frac{nRT_F \ln\left(\frac{V_4}{V_1}\right)}{nRT_C \ln\left(\frac{V_2}{V_3}\right)}$$

hence:

$$\eta_{(\text{ideal})} = 1 - \frac{T_F}{T_C}$$

The answer to Carnot's question, "what maximum amount of work, in theory, can be obtained from the combustion of a given quantity of coal" is therefore: it only depends on the high and low temperatures of the engine!

Two important points should be made here:

- Firstly, this efficiency is not 100% even considering frictionless, leakage-free machines with infinitely slow movements. By contrast, there is nothing to prevent an electric motor or alternator from achieving 100% performance if you can get rid of all friction. Thus, even before addressing the inevitable technological difficulties in setting up real engines, the engine designer is limited by the fundamental nature of the heat in what he or she can obtain from his or her machine. In the following section, we will discuss the irreversibilities observed in real engines, which will further reduce the efficiency calculated above.
- Secondly, this equation is a strong argument for increasing the combustion temperature in engines. Indeed, in practice the low temperature T_F is limited by that of the ambient air. The only remaining parameter to increase the efficiency of an ideal engine is the temperature T_C . This relationship explains the surprising efforts made by engine designers to use high temperatures (and correspondingly high pressures), even though real engines are far from being reversible.

To sum up, we will answer Carnot's question as follows: *the higher the temperature at which coal is burned, the lower the ambient temperature, and the less heat loss - inevitable - from the engine.*

The Carnot receiving (refrigerating) machine

By reversing the engine operating direction described above, a refrigerator, air conditioner, or heat pump is created. The fluid then passes through the same states, but in the opposite direction (1-4-3-2-1). The heat $Q_F > 0$ is taken from the cold source, the work is $W_{tot} > 0$ is received by the machine and the heat $Q_C < 0$ is rejected by the machine to the external source at high temperature. This cycle allows the maximum performance (or the "least bad" performance, as it is not infinite) of a refrigerator, air conditioning system or heat pump operating between two temperatures T_C and T_F . The **CoP of a refrigerating machine** is the comparison between the heat extracted from the cold source (useful transfer, Q_F) and the work consumed (energy expenditure, W_{tot}). The application of

the 1st principle allows us to write:

$$CoP = \frac{Q_F}{W_{tot}} = \frac{Q_F}{-(Q_C + Q_F)} = -\frac{1}{1 + \frac{Q_C}{Q_F}}$$

The CoP of a Carnot refrigerator will always be $CoP > 1$ because $Q_F > 0$ and $Q_C < 0$.

When it comes to a Carnot receiving machine, we can show that this performance is a function of temperature alone (as with the engine) and that we have:

$$CoP_{(ideal)} = \frac{1}{\frac{T_C}{T_F} - 1}$$

The same remarks as above apply here: on the one hand, the CoP of a refrigerator or air conditioner never reaches infinity (a refrigerator of CoP infinity would work without any labour input). On the other hand, the lower the refrigeration temperature T_F , the lower the performance. In other words, when cooling an object with an ideal refrigerator, selecting a lower temperature is more expensive not only because more heat has to be extracted from the object, but also because the extraction performance decreases.

The **CoP of a heat pump** is the comparison between the heat supplied at high temperature and the work consumed. The application of the 1st principle allows us to write:

$$CoP = \frac{-Q_C}{W_{tot}} = \frac{-Q_C}{-(Q_C + Q_F)} = \frac{1}{1 + \frac{Q_F}{Q_C}}$$

The CoP of a Carnot refrigerator will always be $CoP > 1$ because $Q_F > 0$ and $Q_C < 0$.

When it comes to a Carnot heat pump, we can show that this performance is a function of temperature alone (as with the engine) and that we have:

$$CoP_{(ideal)} = \frac{1}{1 - \frac{T_F}{T_C}}$$

As with a refrigerator, the CoP of a heat pump cannot be infinite: it is limited by the extreme temperatures reached in the cycle. The more the heat Q_C is delivered at high temperatures, the lower the maximum achievable coefficient of performance.

7.6 Stake 6 “Operation of thermal machines” (S6)

The different types of thermal machines and their study from a thermodynamic point of view have been presented in section MB6-1. These are generally separated into two main categories: driving machines, which provide work from heat, and receiving machines, which consume mechanical energy to enable heat transfer. From a technological point of view, many solutions have been imagined and optimised since the 19th century, and new ones are still being developed today. The aim of this section is to illustrate the operation of a driving machine, the four-stroke combustion engine, and a receiving machine, such as a refrigerator or air conditioner, by presenting the main components and the associated thermodynamic cycles.

7.6.1 Four-stroke combustion engine

The four-stroke combustion engine is a *reciprocating internal combustion engine*, unlike most steam engines where combustion takes place outside the device. It is currently the most widely used practical device for transport, both land and sea. It is based on the linear movement of a piston in a cylinder (Figure 7.13).

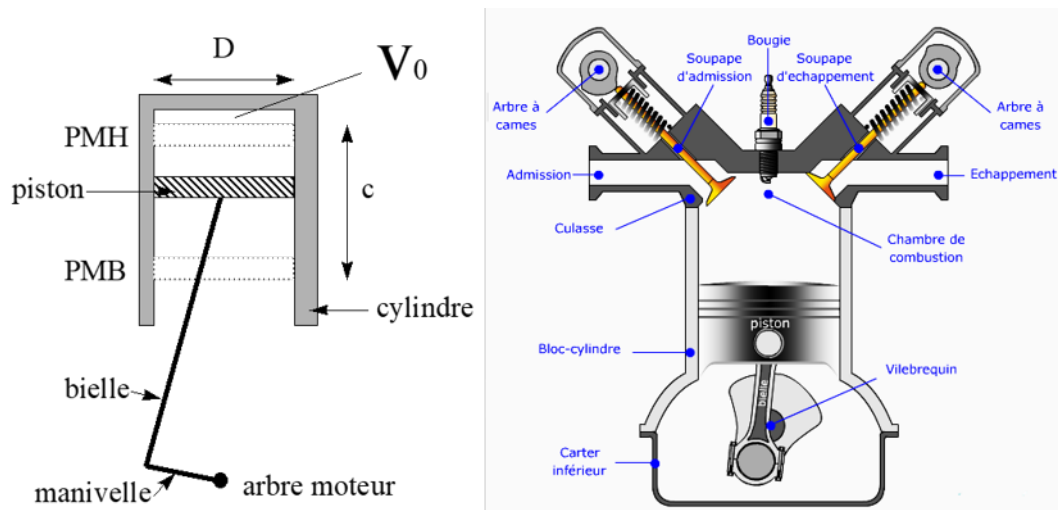


Figure 7.13: Main elements in a reciprocating engine and geometrical parameters.

General description

The process of this movement into continuous rotation is ensured by a "connecting rod/crank" system (in an engine, the crank is called the crankshaft).

The main geometrical characteristics of a reciprocating combustion engine (see Figure 7.13) are as follows:

- Bottom Dead Centre (BDC): lowest position of the piston in the cylinder, and therefore the largest volume of gas.
- Top Dead Center (TDC): The highest position of the piston in the cylinder.
- Dead volume (V_0): at top dead centre, the gas volume is not zero and corresponds to V_0 .
- Piston stroke (c): this is the distance travelled by the piston between TDC and TDC.
- The bore (D) is the inside diameter of the cylinder.
- The cylinder capacity (VC) is the total volume of gas contained in the cylinder when the piston is at BDC.

Four-step operation

We speak of a four-stroke combustion engine because operation can be divided into four main phases (see Figure 7.14):

1. intake (or suction);
2. compression;
3. combustion + expansion;
4. exhaust (or discharge).

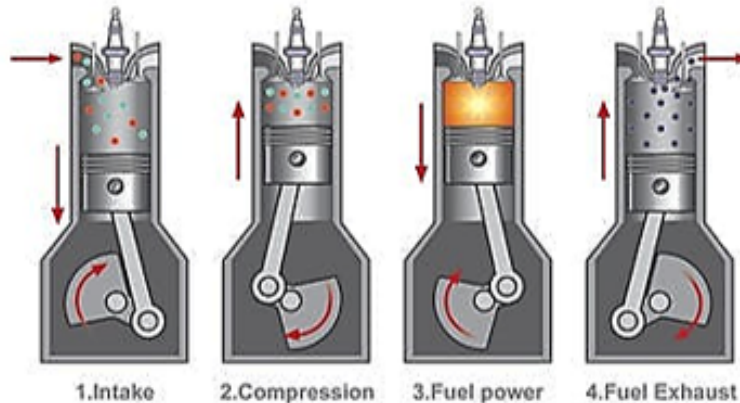


Figure 7.14: Presentation of the four operating phases of a reciprocating internal combustion engine of the "spark-ignition (petrol) engine" type.

In the case of a "petrol" engine, *i.e.* a spark ignition engine, the four strokes are as follows:

- **1st stage: ADMISSION**

Initially, the piston is at TDC, the inlet valve is open, the exhaust valve is closed. The piston descends, aspirating a mixture of air and fuel. The intake phase ends when the piston reaches BDC. This is the cylinder filling phase.

- **2nd stage: COMPRESSION**

Initially, the piston is at the BDC, both valves are closed. The cylinder becomes a hermetic enclosure. The piston moves up from BDC to TDC. As the volume decreases, the pressure of the gas mixture increases.

- **3rd stage: COMBUSTION + RELAXATION**

The piston is at TDC, both valves are always closed. In the case of a spark-ignition engine, combustion is initiated by an arc created by a spark plug. The combustion of the air + fuel mixture causes a very high temperature increase and thus a pressure increase. The combustion gases push the piston downwards and this causes the crankshaft to rotate. This is the expansion phase, which is the driving part of the cycle.

- **4th stage: EXHAUST**

Initially, the piston is at BDC. The inlet valve is closed and the outlet valve is open. The piston moves up towards TDC, pushing the burnt gases back into the exhaust manifold.

At the end of the fourth stroke, the piston and valves returned to their original positions. Engine operation is cyclic. It is important to note that the compression and exhaust phases are receptive. The mechanical energy comes from a "flywheel", or "engine flywheel", which stores the energy of the expansion phase in the form of kinetic energy.

Theoretical and actual cycles of a spark ignition engine

The operating principle of the four-stroke, spark ignition engine was first imagined by Beau de Rochas in 1862, developed by Nikolaus Otto in 1867 and perfected by Gottlieb Daimler and Wilhelm Maybach in 1887. The theoretical cycle can be easily represented in a Clapeyron diagram (*cf.* O8), considering that a constant number of moles of ideal gas undergoes the various reversible processes shown in Figure 7.15.

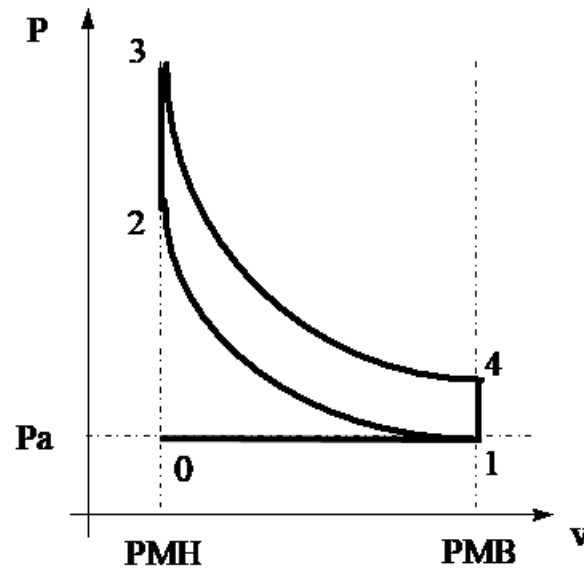


Figure 7.15: Representation of the theoretical thermodynamic cycle of a four-stroke internal combustion engine. This cycle is called "Beau de Rochas cycle" or "Otto cycle" according to the literature.

We find the four stages described above:

- 1st stage between (0) and (1), intake phase at constant pressure;
- 2nd stage between (1) and (2), with isentropic compression (adiabatic + reversible);
- 3rd stage between (2) and (4), with first the combustion at constant volume between (2) and (3) followed by the isentropic expansion between (3) and (4) (adiabatic + reversible);
- 4th stage between (4) and (0), with cooling at constant volume between (4) and (1) followed by the discharge of the gases generated by the combustion between (1) and (0).

It should be noted that the segment (0 - 1) is not always represented because, in theory, the mechanical work associated with processes (0 → 1) and (1 → 0) are strictly opposed (*cf.* O8).

The theoretical cycle assumes a certain number of hypotheses which are not verified in the actual operation of the engine, for thermodynamic and mechanical reasons, as:

- zero gas mass inertia (no consideration of kinetic energy);
- instantaneous combustion phase;
- all gases are ideal gases;
- reversible processes;
- no heat transfer through the engine walls.

For these different reasons, the real cycle measured on an engine test bench (shown in Figure 7.16) differs significantly from the theoretical cycle presented above.

In addition to the points mentioned above (non-instantaneous combustion, non-adiabatic compression and expansion), it is interesting to note that the intake and exhaust phases do not take place at constant pressure and that the associated work no longer compensates for each other. The trigonometric direction for these two processes (*cf.* O8) indicates that the total work is positive (this is called decanting work). This will lead to a reduction in the engine efficiency.

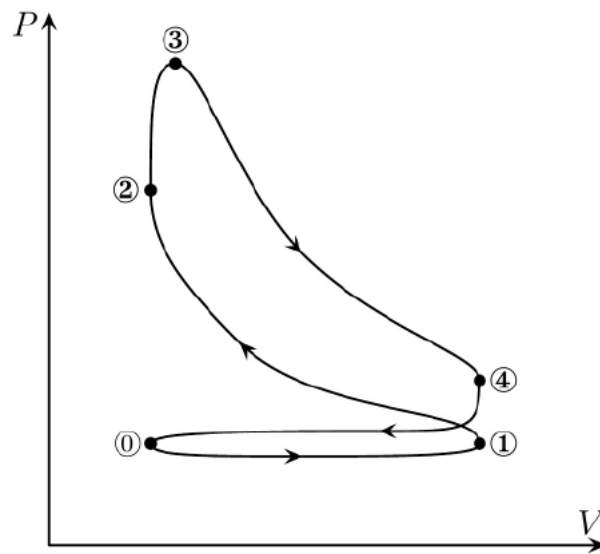


Figure 7.16: Representation of the real thermodynamic cycle of a four-stroke combustion engine.

Theoretical cycles of a diesel engine

There is also another type of combustion engine that is largely used, even if its use is increasingly being questioned for environmental and health reasons: the diesel engine. It was developed by the German engineer Rudolf Diesel from 1893 to 1897. Historically, the advantage of this engine is its ability to use almost any type of fuel, initially coal powder, nowadays vegetable oils for example. Unlike spark ignition engines, the diesel engine is a compression ignition engine. This does not lead to any major changes in the sequence of the four operating phases of the theoretical cycle. The gas sucked into the cylinder is air, and no longer a mixture of air and fuel. The fuel is injected during the cycle at point 2. Combustion is initiated by the extreme conditions in the engine (high temperature and high pressure). It is therefore the combustion phase that represents the main evolution compared to the spark-ignition engine (petrol engine).

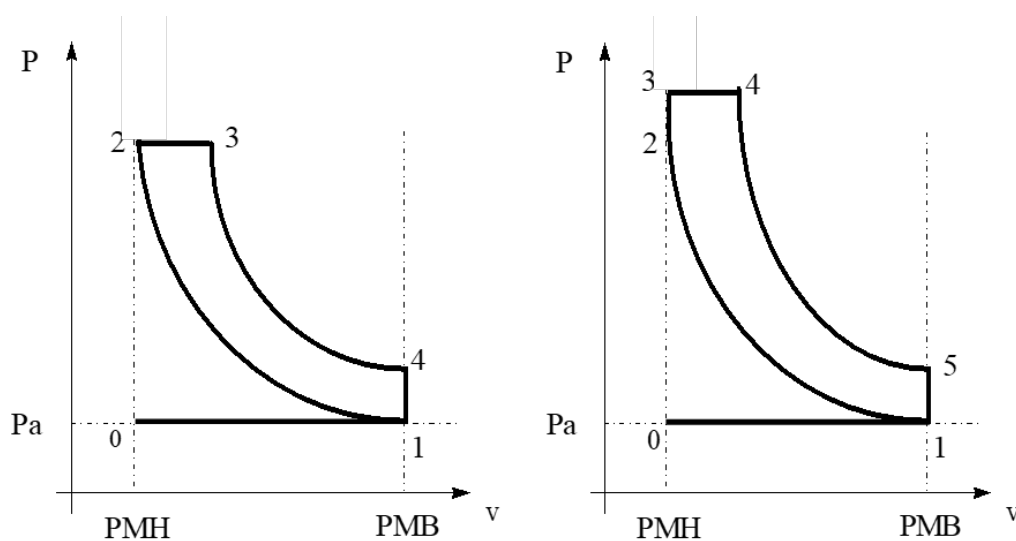


Figure 7.17: Theoretical thermodynamic cycles of the Diesel engine: a slow Diesel cycle (< 1000 rpm) on the left; a mixed Diesel cycle or Sabathé cycle on the right.

Depending on the engine speed, *i.e.* the rotation speed of the piston, two different theoretical cycles can be defined. At low speeds (< 1000 rpm), the combustion takes place at constant pressure ($2 \rightarrow 3$) whereas at higher speeds it takes place in two parts: first at constant volume ($2 \rightarrow 3$) and then at constant pressure ($3 \rightarrow 4$).

7.6.2 Refrigerating machine

A refrigerating machine is a bithermal machine whose aim is the transfer of heat from a cold to a hot source thanks to an external work input. This machine is therefore a receiver.

Refrigerating machines and heat pumps

In the case of a refrigerator or air conditioner, the objective is to move a quantity of heat from the inside of a chamber to the outside. The cold source is therefore inside the refrigerator or chamber, and the hot source is outside. In the case of a heat pump, the operation is "reverse", and the objective is to bring a quantity of heat, from the surroundings of the building at a lower temperature, to inside the building to warm it. The cold source is therefore outside the building, and the hot source inside. However, from a technological and thermodynamic point of view, these two types of refrigerating machine are very close, so we will limit ourselves to the description of refrigerators and air conditioners.

Operation of a refrigerating machine and choice of fluid

The terminology "cold production" is inappropriate because it is a question of extracting a quantity of heat from a system to be cooled by an endothermic phenomenon, and rejecting this quantity of heat outside (first law). Several techniques exist, for example the expansion of a gas, or the use of absorption and desorption phenomena (absorption machine, the first refrigeration machine patented by the Frenchman Ferdinand Carré). Another way is to use the phase change of a pure substance, as you saw in O7. This process was already used in ancient Rome for the preservation of foodstuffs, by taking and storing ice.

Naturally, it is much more convenient to operate cyclically, using a refrigerant fluid. In theory, any fluid with a liquid-gas transition below room temperature could be used as a refrigerant. However, other criteria need to be considered: thermophysical properties (latent heat of vaporization, viscosity, compression ratio), environmental impact (chlorinated and fluorinated fluids, destructive to the ozone layer, were banned since the Montreal Protocol in 1987), health (ammonia, sulphur dioxide) and safety (propane) issues. Currently, the most commonly used refrigerant is R-134a (or HFC-134a), which is a halogenated hydrocarbon with the raw formula $C_2H_2F_4$.

Main elements in a refrigerating machine

In order to operate, a refrigerating machine must work at two pressure levels with a fluid present in two phases, liquid and gaseous. This requires the four elements shown in Figure 7.18:

- Compressor ($1 \rightarrow 2$): it increases the pressure of the refrigerant which is in the gas phase.
- Condenser ($2 \rightarrow 3$): this is a heat exchanger through which the refrigerant passes from the gas to the liquid phase undergoing liquefaction at high pressure (hot source). The other fluid, which receives the amount of heat, is usually air, driven by a fan.
- Expansion valve ($3 \rightarrow 4$): the expansion valve causes a drop in pressure and temperature of the refrigerant fluid, which has is in the saturated liquid state at the valve inlet. At the outlet, the fluid is generally in a liquid-vapour equilibrium, with a very low amount of vapour. This thermodynamic process is somewhat unusual and is carried out in an isenthalpic way, *i.e.* without any change in the enthalpy of the refrigerant. The refrigerant receives neither work nor heat transfer but, thanks to a suitable shape of the pipe in which it flows, its pressure and temperature decrease.
- Evaporator ($4 \rightarrow 1$): this essential part of the refrigeration machine is the cold source. Generally, it is a refrigerant/air heat exchanger. The evaporator is placed inside the refrigerator.

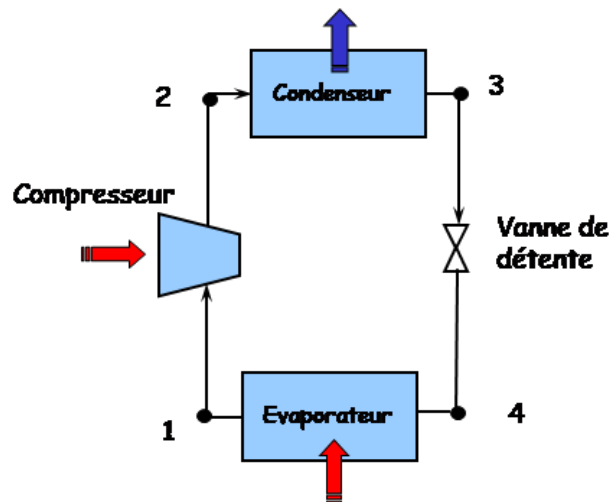


Figure 7.18: Representation of the main components of a refrigeration machine.

Theoretical thermodynamic cycle

The theoretical cycle, consisting of reversible processes, is usually represented in an enthalpy diagram as shown in Figure 7.19, where the enthalpy is on the abscissa and the pressure on the ordinate. The entire operation can be divided into four main phases:

1. stage 1 \rightarrow 2: in state 1, the fluid enters the compressor in the vapour phase and undergoes isentropic compression up to state 2;
2. stage 2 \rightarrow 3: in state 2, the compressed refrigerating fluid is at a temperature higher than the external temperature and it enters the condenser where it releases the heat to the external environment at constant pressure. At the outlet of the condenser (state 3), the fluid is in a saturated liquid state;
3. stage 3 \rightarrow 4: between states 3 and 4, the fluid undergoes an isenthalpic expansion without exchanging heat or work. In state 4 the fluid is at the liquid-vapour equilibrium;
4. stage 4 \rightarrow 1: in state 4, the two-phase fluid enters the evaporator. The entire fluid is evaporated at constant pressure and returns to state 1.

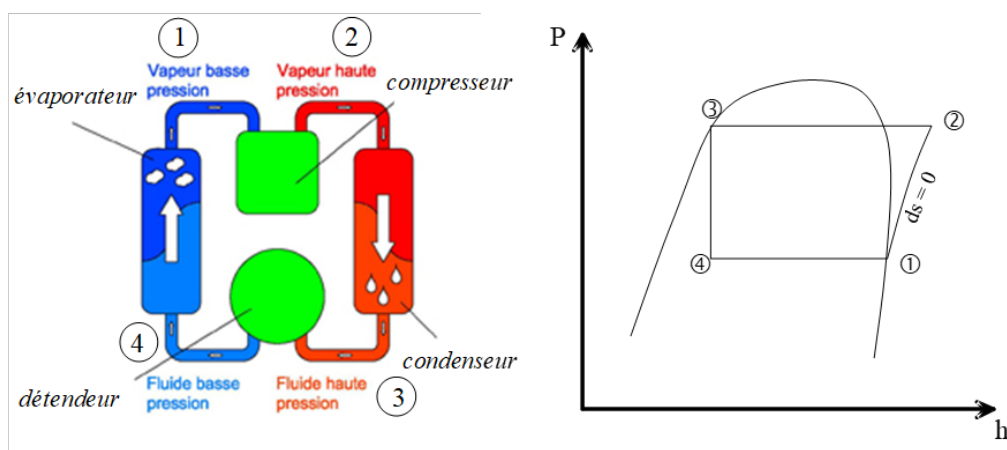


Figure 7.19: Representation of the theoretical cycle of a refrigerating machine in an enthalpy diagram.

7.7 Stake 7 “Properties of a state function - Interest in Thermodynamics” (S7)

This item is largely inspired by the article: "State function", Wikipedia, the free encyclopedia, https://fr.wikipedia.org/w/index.php?title=Fonction_d'etat&oldid=159341808 (page consulted on 19 October 2019).

7.7.1 Observation

Let's consider the altitude function A when hiking in the mountains. The "state" of the group of hikers can be defined, for example, by its GPS coordinates, which can be used to locate it on the hiking trail. Let us assume that to go from a summit $S1$ at 2500 m to a summit $S2$ at 2600 m, the group has two paths:

- a first path that follows the ridge line almost at the level of the two summits,
- a second path that goes down into the valley at 500 m altitude.

Altitude variation ΔA is the same for both paths:

$$\Delta A = A(S2) - A(S1) = 100 \text{ m}$$

The altitude function could be seen as a state function of the hike. On the other hand, the efforts made, work and heat released by hikers will not be the same! Therefore, these quantities are not state functions but quantities related to the path followed (path functions).

7.7.2 Fundamental property of state functions

Reminder of mathematical definitions

The differential of a state function F (function of several independent variables) is exact and therefore can be noted dF . This means that it is equal to the sum of its partial differentials with respect to each variable. For a state function of two variables noted $F(x, y)$:

$$dF = \left(\frac{\partial F}{\partial x} \right)_y dx + \left(\frac{\partial F}{\partial y} \right)_x dy$$

where $\left(\frac{\partial F}{\partial x} \right)_y$ is the partial derivative of F with respect to x at constant y .

Application: if F is a function of several variables in the course of a process, this process can be broken down into several steps in such a way that for each step only one independent variable varies, which makes the study simpler. The overall variation of F will be equal to the sum of the partial variations of each step and will obviously be identical to the variation obtained during the process carried out in a single step; all variables will vary simultaneously.

Let us consider the process shown in Figure 7.20 defined by the initial state A : $F(A)$; $x(A)$; $y(A)$ and the final state C : $F(C)$; $x(C)$; $y(C)$. An intermediate state B is defined: $F(B)$; $x(B) = x(C)$; $y(B) = y(A)$. It is then said that the variation of the state function does not depend on the path followed.

Let's calculate the variation of the function:

$$dF = \left(\frac{\partial F}{\partial x} \right)_y dx + \left(\frac{\partial F}{\partial y} \right)_x dy$$

$$\Delta F_{A \rightarrow C} = F(C) - F(A) = \int_{x(A)}^{x(C)} \left(\frac{\partial F}{\partial x} \right)_y dx + \int_{y(A)}^{y(C)} \left(\frac{\partial F}{\partial y} \right)_x dy$$

Note: the order of variation of the independent variables x and y does not affect the result. This is mathematically justified by the fact that the cross second derivatives of the function F compared to x and y are equal: $\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x}$

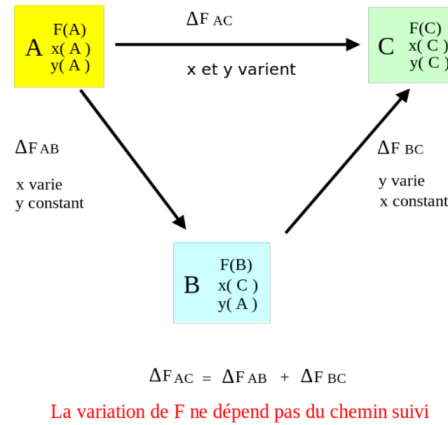


Figure 7.20: Example of the decomposition of the direct process $A \rightarrow C$ into two processes $A \rightarrow B$ and $B \rightarrow C$ in order to pass through the intermediate state B .

Application example: case of the Ideal Gas (see O4)

We consider an ideal gas whose state is given by its temperature T and its pressure P . In order to carry out a process, the pressure or temperature of the gas is varied from the initial values T_i and P_i noted below to final values T_f and P_f . The amount of matter is considered to be constant.

Case of volume: the equation of state of the ideal gas gives us an explicit expression of the volume as a function of these two parameters: $V(T, P) = \frac{nRT}{P}$. The volume appears as a state function. From this expression, one can calculate the volume variation of the gas during the process from the initial state to the final state:

$$\Delta V = V_f - V_i = nR \left[\frac{T_f}{P_f} - \frac{T_i}{P_i} \right]$$

We can verify that we find the same variation by following two different paths for the process. For the first path, we vary the pressure from P_i to P_f keeping the temperature constant and equal to T_i , then the temperature is varied from T_i to T_f by keeping the pressure constant and equal to P_f . In the second path, we proceed in the same way, but by varying the temperature before the pressure.

For an infinitesimal variation in pressure and temperature, one can write:

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

or, using the Ideal Gas Law:

$$dV = \frac{nR}{P} dT - \frac{nRT}{P^2} dP$$

We consider the two different paths defined by the order of variation of P and T . For the first path, the total volume variation can be written as follows by first varying the pressure:

$$\begin{aligned} \Delta V_1 &= \int_{P_i \rightarrow P_f; T=T_i} dV + \int_{T_i \rightarrow T_f; P=P_f} dV = \int_{P_i}^{P_f} -\frac{nRT_i}{P^2} + \int_{T_i}^{T_f} \frac{nR}{P_f} dT = \\ &= \left(\frac{nRT_i}{P_f} - \frac{nRT_i}{P_i} \right) + \frac{nR}{P_f} (T_f - T_i) = nR \left[\frac{T_f}{P_f} - \frac{T_i}{P_i} \right] \end{aligned}$$

For the second path, the temperature is varied first:

$$\Delta V_2 = \int_{T_i \rightarrow T_f; P=P_i} dV + \int_{P_i \rightarrow P_f; T=T_f} dV$$

We find the same result as for the first path, which is obviously the same as the one obtained directly from the Ideal Gas Law.

Since the differential form dV of the function $V(T, P)$ is an exact differential, the order of the derivation of the V compared to T and P is indifferent and the cross second derivatives are equal, which is the case:

$$\frac{\partial^2 V}{\partial T \partial P} = \frac{\partial^2 V}{\partial P \partial T} = -\frac{nR}{P^2}$$

Case of work: on the other hand, the work of the pressure forces depends on the path followed, so it cannot be written as the variation of a state function, and the work provided during an infinitesimal process ∂W is not an exact differential (see MB3).

We have previously established the volume differential of an ideal gas:

$$dV = \frac{nR}{P} dT - \frac{nRT}{P^2} dP$$

but the work of the pressure forces is given by $\partial W = -P_{ext} dV$.

So the differential form of the work associated with an ideal gas, is equal to: $\partial W = -nRdT + \frac{nRT}{P} dP$.

It can be shown that ∂W is not an exact differential by noticing that the cross second derivatives are not equal:

$$\frac{\partial}{\partial P}(-nR) = 0 \neq \frac{\partial}{\partial T} \left(\frac{-nRT}{P} \right) = \left(\frac{nR}{P} \right)$$

This is confirmed by the calculation of the work provided during the process by following the two different paths described above. For the first path, we find a work output of:

$$W_1 = nRT_i \ln \left(\frac{P_f}{P_i} \right) - nR(T_f - T_i)$$

and for the second:

$$W_2 = -nR(T_f - T_i) + nRT_f \ln \left(\frac{P_f}{P_i} \right)$$

The total work obtained in the two cases considered is different. It therefore depends on the path followed and cannot be written as a variation of a state function.

7.7.3 Interest of state functions in Thermodynamics

The real processes are irreversible and their path depends on the way in which they are carried out. Their evolution in a diagram is therefore not mathematically defined and the thermodynamic quantities associated with them are not known at all times. Nevertheless, if the studied quantity is a state function, its variation depends only on the final state and the initial state of equilibrium. To calculate its variation, it is then sufficient to imagine a reversible or ideal process, starting from the same initial state to arrive at the same final state as for the real process. This ideal process is characterized by a succession of equilibrium states. It can now be modelled mathematically and its variation can therefore be calculated. This variation is identical to that observed for the irreversible process and the problem is solved. Moreover, if the state function is a function of several variables, the process can be decomposed into as many ideal intermediate steps as the number of variables; each step being characterized by the variation of a single independent variable. This greatly simplifies the calculations.

The usual state functions in thermodynamics are:

- *internal energy: U expressed in J (joule) (cf. O1 and O10),*
- *enthalpy: $H = U + PV$ expressed in J (cf. O11),*
- *entropy: S expressed in $J \cdot K^{-1}$ (cf. O13),*
- *Gibbs free energy: $G = H - TS$ expressed in J (cf. O17).*

Note: there is also the free energy function $F = U - TS$ expressed in Joules, not covered in this course.