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تلمســـان

Department of Preparatory Education

Chemical Thermodynamics Course for First Year Engineering Students

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This book is primarily intended for students at the beginning of their university studies. It offers a comprehensive course in chemical thermodynamics, accompanied by numerous concrete examples and progressive exercises to promote effective assimilation of the concepts.

The book opens with an introduction to chemical thermodynamics, defining the main thermodynamic quantities. It then addresses the two fundamental principles of the discipline, gradually leading to the central notion of chemical potential—a concept introduced by Gibbs—which allows the study of both physical and chemical transformations of matter.

The First Law is first applied to thermomechanical transformations, involving heat and work exchanges, and then to chemical reactions, illustrated by numerous examples. These concrete cases, integrated throughout the presentation, offer a clear and practical perspective on the fields of application of thermodynamics.

The Second Law introduces the notion of system evolution, before leading to the study of chemical equilibria and their modifications. This final section concludes with various examples of reactions of industrial interest, chosen for their relevance.

This manual brings together a solid base of useful numerical data in chemical thermodynamics and offers a wide selection of corrected exercises, allowing the reader to test their knowledge and strengthen their understanding. It is the result of extensive teaching experience, notably acquired in the preparatory cycle of the Higher School of Applied Sciences of Tlemcen, where I teach this subject. I hope this book will provide both rigorous and accessible support for students and teachers alike.

Chapter I : General definition of a system

I- General definition of a system

I.1 Definition

A **system** is a portion of space under study. It is bounded by a real or fictitious (arbitrary) surface through which **energy and/or matter** are exchanged with **the external medium** (or environment).

Together, the system and the external environment make up the universe.

A system takes on different names depending on the nature of its exchanges with the external environment:

I.2 Open system

An **open system** can exchange energy and matter with the external environment.

A pot of water boiling without a lid Example:

- **Material exchange**: steam escapes.
- **Energy exchange**: heat supplied by the hotplate.

Fig.1. *water boiling without a lid*

A car engine

- **Material exchange:** fuel enters, exhaust gases leave.
- **Energy exchange:** heat produced, mechanical work on wheels.

The human body

- **Exchange of matter:** respiration (O_2, CO_2), food, waste.
- **Energy exchange:** heat production, muscular work, etc.

I.3 <u>Closed system</u>

A closed system can exchange energy but not matter with the external environment.

Example :

An oil-filled radiator:

- The oil remains inside the system (no material exchange), but the system exchanges heat with the room.

Fig.2. *Oil-filled radiator*

A pressure cooker closed during cooking:

- As long as the valve doesn't open, the steam doesn't escape. The system is closed (heat exchange, but no material exchange).

Fig.3. *A pressure cooker*

I.4 Isolated (adiabatic) system

An adiabatic (or thermally insulated) system cannot exchange **energy** with **the outside environment.** In practice, perfect insulation is impossible.

An adiabatic system is one in which heat exchange is minimal.

Example: a Dewar.

An isolated system can exchange **neither energy nor matter with the external environment. Here , too, perfect insulation is impossible in practice.**

Example :

- A perfect (ideal) thermos

- A perfectly thermally insulated, hermetically sealed container that lets neither heat nor matter through (in theory).
- A gas enclosed in a perfectly rigid, insulating box : No exchange of heat (energy) or particles (matter) with the outside.

Fig.4. *A pressure cooker perfect (ideal) thermos*

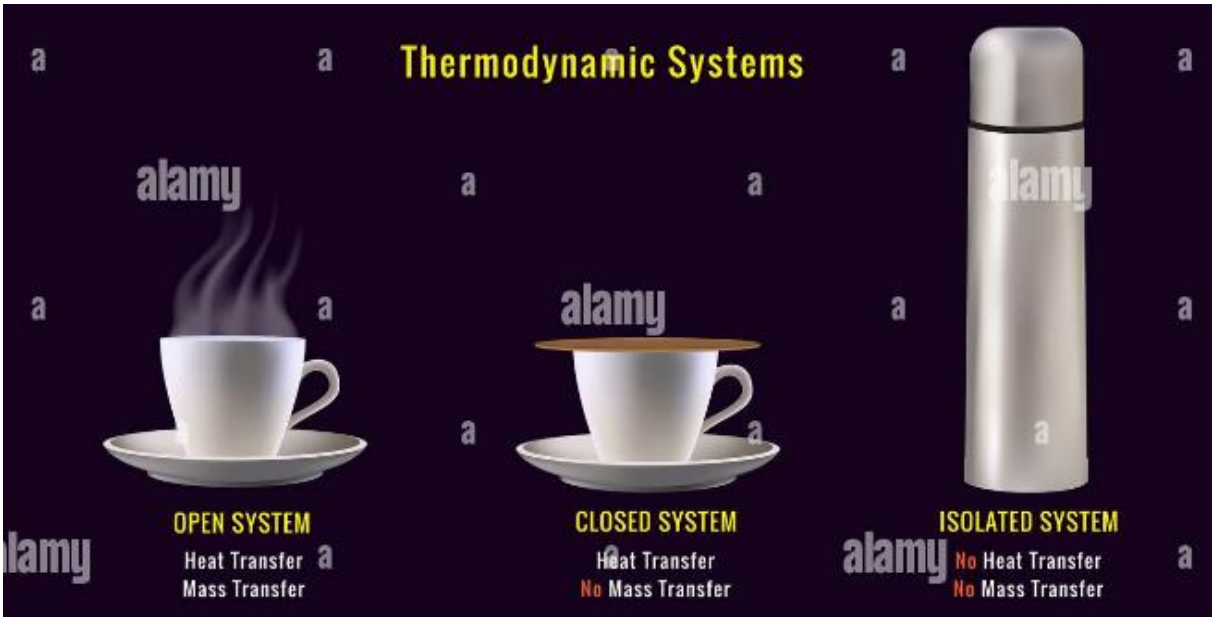
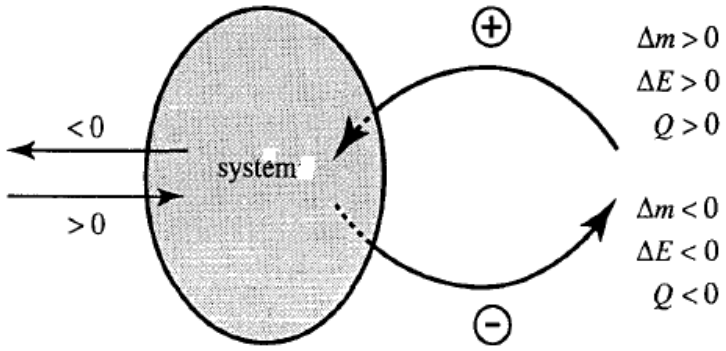


Fig.5.*Tthermodynamics system*

I.5 Sign agreement

The quantity of energy or matter exchanged between the system and the external environment is given an algebraic sign to indicate the direction of the exchange.



Sign assignment refers to the system using the banker's convention:

=> Energy or matter **received (gained)** by the system is counted **positively,**

=> Energy or matter **supplied (lost)** by the system is counted **negatively.**

I.6 State variables

As already mentioned, thermodynamics deals with the energy exchanges accompanying a transformation, which is the passage of a system (physical or chemical) from an **initial state (El)** to a **final state (EF).** To define the transformation, the initial and final states of the system under consideration must be known.

It is the set of values taken by thermodynamic quantities relating to the macroscopic state, known as "state variables" or "state parameters", such as mass (m), pressure (P), volume (V), concentration (C), density (d), temperature of change of state, etc., which define the state of the system.

Many of these state variables are related to each other :

Either by definitional relations, such as, for example, the relation linking quantity of matter, volume and concentration

$$C = \frac{n}{V} = \frac{m}{M}\frac{1}{V} \text{ (Mol L}^{-1}\text{)}$$

• Or by physical formulas called equations of state, such as the equation of state for perfect gases:

$$PV = nRT$$

Thanks to these relationships, we can use a small number of state variables (or parameters) to determine all the others by calculation, in order to fully describe the system under study.

A system can be completely defined by a limited number of state variables: T, P and n (Gibbs variables), for example

I.7 Extensive, intensive variables

There are two types of state variable: **extensive and intensive.**

Extensive variables are proportional to the quantity of matter in the system:

Mass (m), Number of moles (n), volume (V), Electric charge (q), etc.

*Extensive variables are **additive.***

If you double the amount of matter (n) in the system, they also double.

Intensive variables are quantities that are independent of the quantity of matter in the system: temperature (T), pressure (P), concentration (Ci), density (p).

An intensive variable is a quality factor.

It has the same value at any point in the system.

Generally speaking, when 2 systems S1 and S2 are combined into a single system S3, a variable X can take on two values:

$X_1 = X_2 = X_3$ ==> X is an **intensive variable**

$X_1 = X_2 + X_3$ => *X* is an **extensive variable**

Some intensive quantities commonly used in chemistry are obtained by dividing an extensive quantity relating to a given system by its quantity of matter. The quantities thus obtained are called molar quantities and are also referred to as reduced extensive quantities.

I.8 Gibbs variables (T, P, ..., n\)

These are physico-chemical variables (or parameters) that define the state of the system. These are the physical variables defining the thermodynamic state of the system under study:

T: thermodynamic temperature in kelvin (K)

P: pressure in pascal (Pa) or bar

V: volume in m^3 or liter (L)

and chemical variables defining the chemical composition of the system under study (we'll consider a homogeneous system made up of n components Ai).

=> *Xi:* molar fraction of component A; $Xi = \frac{ni}{\sum ni}$ *ni : number of moles of Ai*

=>Pi: partial pressure of component Ai

For a perfect gas : $PiV = niRT$ => $Pi=\frac{ni}{V}RT$

$$\Rightarrow \left(\frac{P}{n} = \frac{RT}{V} \right) x\ ni \Rightarrow \text{Pi= xi Pt}$$

The International System (SI) unit of pressure is the pascal (Pa). We also use the bar (1 bar = 10^5 Pa) and sometimes the atmosphere (1 atm= 1.01325. 10^5Pa).

==> Ci: molar concentration or molarity of component Ai (number of moles of A, per unit volume of solution).

$$\text{Ci} = \frac{ni}{V} = [\text{Ai}]$$

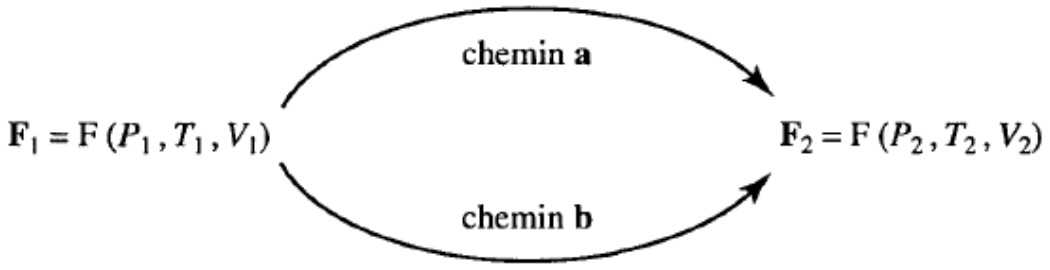
The SI unit of molar concentration is the mole per m^3 (mol. m^{-3}) . In practice, the unit used is the mole per liter: mol. L^{-1}

I.9 Status function

The function F(P, T, V) is a state function if its value corresponding to a state of the system depends solely on the state variables, but remains independent of the transformations previously undergone by the system.

State function properties

1. If F2 takes the same value when the system follows path a or b from state 1 to state 2, then F is a state function.



2. Let be a state function F(x,y) of the variables x and y. The infinitesimal variation dF of this function during a transformation is an exact total differential :

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

(being the partial derivative of F with respect to x, y being constant.

3. The variation of F, dF (or AF for a finite transformation) is independent of the path followed during a transformation; it is entirely defined by the values of the state variables of the initial and final states of the system:

$$\Delta F = \int_{\text{état 1}}^{\text{état 2}} dF(x,y) = F[\text{état 2}(x,y)] - F[\text{état 1}(x,y)]$$

I.10 Reversible transformation

Fig.6. *Exemple of reversible transformation*

When a system transitions continuously from an equilibrium state Sa to an equilibrium state Sb, the successive states cannot be equilibrium states. But if we imagine that the transition occurs through infinitesimal changes in the state variables, two successive states will be very close to each other. The variation in a state function characterizing the transformation will then be infinitesimal, and each state will be an equilibrium state. From this reasoning, thermodynamics assumes (theoretically) that a continuous transformation can be characterized by a sequence of equilibrium states. A reversible transformation is therefore a transformation during which the system must always be able to return to the previous equilibrium state

through an infinitesimal change in a state variable. It is therefore a transformation that can be performed in both directions. The system's state variables must also have values very close to those of the external environment at all times: such a transformation therefore presupposes the absence of dissipative phenomena (frictional forces, for example).

Thus, a reversible transformation appears to be an ideal operation, difficult to achieve in practice.

I.11 Irreversible transformation

Fig.7. *Exemple of irreversible transformation*

Real transformations are irreversible. These are transformations for which the system's transition from the initial state to the final state occurs in one (or more) steps, but without returning to the initial state. The differences between the values taken by the state variables in successive steps are significant.

However, since the variation of a state function is independent of the path followed (i.e., the way in which the transformation is carried out), this variation can always be determined by imagining a reversible evolution path.

Chapter II. The perfect gas

II- The perfect gas

II.1 Definition

Let's start with the most important:

The ideal gas is a mathematical model, allowing us to predict the temperature of a gas based on its pressure.

The ideal gas model itself defines a temperature scale. It is proposed to very simply measure the absolute temperature T with a manometer, stipulating that it is directly proportional to the pressure p and inversely proportional to the density. We can thus say that the ideal gas does not describe reality, that it is not a physical principle, but rather only a simplified model of the behavior of gases. Its range of validity is limited and unclear.

II.2 The equation of state

We will call an ideal gas a fluid in a gaseous state whose pressure and volume multiple, pv, remains proportional to its temperature. The constant of proportionality is called the gas constant, and denoted R; it depends on the nature of the gas.

$$PV = RT$$

The equation is called the ideal gas equation of state.

It can also be expressed as a function of mass:

$$PV = mRT$$

By definition for an ideal gas**,** where **Pis the pressure (Pa),**

V the volume (m3),

T the temperature (K),

R the constant of the gas considered (J K-1 kg-1).

Example 4.1

A mass of 2 kg of gas whose constant is R = 100 J K1 kg1 is contained in a 200 L tank at a pressure of 3 bar. What is its temperature?

We use equation 4/2 to express the temperature:

$T = \frac{PV}{mR} = 3\ 10^5\ 0.2 / 2\ 100 = 300\ K = 26.85\ C.$

The only problem with this equation is the units, which must be converted

to: 200 L = 0.2 m^3 and 3 bar = 3 10^5 Pa. The temperature is always in kelvins.

What does an ideal gas represent?

The ideal gas is the simplest model we can imagine to represent the behavior of a gas.

According to this model, molecules behave like spheres bouncing against each other (Figure 4.1). We can imagine a large number of very small billiard balls in chaotic motion, colliding and bouncing against each other without ever attracting each other or dissipating their energy through friction.

In this chaos, temperature is a measure of the kinetic energy of the molecules.

It is quantified by measuring the force resulting from the impact of the molecules on a wall of the container that is, with pressure. With this model, we can propose a temperature scale such as T/p.

The fewer molecules impacting the surface, the more strongly they must impact it to generate a given pressure. Thus, when the mass volume decreases at a given pressure, it is because the temperature increases.

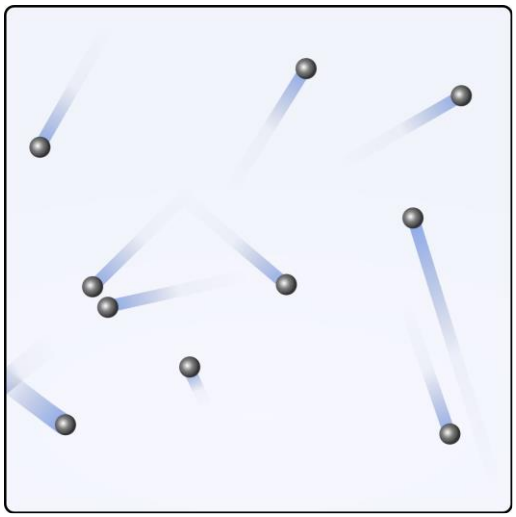


Fig An ideal gas can be visualized as a set of randomly moving balls. They collide without friction or mutual attraction. The speed of each ball changes with each collision.

What does an ideal gas not represent?

The behavior of molecules when they are close to each other is actually very complex, because attractive forces play a decisive role.

The influence of these forces is greater when the molecules are slow and structurally complex (the interaction between two hydrocarbon molecules, for example, is more difficult to model than the interaction between two helium molecules).

For now, we will remember that the ideal gas model works best:

— When molecules collide at high speed, that is, when the gas temperature is high;

— When the average space between molecules is large, that is, when the specific volume of the gas is large.

Limits of the Model

It won't take the student long to find the limits of the 4/2 equation, which states that a non-zero mass of an ideal gas occupies a zero volume at zero temperature.

Strictly speaking, an ideal gas cannot exist—the mathematical model loses its meaning at very low temperatures since it does not take into account the volume of the molecules themselves. Several other equations of state can be used to correspond to real gases over a wider range of properties.

Thus, the van der Waals equation, proposed as early as the 7th century, suggests:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Where a and b are two constants.

Chapter III The First Law

III- The First Law

III.1 defintion

The first law of thermodynamics simply states that: **Energy is indestructible.**

We can also write that "the energy of the universe is constant," or "energy is always conserved": it can be neither created nor destroyed. In other words, when an object receives a joule of energy, it can either store it or release it externally; but under no circumstances can it destroy it.

III.2 Forms of Energy

The different forms of energy that we usually identify have been discovered one by one throughout the history of physics.

III.2.1 Kinetic energy is possessed by a body due to its speed; it is the easiest form of energy to identify. It was long called vis viva ("living force").

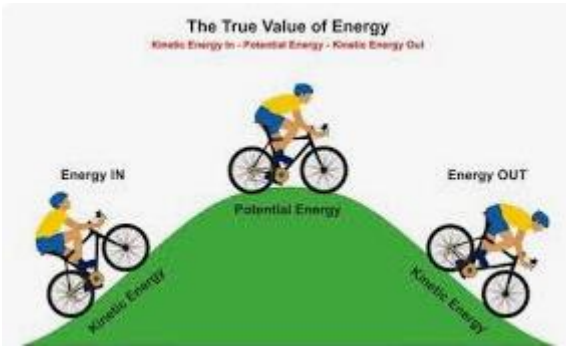


Fig.8. *energy's form*

III.2.2 Potential energy is stored with the interaction between two objects linked by a conservative force. On a macroscopic scale, the most tangible form is potential energy of altitude, resulting from the work done by a mass against its weight. By compressing a spring, we store potential energy of compression, which we recover by relaxing it.

Fig.9. *Exemple of potential energy*

III.2.3 Chemical energy is a combination of potential and kinetic energy between atoms. Human metabolism, as well as the combustion of hydrocarbons with atmospheric oxygen used in almost all our vehicles, are both based on chemical energy transfers.

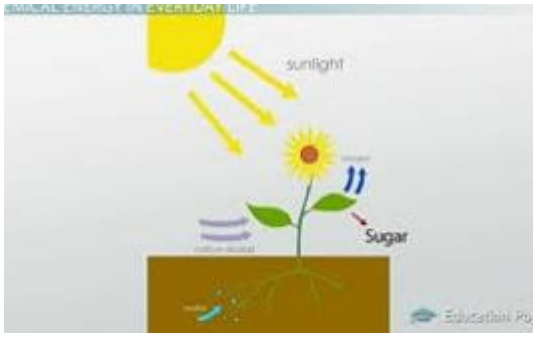


Fig.10. *Exemple of Chemical energy*

III.3 <u>Internal energy, denoted U</u>, is a concept we use to group together all the kinetic and potential energy of a body's molecules. It represents the total amount of mechanical energy stored inside an object.

III.3.1 Heat, denoted Q, is a transfer representing the chaotic transmission of kinetic energy from one body to another;

III.3.2 Work, denoted W, is a transfer representing the coherent transmission of energy from one body to another.

Generally speaking, thermodynamic engineers want to capture heat from bodies they want to cool, or provide work to bodies they want to move. We will therefore study these transfers in detail.

III.4 Thermodynamic Variables

The state of a system is defined using a number of macroscopic quantities called thermodynamic variables or state variables.

Examples: volume, pressure, temperature, density, conductivity, viscosity, etc.

The variables are not all independent: there are relationships between them. Experience shows that it is sufficient to determine the value of a small number of these variables to characterize the system.

III.4.1 Concept of pressure:

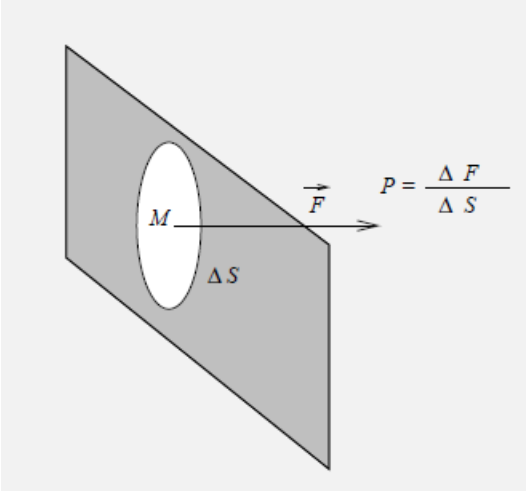
Definition

Consider a point M located on a surface, and surround it with a small surface element ΔS. Let ΔF be the force exerted perpendicular to this element.

The average pressure exerted on this surface element is then defined by the ratio:

$$P=\Delta F /\Delta SP$$

Pressure thus represents the intensity of the force exerted per unit area.



The total work during the transformation will be expressed as:

$$\Delta W = \int_{V_{initial}}^{V_{final}} -P\,dV$$

Notations :

In the following, we assume that only heat and mechanical energy are involved. We call W and Q, respectively, the quantities of work and heat exchanged by the system under study with the outside world.

Sign convention.

W>0	Q>0	Energies received by the system
W<0	Q>0	Energies released by the system

III.4.2 Clapeyron Diagram

This diagram represents the evolution of transformations when the pressure P is plotted on the ordinate and the volume V on the abscissa.Propriete:

Property:

In the Clapeyron diagram, the work **W =- ∫ PdV** will be represented by the area between the curve **P = f(V)**, the volume axis, and the lines parallel to the pressure axis passing through the abscissas Vinitial and Vfinal.

III.5 Reversible Elementary Transformations

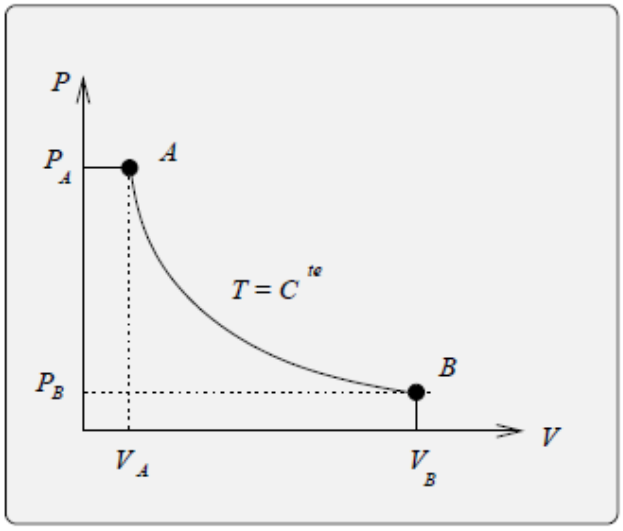
Here, we propose to calculate the properties of an ideal gas, as well as the energy transfers involved when it is compressed or expanded according to completely arbitrary constraints of volume, pressure, or temperature.

III.5.1 Isothermal transformation

It is possible to heat or cool a gas while maintaining its constant temperature (Figure). A gas flow at a constant temperature is said to be isothermal.

For an ideal gas, an evolution at constant temperature always occurs at constant energy. For each joule of heat supplied to the gas, one joule must be removed from it in the form of work; conversely, each heat extraction must be compensated by an equal contribution of work.

The isothermal transformation takes place at a constant temperature. The representation of an isothermal transformation in the Clapeyron diagram is an equilateral hyperbola.



Expression of work in the case of an isothermal transformation :

$$\Delta W_{isoth.} = \int_1^2 -P\,dV$$
$$= \int_1^2 -\frac{n\,R\,T}{V}\,dV$$
$$= -n\,R\,T_1 \int_1^2 \frac{dV}{V}$$
$$= -n\,R\,T_1\,ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta W_{isoth.} = -n\,R\,T_1\,ln\left(\frac{V_2}{V_1}\right) = -n\,R\,T_2\,ln\left(\frac{V_2}{V_1}\right)$$
$$= -P_1\,V_1\,ln\left(\frac{V_2}{V_1}\right) = -P_2\,V_2\,ln\left(\frac{V_2}{V_1}\right)$$

Exemple

For air, we measure Cp(air) = 1005 J kg^{-1} K^{-1}, Cv(air) = 718 J kg^{-1} K^{-1}, Rair = 287 J kg^{-1} K^{-1}.

A mass of 2.5 kg of air in a tank is at a pressure of 2 bar and a temperature of 800°C. We want to supply it with 100 kJ of heat without changing its temperature. What should the work transfer be? What will the volume and pressure be at the final value?

The work is easy to determine: $W_{A\text{-}B} + Q_{A\text{-}B} = U = 0$ here because the temperature does not vary. Thus, $W_{A\text{-}B} = Q_{A\text{-}B} = 100$ kJ (the gas must expend as much work as it receives heat).

The V final properties are obtained using the equation

$W_{A\text{-}B} = RTcst\ Ln(\frac{VA}{VB})$

$\frac{VA}{VB}=\exp\left[\frac{W\,A-B}{RTcst}\right]$

$\frac{VA}{VB}=\exp\left[\frac{-10\,.103}{2.5x287x\,(800+273)}\right] = 0.878207$

And as

$V_A = \frac{RTA}{PA} = \frac{287x\,(800+273)}{2.105} = 1.54\ m^3$

We obtain a final volume V_B $V_B = \frac{VA}{0.878207} = 1.715\ m^3$

The final pressure, finally, is obtained by comparing the final state and the initial state:

$P_A V_A = m\,R\,T_A = m\,R\,T_B = P_B V_B$

$P_B = P_A V_A / V_B = 1.786 \,.\, 10^5$ Pa = 1.786 bar.

The volume increases and the pressure decreases, as the gas works by expanding and receiving heat.

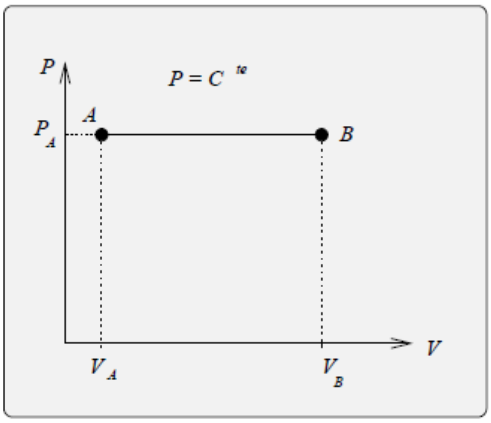
III.5.2 Isobaric transformation

It is possible to heat or cool a gas while maintaining its pressure constant. A process at constant pressure is said to be isobaric. To generate such a transformation, we can:

— with a closed system, heat or cool the gas while maintaining a constant force on the walls;

— with an open system, heat or cool the gas by simply allowing it to flow through a duct, without any moving parts. This is the case, for example, in the combustion chamber of a turbojet engine.

Isobaric transformation takes place at constant pressure.



Expression du travail dans le cas d'une transformation isobare

$$\begin{aligned}\Delta W_{isob.} &= \int_1^2 -P\,dV \\ &= -P_1 \int_1^2 dV \\ &= -P_1 (V_2 - V_1) \\ &= -P_2 V_2 + P_1 V_1\end{aligned}$$

$$\begin{aligned}\Delta W_{isob.} &= P_1 V_1 - P_2 V_2 \\ &= n R T_1 - n R T_2\end{aligned}$$

Exemple

For air, we measure cp(air) = 1005 J kg^{-1} K^{-1}, cv(air) = 718 J kg^{-1} K^{-1}, Rair = 287 J kg^{-1} K^{-1}

How much energy does it take to heat the air in a 30m² apartment from 10°C to 20°C?

Heating will likely occur at constant pressure (unless the apartment is hermetically sealed, the pressure will be atmospheric throughout and the air will "leak" under the doors). We assume a pressure of 1 bar and a ceiling height of 2.5 m. We are using a closed system encompassing all the heated air.

We have a volume of 75m^3, which brings the total mass of air to

$m_A = \frac{PAVA}{R\,TA}$ = 1. 105. 75/ 287 (273+10) = 92.29 Kg

The heat required to heat this quantity of air at constant pressure is quantifiable

$Q_{A\text{-}B}$ = m c_p ΔT = 92.29 . 1005 (20 -10) = +9.28 x 10^5 J = +928 kJ.

This result represents the final net heat transfer to the air (including losses to walls and windows, as well as the heat transfers that compensate for them).

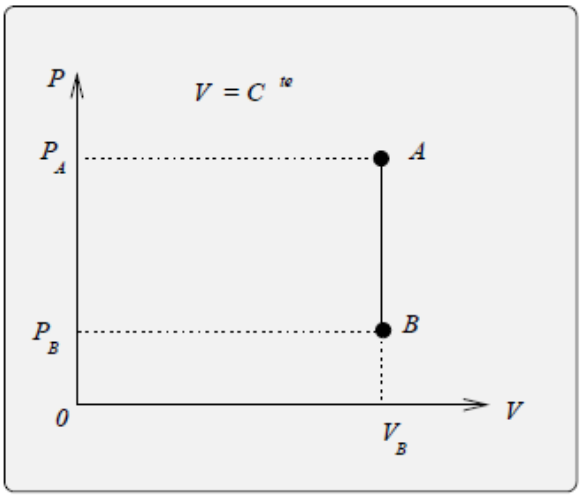
Conversely, cooling would cause the inflow of outside air, which would need to be taken into account in the mass calculation.

III.5.3 Isochoric Transformation

It is possible to heat or cool a gas while maintaining its constant volume. A constant volume flow is called isochoric.

With a closed system, we can heat or cool a gas in a fixed, closed reservoir. This is the case, for example, during the combustion phase ("explosion") in a gasoline engine.

The isochoric transformation takes place at constant volume.



Expression of work in the case of an isochoric transformation

$$\Delta W_{isoch.} = \int_1^2 -P\,dV = 0$$

Exemple

For air, we measure cp(air) = 1005 J kg^{-1} K^{-1}, cv(air) = 718 J kg^{-1} K^{-1}, Rair = 287 J kg^{-1} K^{-1}.

In a gasoline engine cylinder, air is at a pressure of 17 bar with a density of 9.4 kgm3.

The combustion of the fuel (so rapid that the volume does not have time to change) results in the input of 1450 kJ kg^{-1} of heat .

What values do the temperature and pressure reach?

Initially, the temperature is $T_A = P_A V_A / R = P_A / \rho_A R = 17.\ 10^5 / 9.4 \text{ X} 287 = 630.\text{K}$

We use a closed system consisting of the air mass. Since the volume does not vary, the work is zero. and it is the heat that causes the internal energy to vary.

$qA\text{-}B = \Delta U = Cv\ \Delta T = Cv(T_B\text{-}T_A)$

Thus

$T_B = 2\ 649.\ 6\ K$

The final pressure is obtained by comparing the final condition and the initial condition

$P_B = \frac{TB}{TA} P_A = 71.5bars$

Be careful to count the temperatures in kelvins in the fractions.

The maximum temperature, above 2300°C, exceeds the melting point of most metals. In a gasoline engine, this temperature is reached only sporadically, during each combustion.

Note:

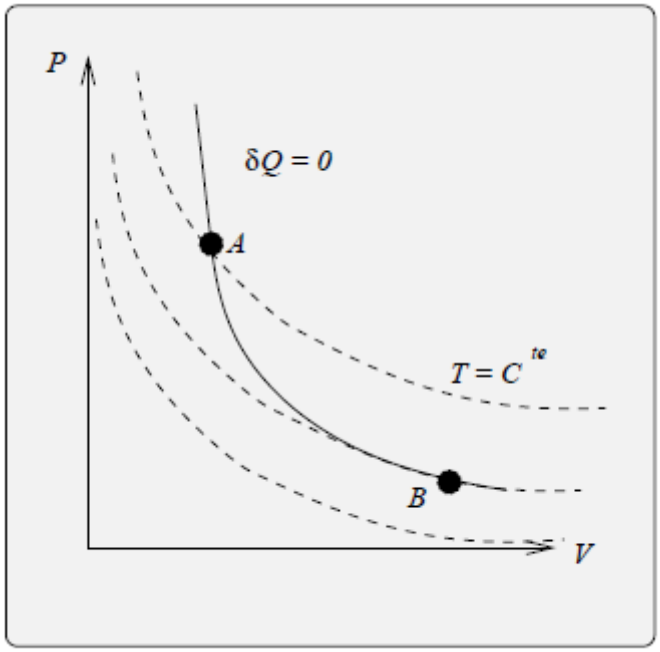
In isothermal, isobaric, and isochoric transformations, the exchange of energy between the system and its surroundings always occurs with the exchange of heat and work with the exterior, except in the case of isochoric transformation where the work of the pressure forces is zero.

III.5.4 Adiabatic Transformation

An adiabatic process is one in which there is no heat transfer. This can be forced by covering the container or gas pipe being compressed or expanded with a thick layer of thermal insulation.

A reversible adiabatic process is carried out infinitely slowly. For this to happen, a piston in a cylinder must move infinitely slowly, and a continuous-flow compressor must be infinitely long.

If the system is thermally insulated, the only exchange with the outside world occurs solely in the form of work. The transformation that occurs under these conditions is called an adiabatic transformation.



Note:

When moving from A to B, the system cools; the pressure, volume, and temperature vary simultaneously. Curves representing an adiabatic transformation are called isentropic curves.

Exemple

For air, we measure cp(air) = 1005 J kg1 K1, cv(air) = 718 J kg1 K1, Rair = 287 J kg1 K1, and air = 1.4.

A 50 L compressed air tank contains air at 40 bar and 50°C. The ambient atmosphere is at 1 bar. What is the maximum amount of work that can be extracted from the compressed air without adding heat?

The maximum work will be obtained if the expansion is reversible. Since we cannot add heat, our best option here is to perform a reversible adiabatic expansion from 40 bar to 1 bar.

We want to calculate the temperature Vnal, as this will give us the energy variation, therefore the work lost by the gas.

we are interested in: $\frac{TA}{TB} = \left(\frac{PA}{PB}\right)\frac{\gamma-1}{\gamma}$

$T_B = T_A \left(\frac{PA}{PB}\right)-\frac{\gamma-1}{\gamma} = (50+273)\ (40/1)^{(1.4-1/1.4)} = 112.6$ K = -160.5 ◦C.

The work done by the closed system consisting of the gas is therefore

$w_{A-B} = \Delta u - q_{A-B} = c_v \Delta T - 0 = 718 \times (-160.5 - 50) = -1.5115 \times 10^5$ J kg^{-1} = -151;1 kJ kg^{-1}

III.6 <u>Closed systems</u>

III.6.1 Principle of Equivalence: **Statement 1**

Evidence There are phenomena in nature that involve both exchanges of mechanical work and heat. These two quantities are not conserved separately but appear linked to each other.

Examples:

1. The brakes of a vehicle descending a slope at constant speed become heated. External forces (gravity) provide the system with work that is transformed into heat.

2. In thermal engines, there is a continuous transformation of heat into mechanical work.

3. Friction phenomena transform work into heat. Equivalence Principle: Statement 1

When a system returns to its initial state by performing a cycle of transformations in which it exchanges only work and heat with the external environment,

if it has received work, it has provided heat to the external environment.

if it has received heat, it has provided work to the external environment.

III.6.2 Principle of Equivalence: Statement 2

In a closed cycle carried out with only exchanges of work and heat, the algebraic sum of the mechanical and caloric energies received or released by the system is zero.

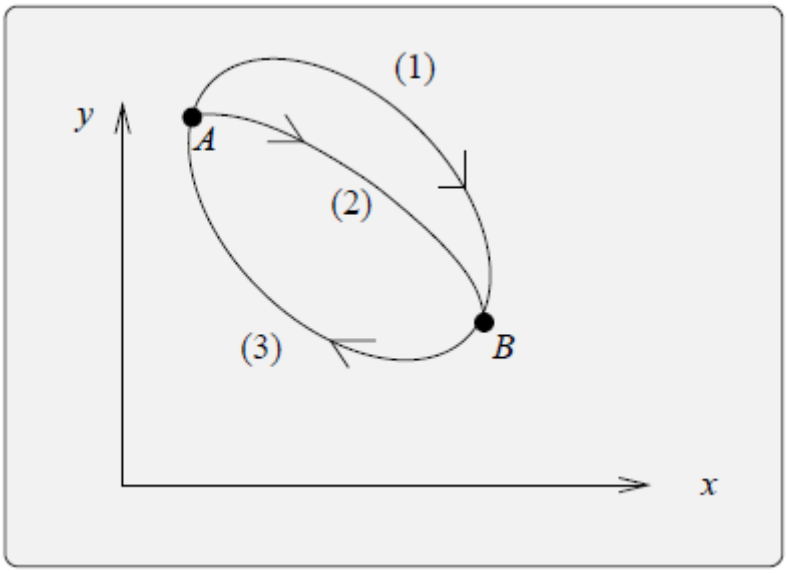
$$W + Q = 0$$

III.6.3 Principle of the Initial State and the Final State

Consider the following two cycles:

_ A (1) B (3) A

_ A (2) B (3) A



For each of the two cycles let us apply the principle of equivalence

Cycle A (1) B (3) A :

$W_1 + Q_1 + W_3 + Q_3 = 0$

Cycle A (2) B (3) A :

$W_2 + Q_2 + W_3 + Q_3 = 0$

either :

$$W_1 + Q_1 = W_2 + Q_2$$

When a system evolves from an initial state A to a final state B, the algebraic sum of the mechanical and caloric energies received or released by the system to the outside world depends only on the initial state and the final state, and not on the path taken to get from A to B. **W + Q does not depend on the path taken.**

III.7 Internal energy:

III.7.1 Definition

The quantity W + Q, homogeneous to work, measures the change in internal energy of the system ΔU. Kinetic and potential energies are not taken into account.

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

$\Delta U = U_B - U_A$ Only depends on states A and B and not on the path followed.

III.7.1 Applications of the first principle

a- Isolated system:

W = 0; Q = 0

$\Delta U = U_B - U_A = W + Q = 0$

b- **Isochoric transformation**:

$\Delta U_V = U_B - U_A = Q_V$

Remarq :

Consider the inverse transformation of an isochoric transformation.

We will have:

$\Delta U_V = U_{A-B} = Q_V$

And so :

$U_{B-A} = - Q_V$

Conclusion :

The amount of heat supplied to a system during an isochoric transformation is equal to the amount of heat it gives up during the reverse transformation.

Application :

When there is heat exchange without work exchange (isochoric transformation) between two parts of the same system, the amount of heat received by one part is equal to that given off by the other part.

In fact:

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

c- Isobaric transformation

The internal energy variation is written as:

$$\begin{aligned}\Delta U &= U_2 - U_1 \\ &= \Delta W + \Delta Q_P \\ &= -\int_{V_1}^{V_2} P\,dV + \Delta Q_P \\ &= -P_1 \int_{V_1}^{V_2} dV + \Delta Q_P \\ &= -P_1 (V_2 - V_1) + \Delta Q_P\end{aligned}$$

$$(U_2 + P_2V_2) - (U_1 + P_1V_1) = \Delta Q_P$$

III.8 Enthalpy function

The heat ΔQ_P exchanged by the system during an isobaric transformation is equal to:

$\Delta Q_P = (U_2 + P_2V_2) - (U_1 + P_1V_1)$

Let:

$H = U + PV$ enthalpy function

$\Delta Q_P = H_2 - H_1 = \Delta H$

Note:

Like the internal energy U, H is a state function. It is expressed in Joules.

The enthalpy change H depends only on the initial state and the final state: for a cycle, we have:

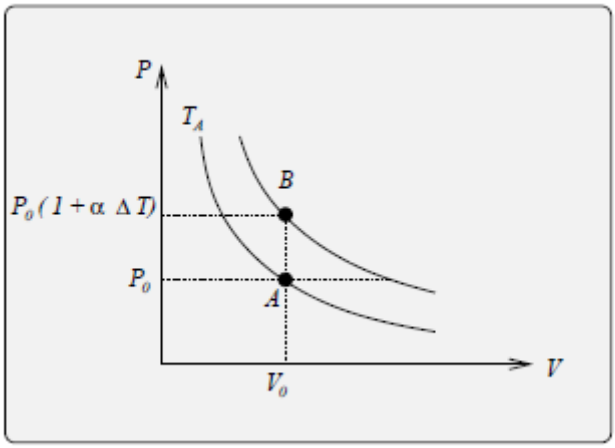
cycle) $\Delta U = \Delta H = 0$

III.9 **Perfect gas equation**

Let's consider two points A and B defined by :

A(P_0, V_0)

B($P_0(1+\alpha\Delta T)$, V_0)



Ideal Gas Law:

Statement

The product P_B V_B is equal to:

$P_B V_B = P_0 (1 + \alpha\Delta T) V_0$

With $\alpha = \frac{1}{T0}$

$$\frac{P_0 V_0}{T_0} = \frac{P_B V_B}{T_B} = C^{te}$$

The ideal gas law for one mole is written in the form:

Pour n moles : $PV = nRT$

Note:

According to Avogadro's law, the molar masses of all gases occupy the same volume under the same temperature and pressure conditions.

Therefore, R has the same universal value for one mole of ideal gas.

R = 8; 314,848 J . mole $^{-1}$. K $^{-1}$

III.10 Standard Molar Volume of an Ideal Gas

The standard molar volume of a gas is the volume of one mole at 0°C under standard atmospheric pressure.

$$V_0 = \frac{RT_0}{P_0} = \frac{(8,314848)\ (273,15)}{101\,325} = 22,415\ l$$

III.11 Heat Capacity

Heat capacity, generally denoted by a capital letter C accompanied by subscripts, is a physical quantity that measures the amount of heat required to cause a change in temperature of a body. In the International System of Units (SI), it is expressed in joules per kelvin (J/K).

There are derived quantities that make this property intensive, that is, independent of the size or mass of the sample. These include molar heat capacity, which corresponds to the heat capacity per mole of a substance, and specific heat capacity—better known as specific heat—which refers to the heat capacity relative to a unit of mass.

Temperature is related to the average kinetic energy of the particles constituting matter, while heat represents a transfer of thermal energy, propagating naturally from a hotter medium to a cooler medium. Thermal energy can be stored in the form of kinetic energy in random translational motions (particularly for monatomic gases), but also in the rotations and vibrations of polyatomic molecules. In particular, vibration modes involve both kinetic energy and potential energy, the latter being linked to interatomic bonds.

These different motions—translation, rotation, vibration—are called degrees of freedom, and each contributes to a system's thermal capacity within the framework of classical physics. However, quantum mechanics imposes certain restrictions: at low temperatures, certain degrees of freedom become inactive or partially accessible, which limits a system's ability to store thermal energy. Thus, as the temperature decreases and tends towards absolute zero, the specific heat capacity of a system gradually vanishes. This phenomenon, explained by quantum mechanics, also makes it possible to predict heat capacities in simple systems with good accuracy.

Thermodynamic relations and definition of heat capacity The internal energy of a closed system changes either by adding or removing heat to the system, or by the system performing work or having work done on it, written mathematically we have

$$dU = dQ + dW$$

For work as a result of compression or expansion of the system volume we may write

$$dU = dQ - PdV$$

If the process is performed at constant volume, then the second term of this relation vanishes and one readily obtains,

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

This defines the heat capacity at constant volume, C_v Another useful quantity is the heat capacity at constant pressure, . We start with the enthalpy of the system given by,C_p

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

Which from our equation for simplifies to dU , and therefore at constant pressure we have,

$$dH = dQ + VdP,$$

and therefore at constant pressure we have,

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

III.12 How to characterize the heat capacity of gases

III.12.1 Mayer's Relation

In the case of an ideal gas, unlike the condensed state, there is a significant difference between C_P and C_V. For such a system, since U depends only on temperature, the infinitesimal variation of U simplifies as follows: $dU = C_V dT$

C_V can be determined by counting the number of degrees of freedom. Regarding C_P, we will immediately use the properties of enthalpy we have just seen: at constant pressure, dH reduces to $dH = \delta Q = C_P dT$

Now, $H = U + PV = U + nRT$ for n moles of gas.

Thus: $dH = U + nRdT = (C_V + nR)dT$

Note that this relationship shows that H depends only on T, which constitutes Joule's second law. Identifying the two expressions for d leads to Mayer's relation: **$C_P - C_V = nR$**

Caractérisation de C_P et C_V à l'aide du coefficient γ

Thanks to the Mayer relationship, it is sufficient to know one of the two heat capacities

to know the other. Physicists could have characterized these heat capacities via C_V, as our presentation might encourage. But this did not appear to be the most effective method, as practice has shown that many properties depend not on C_V or C_P, but on the C_P/C_V ratio.

Method: How can we trace C_P and C_V knowing γ?

This is done using Mayer's equation and the definition of γ, which gives two equations:

$C_P - C_V = nR$

$C_P/C_V = \gamma$, which is equivalent to $C_P - \gamma C_V = 0$

We therefore have a system of two linear equations with two unknowns consisting of C_P and C_V. Solving this system gives the following solution:

$$C_V = \frac{nR}{\gamma - 1} \quad \text{et} \quad C_P = \frac{\gamma nR}{\gamma - 1}$$

III.12.2 Experiment characterizing ideal gases

a- Joule-Gay-Lussac expansion

The Joule expansion, also called the Joule–Gay Lussac expansion, is an experimental device used to determine whether a gas obeys Joule's first law (i.e., whether it satisfies the ideal gas model) by verifying whether the internal energy of the gas depends only on temperature.

In the Joule–Gay Lussac expansion, a container C_1 of volume V_1, initially containing the gas at temperature T_0, is connected via a tap (R) to another container C_2 of volume V_2. Container C_2 is initially empty. The walls of both containers are assumed to be rigid and perfectly athermal (see figure below):

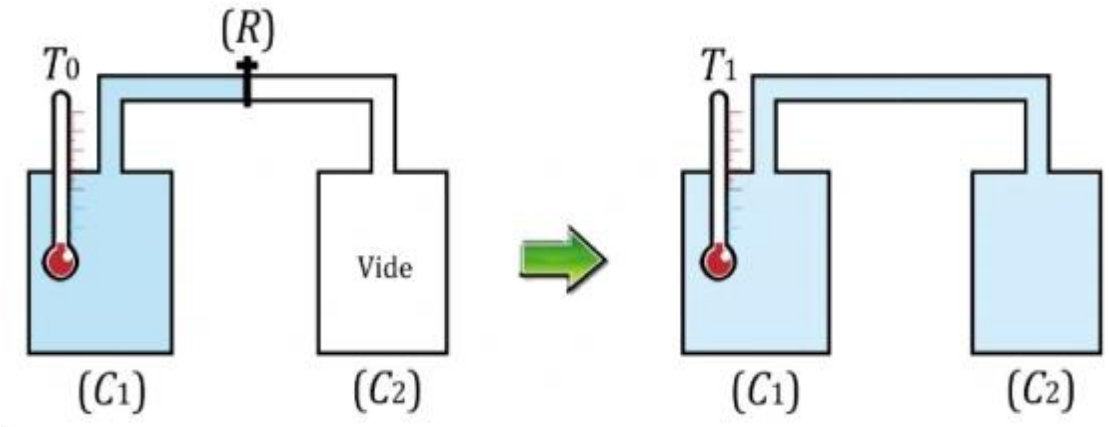


Fig.11. *Joule-Gay-Lussac expansion*

When the valve (R) is opened, the gas rushes into the container C_2 and, after a few moments, the gas pressure stabilizes: a new state of thermodynamic equilibrium is reached and the temperature of the gas in this new state of equilibrium is noted as T_1.

Experimentally, it is measured that during this expansion, most gases cool ($T_0 > T_1$), however, for so-called ideal gases, this difference remains very small ($\Delta T \sim 0$ thus Tfinal = Tinitial) → ($\Delta U=0$).

But in this experiment P and V vary. Therefore ΔU depends neither on P nor on V. The internal energy of an ideal gas therefore depends only on the temperature:$\Delta U = f(T)$

Note:

If the internal energy of an ideal gas depends only on temperature,

the enthalpy of an ideal gas depends only on temperature:

$\Delta H = \Delta U + \Delta (P V)$

$= \Delta U + \Delta nRT$

b- Joule-Thomson expansion

Joule-Thomson expansion is a very common transformation, which occurs in a steady state. On one side, there is a reservoir of fluid under high pressure P_0.

In practice, the pressure in this reservoir is maintained by a compressor. On the other side of the expansion valve, the pressure is lower, denoted P_1. Between the two, a device limiting the flow rate is placed, so that the pressure can be considered constant on each side. The entire system is thermally insulated so that there is no heat exchange.

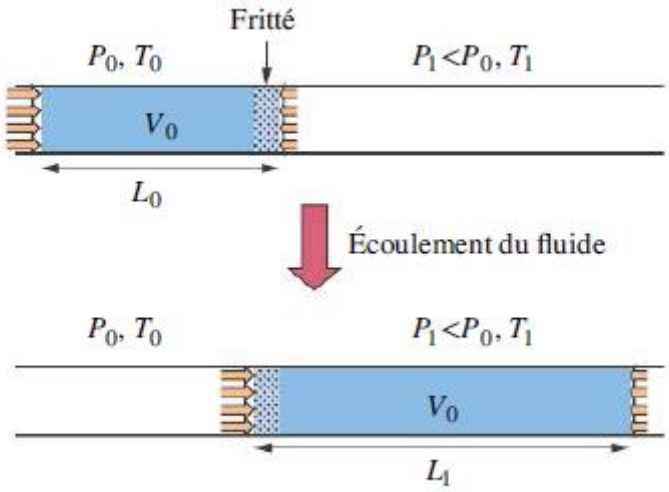


Fig.12. *Joule-Thomson expansion*

The pressure regulator can be a very simple system such as a capillary constriction through which the fluid circulates, a small frit, or even a piece of cotton, as in the historical experiment; this is sufficient to limit the flow. It can also be a more sophisticated device using a valve that gradually opens thanks to a spring system when the pressure difference exceeds a certain value.

How does the temperature vary during such an expansion? Consider a volume V0 (Figure 2.9) of fluid whose end just reaches the regulator.

Due to the pressure difference, the quantity of fluid initially contained in volume V_0 is gradually pushed to the other side. This volume of fluid is subjected to two forces:

• The resultant force F_0 originating from the pressure forces exerted by the adjacent fluid on the high-pressure side. This force is equal to P0S, where S is the cross-sectional area of the pipe. The work done by this force during the considered path is equal to P_0SL_0. Now SL_0 is identified with the initial volume V0 of our system, so the work of this force is $W_0=P_0V_0$.

• The resultant force comes from the pressure forces exerted by the adjacent fluid on the low-pressure side (this volume of fluid must push the gases on the low-pressure side to make room). This force is equal to $-P_1S$, its work is equal to $W_1=-P_1SL_1=-P_1V_1$, where V_1 denotes

the volume occupied by the quantity of fluid in question when it is entirely on the low-pressure side.

All that remains is to apply the first law, knowing that Q=0:

$\Delta U = U_1 - U_0 = W_0 + W_1$

This can finally be rewritten as follows:

$U_1 - W_1 = U_0 - W_0$ or $U_1 + P_1V_1 = U_0 + P_0\ V_0$

Here we recognize the definition of enthalpy: $H_1 = H_0$. This is a very general property of Joule-Thomson expansion; it is sometimes called isenthalpic expansion because of this result.

In the case where the fluid is an ideal gas, $\Delta H = C_P \Delta T$. Therefore, as with the Joule-Gay-Lussac expansion, the temperature is invariant during such an expansion for an ideal gas. With real gases, experience has shown that this is not entirely the case.

There is a more interesting case: in a domestic refrigerator, there is a Joule-Thomson expansion; the fluid arriving at the expansion valve is a liquid, and the fluid obtained at the outlet is a liquid-gas mixture.

Chapter IV Second law of thermodynamics entropy

IV- Second law of thermodynamics entropy : (spontaneous and non-spontaneous evolution)

IV.1. Introduction

The first law of thermodynamics asserts the conservation of energy during a transformation. However, this law does not allow us to predict the direction in which a transformation will naturally occur. This is where the second law comes in, distinguishing ideal, theoretically invertible reversible transformations from irreversible transformations, which occur spontaneously in a single direction.

Observation of natural phenomena highlights the existence of numerous spontaneous transformations, always oriented in a specific direction. These processes are irreversible. Here are two typical examples:

1. If a hot body and a cold body are placed in a thermally insulated (adiabatic) environment, their temperatures change until they equalize. Heat transfer naturally occurs from the hot body to the cold body, never vice versa.

2. When a moving wheel is braked, it eventually comes to a standstill due to frictional forces. This action generates heating of the brake. The kinetic energy of the wheel is thus transformed into internal energy (heat) in the brake. The reverse a spontaneous cooling of the brake restoring kinetic energy to the wheel although consistent with the first law, never occurs in reality.

Two factors of spontaneous evolution: energy and disorder One of the major concerns of thermodynamics is predicting whether a transformation is spontaneous or not. Generally speaking, when the final state is more stable than the initial state of the system, the transformation will be spontaneous under given conditions. In the case of chemical reactions, we compare the set of products (EF) and the set of reactants (EI). A reaction for which the

reactants are more stable than the products is not spontaneous. Some transformations are spontaneous under all conditions, some transformations are non-spontaneous under all conditions. But most transformations are spontaneous under some conditions and non-spontaneous under other conditions. With regard to chemical systems, we note that most spontaneous reactions are exothermic: the energy of the final system formed by the reaction products, measured by its enthalpy, is lower than that of the chemical system in the initial state.

Entropy is a property of bodies. Its variations allow us to measure the irreversibility of energy transfers (always undesirable for engineers). Total entropy always increases during irreversible transfers: of work (with sudden movement), of heat (with temperature gradient).

IV.2. Entropy is a Property

Let's begin by recognizing that entropy is a physical property, that is, something that characterizes the state of a system. In other words: if we consider a portion of the universe at a given time (a system), we find that this system has a mass, a volume, and a temperature: these are its properties, absolute descriptions of its state. Entropy is one of these properties.In contrast, we could say that heat, work, or electric current are not properties: they are not quantities that describe an object, but rather a transfer between two objects.

We will therefore always think of entropy as the entropy of "something" (perhaps as we would say color or temperature "of something"). We will say, for example, "this body has entropy" or "the entropy of this body increases/decreases," and not "we take/give entropy to this body."

Entropy is a physical property denoted by **S.**

When a system follows a reversible evolution, its entropy varies in such a way that:

$$dS \equiv \left(\frac{dQ}{T}\right)_{\text{rév.}}$$

Where the rev. index specifies that the calculation is performed along a reversible path;

dS is the infinitesimal change in entropy (J K^{-1});

dQ is the infinitesimal quantity of heat supplied reversibly (J);

and T is the temperature at which the heat transfer takes place (K).

When it passes from state A to state B reversibly, the entropy of a system therefore changes by a quantity S:

$$\Delta S = \int_{A}^{B} \left(\frac{dQ}{T}\right)_{\text{rév.}}$$

In practice, the term "entropy" is often used even when referring to specific entropy; the symbol and context help determine which variable is being referred to.

IV.3. Statements of the second principle

IV.3. 1 Clausius' statement

"Heat cannot spontaneously pass from a cold body to a hot body."

This means that any heat transfer from a cold body to a hot body requires an external expenditure of energy. This statement highlights a preferred direction for heat exchange and constitutes a specific formulation of the general principle of irreversibility of real transformations. These transformations only occur in a specific direction and are irreversible. One of the major causes of this irreversibility is the presence of dissipative forces, such as friction.

IV.3. 2. Kelvin statement

«It is impossible to design a heat engine which, operating in a cycle, would extract heat from a single source and convert it entirely into work.. »

In other words, it is impossible to transform all of a quantity of heat into work without losses. This statement highlights another form of irreversibility, inherent in thermal machines, and implies that 100% efficiency is unattainable for any device using only a thermal source.

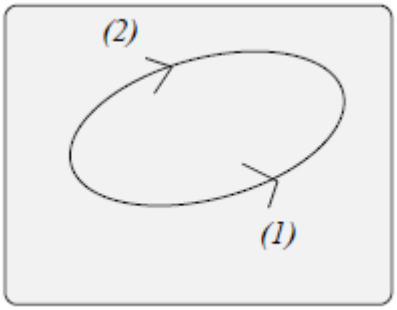
Reversible monothermal cycle

In a monothermal cycle: $W \leq 0$; $Q \geq 0$ **impossible**

In a monothermal cycle: $W \geq 0$; $Q \leq 0$ **possible**

Consider a system undergoing a cycle of reversible transformations in the presence of a single heat source. This cycle proceeds either in direction (1) or in direction (2).

According to the second law, in a monothermal cycle: $\mathbf{W \geq 0}$ **;** $\mathbf{Q \leq 0}$



Or:

Direction (1): $W1 \geq 0$; $Q1 \leq 0$

Direction (2): $W2 \geq 0$; $Q2 \leq 0$

When we change the direction of a cycle, we change the sign of the work and the quantities of heat, i.e.: $\Delta W_2 = -\Delta W_1$ et $\Delta Q_2 = -\Delta Q_1$

Conclusion :

$\Delta W_2 = -\Delta W_1 = 0$ et $\Delta Q_2 = -\Delta Q_1 = 0$

The reversible monothermal cycle is impossible

IV.3. 3 Mathematical statement of the second principle:

The first law of thermodynamics is a principle of conservation of energy, according to which energy can neither be created nor destroyed, but can only be transformed into different forms.

The first law also allows us to predict the amount of energy exchanged by a system with its external environment.

Thus, we have linked the heat exchanges observed during a chemical reaction to variations in the two state functions, internal energy (U) and enthalpy (H). Finally, the first law alone allows us to state that between two states A and B, the transformations:

A ——*- B $\quad\quad \Delta H = Hb - Ha$ ou $\Delta U = Ub$- Ua

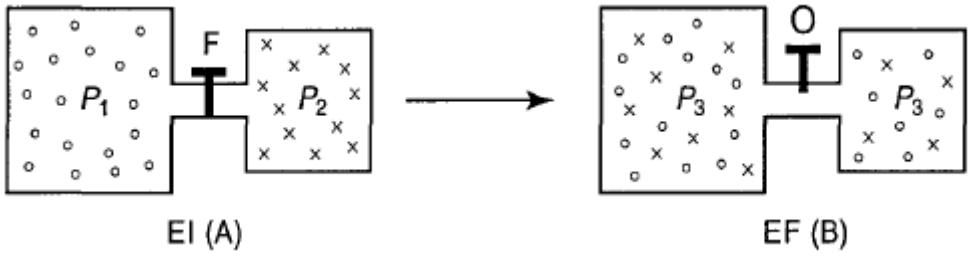
B —*-A $\quad\quad \Delta H = Ha - Hb$ ou $\Delta U = U$a- Ub

However, experience shows that when a transformation is spontaneous, the reverse transformation does not occur spontaneously; it can only possibly be achieved by the supply of energy from the external environment.

Exemples

Exemple 1

When two containers each containing a different gas are placed in communication, the mixing of the two gases is spontaneous.



According to the first principle, the transformation **B** to **A** is **possible**. But in reality, we never observe the separation of these two gases without external intervention.

Example 2

The same is true for chemical systems. A carbon-oxygen mixture spontaneously produces carbon dioxide at 100°C:

$$C(s) + O2(g) \rightarrow CO2(g)$$

The reverse reaction, although conceivable according to the first law, is never spontaneous without external intervention.

Example 3

Natural gas CH_4 produces a spontaneous combustion reaction in air:

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2(g) + 2\ H_2O\ (g)$$

The reverse reaction is not spontaneous. If it were, fuel could be produced from abundant and cheap products, and therefore there would no longer be an energy crisis.

These observations can be generalized without extending the list of examples:

Spontaneous (or natural) transformations cannot be reversed under the conditions in which they occur. That is, an isolated system always evolves toward the same final state. The evolution of the system toward the final state is spontaneous: it occurs without external intervention.

IV.4 Entropy Changes of an Ideal Gas

From now on, we want to be able to quantify the entropy change of the Wuides for any arbitrary evolution. In the case of an ideal gas, this quantification is actually surprisingly simple. For any evolution of a fixed Wuide quantity, we have :

$q1\text{-}2 + w1\text{-}2 = \Delta u$

If we imagine a reversible path between 1 and 2, we can quantify it

$$q_{1\to 2} = -\int_1^{\bar{2}} T\,\mathrm{d}s \qquad w_{1\to 2} = -\int_1^2 p\,\mathrm{d}v$$

We can therefore write:

$$\int_1^2 T\,\mathrm{d}s - \int_1^2 p\,\mathrm{d}v = \Delta u$$
$$T\,\mathrm{d}s - p\,\mathrm{d}v = \mathrm{d}u$$
$$\mathrm{d}s = \frac{\mathrm{d}u}{T} + \frac{p}{T}\,\mathrm{d}v$$

Now, if we use an ideal gas, we have

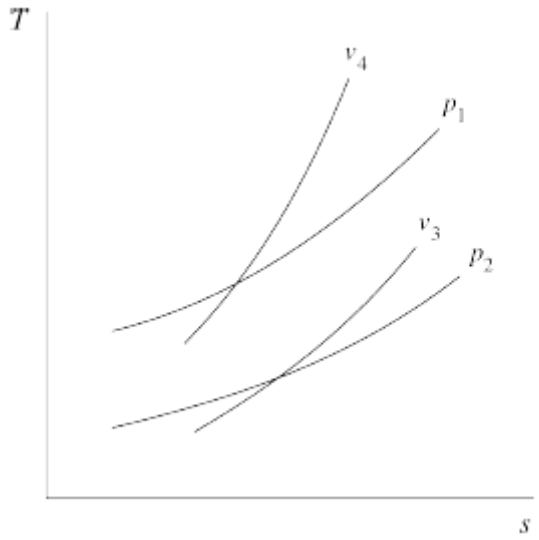
$$\mathrm{d}s = \frac{c_v\,\mathrm{d}T}{T} + \frac{R}{v}\,\mathrm{d}v$$
$$= c_v\frac{\mathrm{d}T}{T} + R\frac{\mathrm{d}v}{v}$$
$$\Delta s = s_2 - s_1 = c_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$
$$\Delta s = s_2 - s_1 = c_p \ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1}$$

This equation is interesting because it tells us that the entropy variation s during an evolution from 1 to 2 depends only on the initial and final states.

In the case where the specific pressure or volume are kept constant

$$\Delta s_{v_{\text{cst.}}} = c_v \ln\frac{T_2}{T_1}$$
$$\Delta s_{p_{\text{cste}}} = c_p \ln\frac{T_2}{T_1}$$

These two equations allow us to plot isochoric (constant volume) and isobaric (constant pressure) curves for an ideal gas on a T versus S diagram, as shown in figure 1.



Figure– Isobaric and isochoric curves on a T diagram as a function of s, for an ideal gas. p1 > p2 and v3 > v4.

Chapter V Carnot Cycle

V- Carnot Cycle

V.1. Definition

A system undergoes a dithermic cycle when it exchanges heat with two heat sources.

A Carnot cycle is a fully reversible dithermic cycle, consisting of:

- Two isothermal transformations, in contact with the sources,
- Two adiabatic transformations, which allow the passage from one source to the other.

The Four Stages of the Carnot Engine

We can describe the Carnot cycle with a quantity of mass trapped in a cylinder that undergoes four transformations (Figure 7.9). It thus evolves between temperatures TH (high-temperature "hot" source) and TB (low-temperature "cold" source), to produce a net work:

V.2 Reversible Adiabatic Compression from 1 to 2

In this step, we want to bring the fluide to a high temperature without adding heat.

The cycle begins at 1, when the fluide is in the cylinder at a low temperature Tc.

To bring it to a high temperature (and thus enable reversible heat transfer in phase 2-3), the fluide is compressed reversibly adiabatically. The fluide's temperature increases from Tc to TH.

This phase consumes work ($W_{1-2} > 0$).

V.3 Isothermal Heating from 2 to 3

In this step, we want to capture a quantity QTH of heat from the high-temperature source.

In 2, the fluid is compressed in the piston, at temperature TH. The cylinder is brought into contact with the hot source (temperature TH) and heat is supplied with an infinitesimal

temperature difference: this is an isothermal expansion . The fluid temperature remains constant at TH.

This phase produces work ($W_{2-3} < 0$).

V.4 Reversible adiabatic expansion from 3 to 4

In this step, we want to lower the temperature of the Wuide to that of the cold source (Tc).

At 3, the Wuide is still at temperature TH. The cylinder is then thermally insulated and the Wuide is expanded to extract work and reduce its temperature without heat transfer: this is a reversible adiabatic expansion.

The piston continues its slow recoil, and the temperature of the Wuide drops to Tc.

This phase produces work ($W_{3-4} < 0$).

V.5 Isothermal Cooling from 4 to 1

In this final step, we want to reject a quantity QTc of heat into the low-temperature well.

At 4, the Wuide is at a low temperature Tc. To return it to its initial volume, heat must be removed. We perform isothermal cooling: the piston is gradually advanced, and the Wuide temperature is kept constant at Tc.

This phase consumes work ($W_{4-1} > 0$).

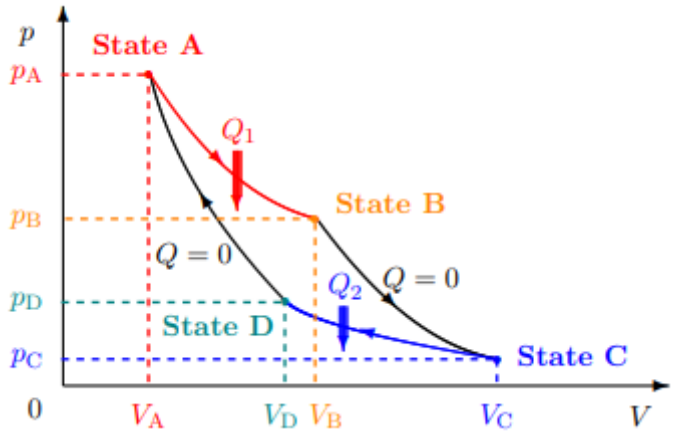
At final, the engine has received a quantity Q_{TH} of heat at a high temperature,and rejected a smaller quantity QTc at a low temperature. The difference between these two quantities is the work produced, $W_{net} = W_{1-2} + W_{2-3} + W_{3-4} + W_{4-1} = Q_{TH} \leq Q_{Tc}$

This amount of work Wnet represents the maximum that can be obtained from a given amount of heat QTH, between two given temperatures Tc and TH.

The Carnot engine cycle can be plotted on a pressure-volume diagram. In particular, we observe that the compression phases occur at a lower pressure and volume than the expansion

phases: the cycle produces work. Since all changes are reversible, the area circumscribed in the 1-2-3-4-1 path represents the amount of net work Wnet produced..

V.6 Clapeyron diagram



A-B isothermal: T_1

B-C adiabatic: from T_1 to T_2

C-D isothermal: T_2

D-A adiabatic: from T_2 to T_1

Balance of heat exchanges

A - B: isotherm at temperature T_1

$dU_{AB} = 0 = - P\,dV + \delta Q_{AB}$

$\delta Q_{AB} = P\,dV = \frac{nRT}{V}\,dV$

$$\Delta Q_{AB} = nRT_1 \ln\left(\frac{VB}{VA}\right)$$

C -D: isotherm at temperature T_2

$dU_{CD} = 0 = - P\,dV + \delta Q_{AB}$

$\delta Q_{CD} = P\,dV = \frac{nRT}{V}\,dV$

$$\Delta Q_{CD} = nRT_1 \ln\left(\frac{VD}{VC}\right)$$

B-C: adiabatic from T_1 to T_2

$$\Delta Q_{BC} = 0$$

D-A : adiabatic from T_2 a T_1

$$\Delta Q_{DA} = 0$$

Relationship between temperatures T_1 and T_2 and volumes V_A; V_B; V_C and V_D

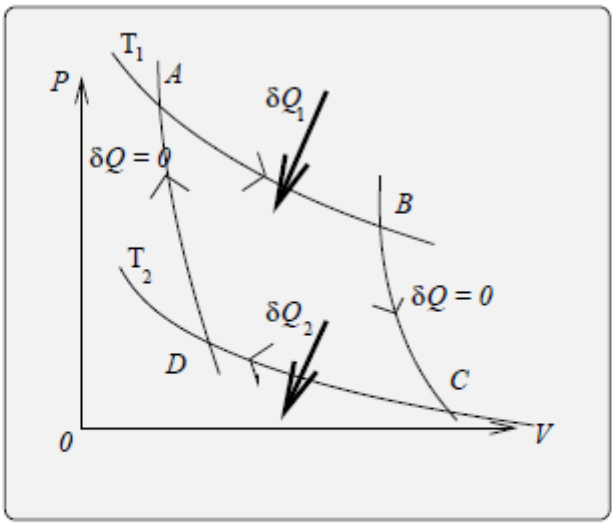
According to Laplace's law

B –C: Adiabatic: $T_B V_B^{\gamma} = T_C V_C^{\gamma}$

D-A: Adiabatic: $T_D V_D^{\gamma} = T_A V_A^{\gamma}$

Note:

Signs for heat quantities:



$$\Delta Q_1 = R T_1 \, ln\left(\frac{V_B}{V_A}\right) > 0 \qquad \Delta Q_2 = R T_2 \, ln\left(\frac{V_D}{V_C}\right) < 0$$

Chapter VI Thermodynamic Cycles

VI- Thermodynamic Cycles

When a compressed fluid is heated, it produces more work during expansion than was expended during compression. By expanding a fluid, its temperature drops and heat can thus be absorbed from a "colder" body. With these two processes, we convert heat into work and vice versa.

We want to formalize the concept of a cycle by answering two questions:

— How do motors, refrigerators, and heat pumps work?

— How can we quantify their efficiency?

VI.1. Graphical Conventions

We begin by agreeing on some graphical and notational conventions, which are summarized in **Figure .**

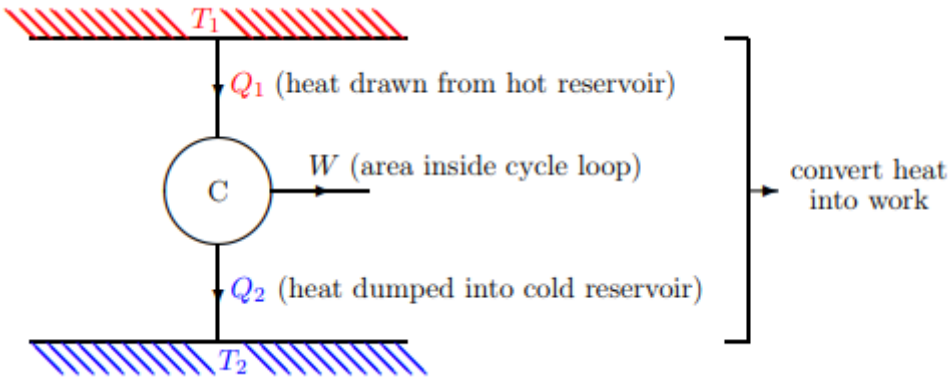


Fig.13. *Diagram of a (Carnot) engine, C.*

We use large white arrows to represent the physical direction of transfers. We do not change our sign convention (transfers are positive toward the system and negative when they come

from it), but only the graphical convention for orienting them, in order to make visualizing transfers in machines more intuitive.

The algebraic sum of the work received Win and provided Wout by a machine is called net work Wnet. Net work can be positive (received by the machine from the outside) or negative (provided by the machine from the outside), depending on the type of application.

$$W_{net} = W_{in} + W_{out}$$

Net heat is defined in the same way:

$$Q_{net} = Q_{in} + Q_{out}$$

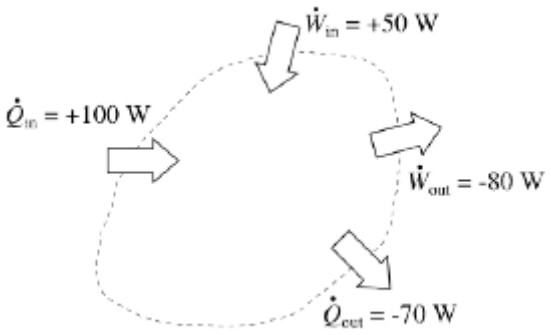


Fig.14. *Graphical and notational conventions of energy transfers*

For example, a car engine receives positive net heat and produces negative net work.

VI.2. Transforming Heat and Work

VI.2.1 Constructing Thermodynamic Cycles

We want to compare different ways of transforming work and heat.

For these comparisons to be valid, we must always take into account all the transformations undergone by the fluid until it returns to its initial state.

For example, it is easy to cool a room with a cylinder of compressed air (it is enough to make the fluid do work while it expands for its temperature to drop); but if we want to cool the room continuously, then we must also consider the energy required to return the air in the cylinder, at its initial pressure and temperature, to the Vn of the process.

A second example is that of a car engine, which rejects heat carried away by the exhaust gases. To account for this lost energy, we calculate the heat that would have to be extracted from the gases to bring them back to the engine's inlet temperature. This imaginary cooling takes place outside the engine in practice, but from a thermodynamic point of view, it is an integral part of the energy transformation process.

Thus, each time we analyze the operation of a heat engine, we take care to continue the evolution of the Wuide until it returns to its initial state (same temperature, same pressure, same internal energy, etc.). We then say that it has completed a thermodynamic cycle

VI.2.2 Producing Work from Heat

Let's start by compressing a fluid: we increase its pressure and reduce its specific volume, which requires a certain amount of work. After that, let's heat this fluid: its pressure and volume tend to increase. By expanding the fluid to its initial pressure, we will recover more work than we invested on the way out. To finally return the fluid to its initial state, we must cool it.

At the end, the fluid has expended less work on the return journey than it received on the way out. Over a cycle, it will therefore have produced work and absorbed (more precisely, transformed) heat. This is the operating principle of an engine. There are countless possible cycles to carry out this transformation, but they all involve at least four energy transfers: compression, heating, expansion, and cooling. We can separate these evolutions in space, as shown in Figure 6.2, or in time, as shown in Figure 6.3. Depending on technological and practical constraints, some of these transfers may be performed simultaneously.

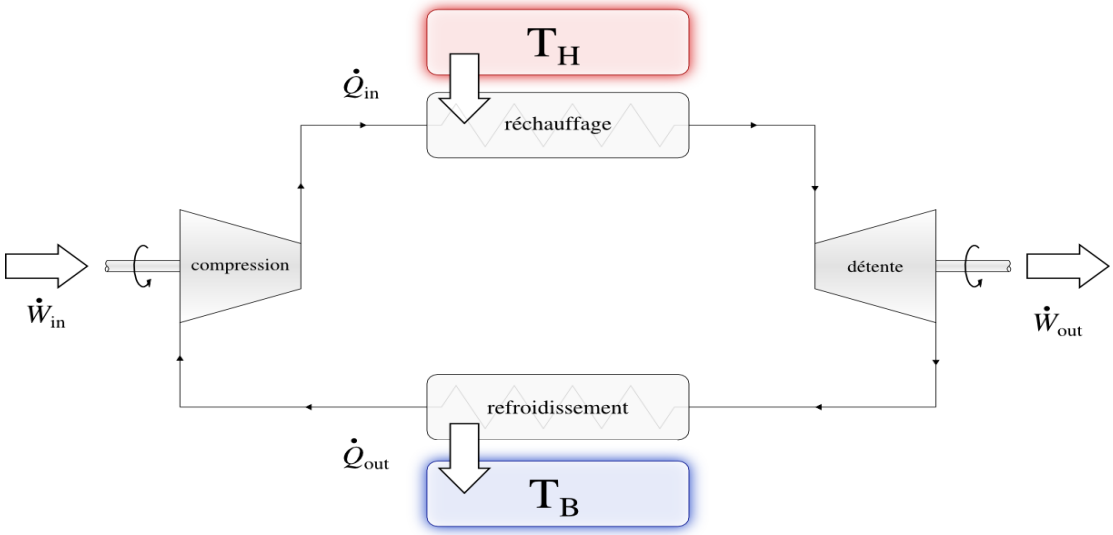


Fig.15. *Thermodynamic engine cycle.*

The fluid absorbs heat supplied at high temperature TH. Compression power is lower than expansion power: the net power in the form of work ˙Wnet = Win + Wout is negative.

VI.2.3 Extracting Heat with Work

When work is applied to a fluid, its temperature increases, and it can thus provide heat to a body that was initially at a higher temperature (‘hotter’) than itself.

Conversely, when a fluid is expanded, its temperature drops, and it can thus extract heat from a body that was initially ‘colder’ than itself.

By performing these steps one after the other, we obtain a refrigeration cycle: a machine capable of extracting heat at a low temperature and releasing it at a high temperature. Such a cycle is represented in Figure 6.5 (steps separated in space) and 6.6 (steps separated in time).

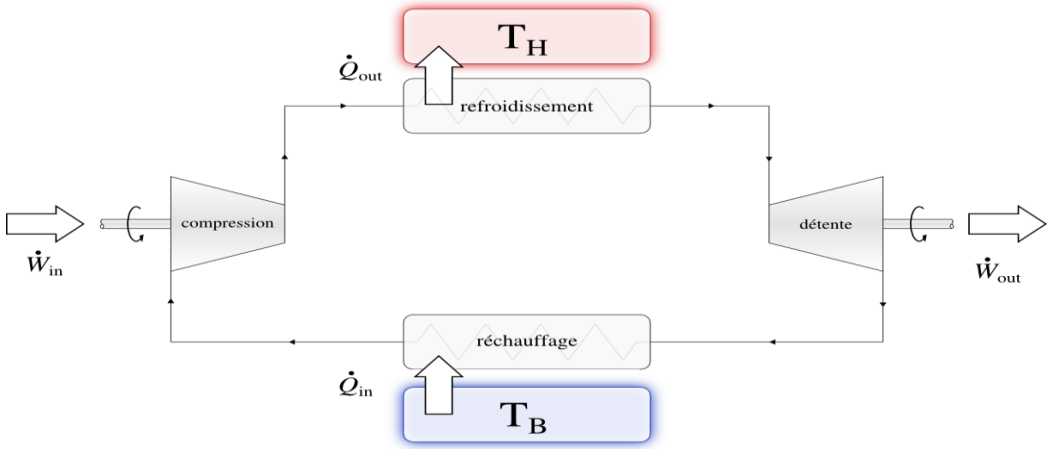


Fig.16. *Thermodynamic cooling cycle, used in refrigerators, air conditioners, and heat pumps.*

A power Q_{in} in the form of heat is captured at low temperature (the fluide is heated) while a power Q_{out} is rejected at high temperature (the fluide is then cooled).

VI.2.4 Expression of efficiency

1. **Efficiency of reversible thermal engines:**

$$\eta = \frac{work\ produced}{energy\ dispensed} = \frac{W}{Q1} = \frac{Wnet}{Qin}$$

$$\eta = \frac{-Q1-Q2}{Q1} = 1 + \frac{Q2}{Q1}$$

$$\eta = 1 + \frac{Q2}{Q1} = 1 - \frac{T2}{T1}$$

NB: The efficiency of a reversible heat engine depends only on temperature, not on the nature of the fluid.

2. **Performance of a refrigeration machine**

In the case of a refrigerating machine, the desired effect is the quantity of heat Q2 removed from the cold source. The energy supplied is the work provided to the compressor

$$\eta = \frac{Q2}{W} = \frac{Q2}{-Q1-Q2} = \frac{Qin}{Wnet}$$

$$\eta = \frac{Q2}{-Q1-Q2} = \frac{T2}{T1-T2}$$

$$\eta = \frac{Q2}{-Q1-Q2} = \frac{T2}{T1-T2}$$

The refrigerating efficiency coefficient depends only on temperatures; it does not depend on the nature of the fluid. It can be less than or greater than 1.

3. Heat pump performance coefficient

In the case of a heat pump, the desired effect is the quantity of heat Q1 returned to the heat source. The energy input is the work provided to the heat pump.

$$\eta = \frac{Q1}{W} = \frac{Q1}{Q1+Q2}$$

$$\eta = \frac{Q1}{Q1+Q2} = \frac{T1}{T1-T2}$$

$$\eta = \frac{Q1}{Q1+Q2} = \frac{T1}{T1-T2}$$

The performance coefficient of heat pumps is greater when the temperatures of the two sources are close**.**

Example

A car engine receives 100 kW of power in the form of heat from the combustion of gasoline; it provides 55 kW in the form of work to the driveshaft. What is its efficiency?

$$\eta = \frac{work\ produced}{energy\ dispensed} = \frac{Wnet}{Qin} = \frac{55}{100} = 0.55$$

This engine performs a rejection: $Q_{out} = -W_{net} - Q_{in} = -(-55 .10^3) -100 .10^3 = -45$ kW.

This heat is mostly evacuated through the exhaust pipe.

Example

A refrigerator consumes 100W of electrical power; it extracts heat from the cold room with 120W of power. What is its efficiency?

The efficiency is $\boldsymbol{\eta = \frac{Q2}{W} = = \frac{Qin}{Wnet} = \frac{120}{100} = 1.2 = 120\%}$

This refrigerator performs a rejection: $\dot{Q}_{out} = -W_{net} - Q_{in} = -100-120 = -220$W outside the cold room

Domestic refrigerators and air conditioners often have efficiency **greater than 1,** but depending on the temperatures required, the efficiency can be quite lower.

Example

A heat pump consumes 100W of electrical power; it heats the interior of a room with 350W of power. What is its efficiency?

The efficiency is $\boldsymbol{\eta = \frac{Q2}{W} = = \frac{Qout}{Wnet} = \frac{350}{100} = 3.5 = 350\%}$

The heat pump rejects more heat than it consumes in work that's its whole point.

If the efficiency were equal to or less than 1, it would be more economical and much simpler to use an electric radiator.

Chapter VII different types of engines (an overview)

VII- The different types of engines

VII.1 A bit of history: the number of engine strokes

VII.1.1 Two-stroke engine

The development of the two-stroke engine was paralleled by that of the four-stroke engine, but its development reached its peak after the Second World War. German engineer Walter Kaaden's refinement of an ingenious exhaust system, whose geometry alone increased the airflow escaping during expansion and reduced it during compression, made the engine very competitive on racing motorcycles; this tuned expansion muffler (Figure 6.17) was adopted on many production models.

At the same time, the ideas formulated by English entrepreneur Joseph Day in the 7th century regarding the mechanism controlling intake were widely disseminated. With its ingenious intake crankcase, the piston itself served as a valve (Figure 6.18). The intake air first passes through the crankcase where the crankshaft rotates, then is slightly compressed by the movement of the piston during expansion before entering the cylinder. The engine thus operates without any moving valves; lubrication can even be provided simply by injecting oil directly into the intake air. With these two advantages, the engine finds application wherever constraints of weight, volume, acquisition cost, and maintenance take precedence over efficiency.

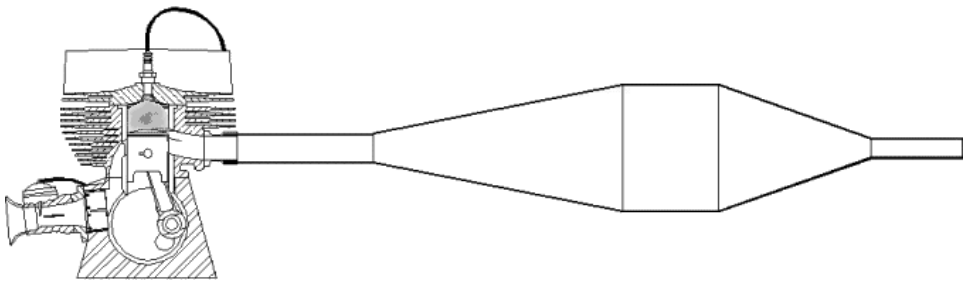


Fig.17. *Tuned expansion chamber (sometimes called "harmonic") mounted on a two-stroke engine.*

Since the flow is unsteady, it is possible to adjust the pressure exerted by the Vxed quantities of gases released on the exhaust port as they pass through the chamber. Passing through the expanding portion reduces pressure (and therefore facilitates emptying during the piston's descent), while passing through the constriction, on the contrary, increases this pressure (and therefore reduces gas losses during the piston's ascent).

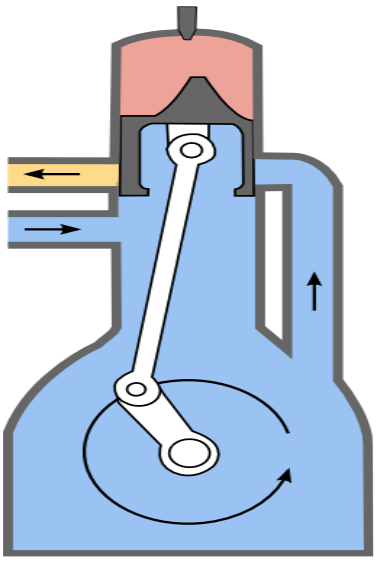


Fig.18. *Crankcase intake system*.

The intake air, loaded with fuel for combustion and oil to lubricate mechanical parts, first enters the crankcase. It is compressed and then inserted into the cylinder with the piston's downward movement alone. No valves or relief valves are required.

After powering three million Trabants in East Germany, it was adopted on almost all outdoor handheld tools (chainsaws, lawnmowers, etc.).

The engine miniaturized easily, left legroom on a scooter, allowed snowmobiles to start easily. In short, until the 1990s, nothing—not even neighborhood associations!—seemed able to slow its progress.

At the beginning of the 20th century, however, these attractions had to be abandoned. One could wearily accept the irritating sound emitted by the two-stroke engine, but its polluting

emissions were alarming. Lubrication by injecting oil into the intake air caused the atmospheric release of smoke, odors, and harmful particles. In addition, the always incomplete emptying of the cylinder severely limited combustion efficiency and thermal efficiency. Tighter regulations controlling emissions are gradually forcing the replacement of these engines with four-stroke engines or electric systems – whose batteries are often charged with energy from power plants... steam-powered. We can see that seemingly minor technological decisions sometimes have consequences on a global scale!

VII.1.2 Four-stroke engine

Historically, we learned to transform heat into work by manipulating fixed quantities of fluid trapped in enclaves. These enclaves have always been cylindrical, which greatly facilitates the manufacture of pistons that exploit variations in fluid volume to extract work.

When the fluid is water, the heat is supplied in a boiler and the steam is then transferred to the cylinder for expansion . In the 7th century, however, air began to be used, a fluid within which heat could be directly generated by combustion. The complex process, which until then consisted of performing a separate combustion to heat a metal boiler, which itself heated the engine's water, was eliminated, along with all the heat and temperature losses it engendered. This marked the birth of the internal combustion engine, whose development was led in particular by the German engineers Nikolaus Otto and Rudolf Diesel . Combustion and expansion were now carried out in the same place, directly in the cylinder.

However, to achieve internal combustion, a new problem must be solved: since the oxygen in the air is used during combustion, it can only be performed once. After each combustion , it is therefore essential to expel the reaction products (mainly CO_2 and H_2O) from the cylinder and reintroduce "fresh" air containing the oxygen O_2 needed to break down the hydrocarbon molecules C_xH_y, which produce heat. Two different solutions are then adopted. The most

common method is to dedicate one piston movement to each stage: the first for compression, the second for expansion (after or during combustion), the third to expel the burnt gases (exhaust), and the last to admit fresh air (intake). Engines using this method are called four-stroke (Figure), and they have always been the most widely used.

The second method will surely surprise purists: it involves performing these four operations in just two stages. In these engines, part of the gas expansion is devoted to their exhaust, which is carried out simultaneously with the air intake (Figures). Certainly, none of the four stages can be performed optimally: the compression and expansion phases are only carried out over a portion of the travel, and the emptying is necessarily incomplete due to the mixing of fresh and used gases. On the other hand, combustions are twice as frequent, since the intake and exhaust stages are omitted, during which no thermodynamic operations take place.

Thus, with equal displacement and rotation speed, two-stroke engines are much more powerful than their four-stroke counterparts, even if they are also significantly less efficient.

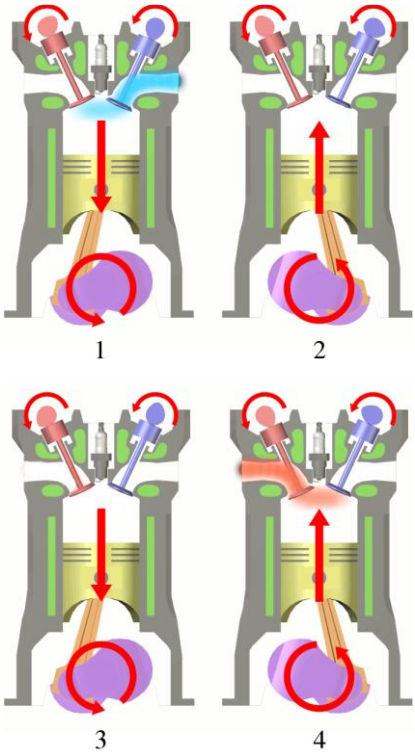


Fig.19. *The four stages of a four-stroke engine.*

The piston descends to admit fresh air from the right (intake, 1); it then rises to increase the air temperature (compression, 2); useful work is produced during a descent (expansion, 3); at Vn, the air is expelled to the outside during a fourth and final movement (exhaust, 4) before starting the cycle again. Most current piston-cylinder engines follow this process.

VII.1.3 Four-stage or four-stroke?

Reciprocating engines are often classified according to their operating mode. Two-stroke engines perform one expansion per crankshaft revolution (every two piston movements); while four-stroke engines (perform one expansion every two revolutions. The distinction lies in the method of draining the burnt gases and replacing them with fresh air.

Translating the Carnot engine to reality, in which the fluid may need to be drained or transferred to a separate cylinder for cooling, can be done with two or four strokes, depending on the engineer's choice.

Thus, the Carnot cycle, even though it does consist of four stages, cannot be associated with either of these two operating modes in particular.

VII.2 Gas Engine Cycles

Gas engines are more compact and lighter than steam engines. Numerous thermodynamic compromises are made to reduce weight and adapt to the speed and temperature limits of engine components.

VII.2.1 Why use a gas engine?

Using air as the driving fluid, rather than steam, offers several advantages.

— First, it is possible to completely eliminate the need for condensers and coolers. The cooling phase takes place directly in the atmosphere, which easily absorbs all the hot gases that are expelled, and which serves as a reservoir from which fresh air can be drawn to repower the engine.

At equal power, the mass, volume, and often the cost of gas engines are therefore significantly reduced compared to their steam counterparts.

This is particularly advantageous when the engine must contribute to its own weight.

— Second, the heat input is lossless. Indeed, it is possible to perform combustion directly inside the working fluid – this is called internal combustion.

While steam engines release large amounts of heat above the boiler, air engines lose very little heat during the combustion phases.

The main drawback of gas engines is that internal combustion requires high fuel quality. Since the combustion residues must circulate within the thermodynamic part of the machine itself, we cannot use attractive or economical heat sources such as burning waste, wood, or even coal.

Ultimately, the relative lightness of air engines compared to their steam counterparts means that they are systematically used when mass plays an important role, such as in air or road transport. It now goes without saying that we always seek to achieve high thermal efficiency, keeping in mind that it cannot exceed its theoretical maximum.

As we have already suggested,

$$\eta = 1 + \frac{Q2}{Q1} = 1 - \frac{T2}{T1}$$

However, thermal efficiency should not be maximized at the expense of other important parameters, the most notable of which for gas engines are presented below.

Work margin

In an operating engine, the irreversibility of compression and expansion is not independent of speed. When operating outside their optimal operating range, engines experience a decrease in their specific power. Irreversibilities can even reduce efficiency to zero, with the engine

running without producing any useful work (just like a disengaged automobile engine). Work margin is a concept that allows us to assess the robustness of a cycle to the increase in these irreversibilities.

To address this concept, let's first study the case of an engine with reversible compression and expansion. The energy transfers of the cycle are described in Figure 10.1. If, instead of being ideal, the turbine of this first engine were suddenly given an isentropic efficiency of 95%, it would only deliver 95W. The effective power of the engine would then drop from 10W to 5W, a reduction of 50%.

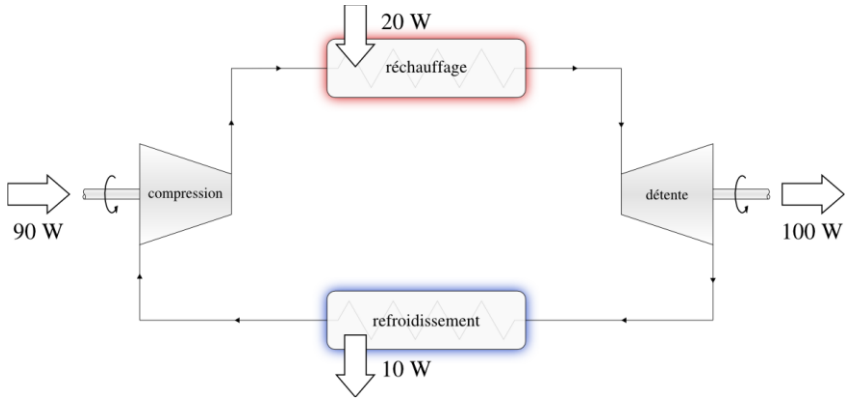


Fig.20. *The cycle of a (hypothetical) low work margin engine.*

The power developed is $\eta = \frac{Wnet}{Qin} = \frac{10}{20} = 50\%$

Let's now compare this case with an engine with the same efficiency and power, but with a different cycle, as shown in Figure . In this engine, if the turbine's isentropic efficiency were to drop from 100% to 95%, the net power would drop from 10 to 9W—a decrease of only 10%. We can thus see that the greater the turbine's share of the net power developed, the less the cycle's efficiency is affected by irreversibilities. We generalize and formalize this with the concept of work margin (Mw), defined as the ratio between the net power and the gross power of an engine.:

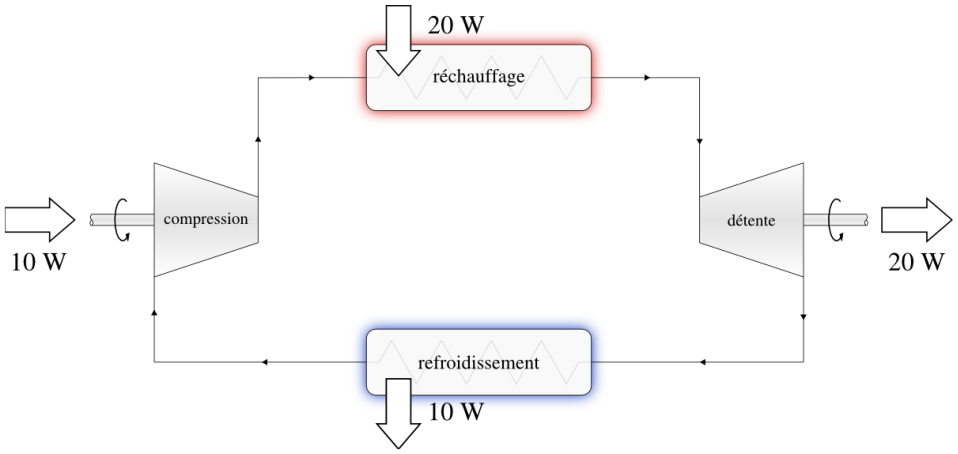


Fig.21. *The cycle of a second (hypothetical) engine, with a high work margin . The power Developed*

The power developed is $\eta = \frac{Wnet}{Qin} = \frac{10}{20} = 50\%$

The yields are identical to those of the engine described in the previous figure

A machine with a wide operating range maintains relatively stable efficiency, even when operating outside of its optimal conditions. This makes it a more flexible and adaptable system. This operating range, or "working margin," is a key indicator of an engine's responsiveness—in other words, its ability to quickly adjust its power and rotational speed.

This concept can be illustrated with an economic analogy: selling a product purchased at 2 monetary units for 3 is more profitable than selling a product at 101 after purchasing it at 100. Although the net profit is identical (1 unit), the latter is much less exposed to market fluctuations in the former case, illustrating a greater "safety margin."

The Carnot engine is often cited as a model of maximum thermal efficiency, but it has an extremely narrow working margin. This is clearly visible on the pressure-volume diagram, where the compression and expansion curves are virtually superimposed. The adaptation proposed by Rankine aims precisely to extend this margin, making the cycle more usable in practice.

Typically, maximizing thermal efficiency requires a high compression ratio to reach a sufficient temperature before heat transfer. Conversely, a wide work margin requires limiting compression work to reduce the engine's vulnerability to irreversible phenomena. Since these two objectives are often in conflict, the thermodynamic engineer must find a judicious compromise based on the system's constraints.

VII.2.2 Specific Thrust and Power

To simplify the comparison of different engine cycles, we use the concepts of specific thrust ($P/\dot{m}$) and specific power (w net), which correspond respectively to the engine's thrust and power relative to the mass flow rate of air passing through it. These quantities are particularly useful in cases where a high power-to-weight ratio is desired.

In the aeronautical field, for example, an improvement in engine efficiency does not always translate into an overall benefit if it is accompanied by an increase in weight or volume. A heavier aircraft will require greater lift, which leads to increased drag, and therefore greater thrust and power to maintain flight performance.Autres aspects à considérer

Beyond the criteria explored in this work, many other factors must naturally be considered when designing an engine, although their analysis is beyond the scope of our study. These include, briefly, the following:

— Purchase price, often determined by the complexity and dimensions of the engine;

— Environmental impact;

— Ease of maintenance and overall reliability;

— Engine responsiveness;

— Vibrations generated during operation.

Taking these factors into account can lead to compromises on pure engine performance. For example, it's reasonable to assume that a student, when purchasing their first vehicle, will prioritize a moderate acquisition cost over low fuel consumption. It's also unlikely that they will choose a racing-type engine, which requires constant technical support.

This principle of compromise between ideal efficiency and practical reality had already been aptly articulated in 1824 by a leading thinker of the time. According to him, it would be unrealistic to attempt to fully exploit the energy potential of fuels. Such ambitions would even risk becoming counterproductive if they ignored other essential considerations. Fuel economy, while important, is not always a priority: depending on the context, safety, robustness, longevity of the equipment, its compactness, or even its installation cost may take precedence.

Thus, the essential skill of those who design or supervise such systems lies in their ability to evaluate, weigh, and balance all of these requirements to achieve the best possible compromise within the specific constraints of the project.

VII.2.3 Reciprocating Engines

Reciprocating engines, also called piston engines, operate by introducing a fixed amount of air, which they use to complete their thermodynamic cycle. This cycle can be repeated simultaneously on multiple pistons and continuously over time, producing consistent power. For example, an automobile engine can complete approximately fifty cycles every second.

VII.2.4 Advantages of Piston Engines

From a thermodynamic perspective, these engines offer a major advantage: it is much easier to control a fixed mass of air than a continuous airflow. This notably allows for constant-

temperature combustion, in accordance with Carnot's principles, by modifying the volume during combustion. This type of combustion remains difficult to achieve in a continuous flow, as it would require it to occur within a turbine itself, which has not yet been mastered on a large scale.

Another advantage of piston engines is that the maximum temperature of the cycle is reached only occasionally, and for short periods of time. This temporarily allows temperatures to exceed the strength limits of the materials used, which can improve efficiency, as discussed in the chapter on the second law of thermodynamics.

However, these engines are disadvantaged by the complexity and weight of their mechanical architecture (connecting rods, crankshaft, valves, auxiliary circuits). This makes them less suitable for applications requiring very high power or high rotational speeds.

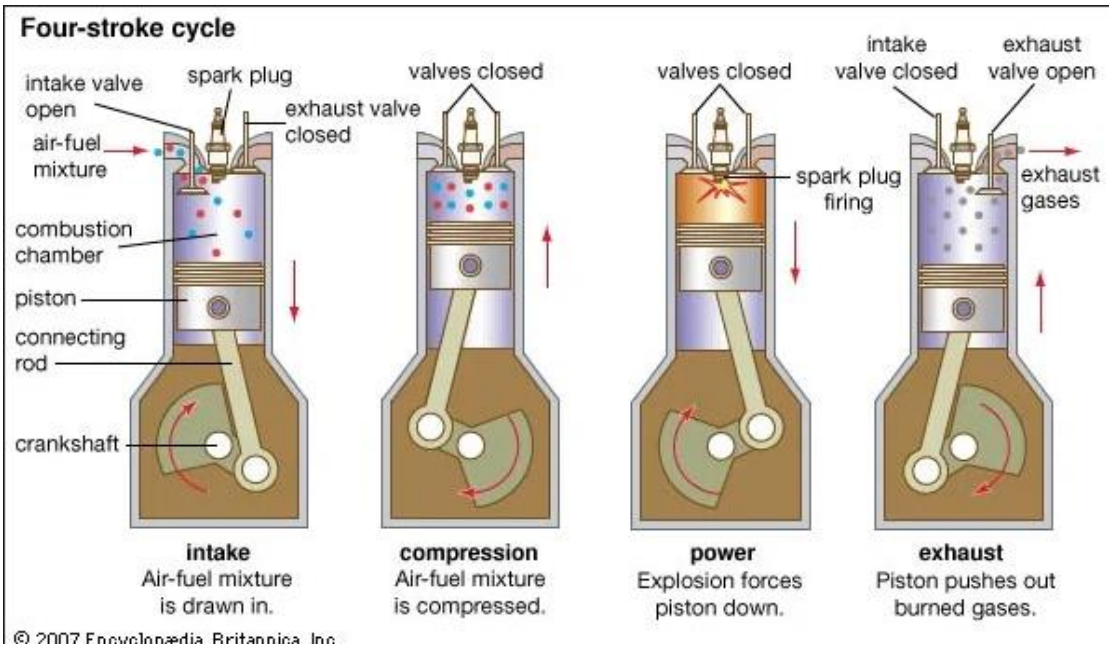


Fig.22. *Four –stroke cycle (piston engine)*

VII.3 Otto cycle: the ideal cycle for spark-ignition engines

The Otto cycle is the ideal cycle for spark-ignition reciprocating engines. It is named after Nikolaus A. Otto, who built a successful four-stroke engine in 1876 in Germany using the cycle proposed by Frenchman Beau de Rochas in 1862.

Fig.23. *Nicolaus August Otto (10 June 1832 – 26 January 1891)*

In most spark-ignition engines, the piston executes four complete strokes (two mechanical cycles) within the cylinder, and the crankshaft completes two revolutions for each thermodynamic cycle. These engines are called **four-stroke** internal combustion engines.

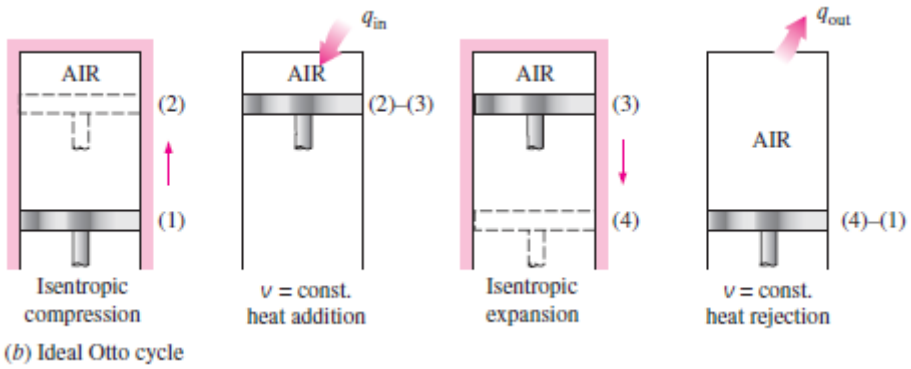
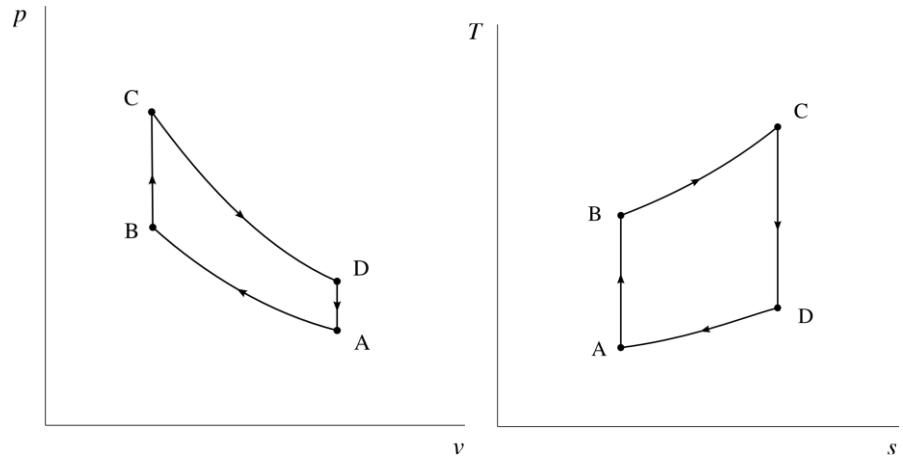


Fig.24. *Fig four-stroke internal combustion engines.*

Initially, both the intake and the exhaust valves are closed, and the piston is at its lowest position. During the compression stroke, the piston moves upward, compressing the air–fuel mixture. Shortly before the piston reaches its highest position , the spark plug fires and the mixture ignites, increasing the pressure and temperature of the system. The high-pressure gases force the piston down, which in turn forces the crankshaft to rotate, producing a useful

work output during the expansion or power stroke. At the end of this stroke, the piston is at its lowest position (the completion of the first mechanical cycle), and the cylinder is filled with combustion products.

Now the piston moves upward one more time, purging the exhaust gases through the exhaust valve (the exhaust stroke), and down a second time, drawing in fresh air–fuel mixture through the intake valve (the intake stroke). Notice that the pressure in the cylinder is slightly above the atmospheric value during the exhaust stroke and slightly below during the intake stroke.



Cycle théorique d'Otto représenté sur des diagrammes pression-volume et température-entropie. Ces graphiques représentent le trajet idéal, sans irréversibilité de compression ou détente.

The resulting cycle, which closely resembles the actual operating conditions, is the ideal Otto cycle. It consists of four internally reversible processes:

1-2 Isentropic compression

2-3 Constant-volume heat addition

3-4 Isentropic expansion

4-1 Constant-volume heat rejection

The Otto cycle was designed to allow for simple implementation of the heat input phase. The fuel was mixed with air before being inserted into the engine, and very rapid combustion was induced by a spark when the volume in the cylinder was minimal: this is called spark ignition.

Otto intended his engine for static applications, but its relative simplicity and responsiveness ensured its success in transportation (notably with his son Gustav Otto, an aircraft manufacturer whose company would later become BMW).

The efficiency of the theoretical Otto cycle can be calculated without much difficulty.

The heat input qcombustion = Cp (Tc - T_B) and the heat rejection qcooling = Cp (T_A - T_D) are both carried out at constant volume. Thus, since in theory no heat transfer takes place in the compression and expansion phases, and if we consider that the properties (cv) of the gas do not change during combustion, the efficiency η Otto of the theoretical cycle is simply:

$$\eta_{\text{Otto}} = \left| \frac{-q_{\text{combustion}} - q_{\text{refroidissement}}}{q_{\text{combustion}}} \right| = 1 + \frac{q_{\text{refroidissement}}}{q_{\text{combustion}}} ;$$

VII.4 The Diesel cycle

The history of the Diesel engine begins discreetly, on the sidelines of a thermodynamics course. In 1878, in Munich, a student named Rudolf Diesel asked himself in his notes: "Can we design a steam engine capable of performing a perfect thermodynamic cycle without being excessively complex?" Noting that the steam engines of his time suffered from very low efficiency, he began to consider a more rational alternative.

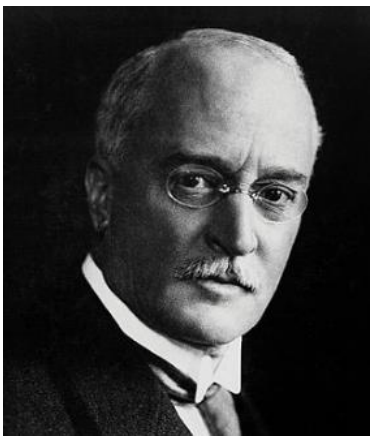


Fig.25. *Rudolf Christian Karl Diesel (un ingénieur allemand) 1858 - 1913*

Over the years, this idea matured and culminated, in 1893, in the publication of a groundbreaking concept: a heat engine based on strictly physical principles. Diesel openly criticized gas and air engines, asserting that their operation was based on a flawed principle, incapable of delivering satisfactory efficiency, regardless of technical improvements. He was just as harsh toward steam engines.

The core of his approach was to approximate the Carnot cycle, reaching the maximum temperature—the combustion temperature—not during combustion itself, but by preceding it, solely through air compression. The fuel was then injected progressively, allowing combustion at a constant temperature.

The only differences from the Carnot cycle lay in the intake and exhaust phases, which were carried out at constant pressure in a four-stroke cycle. Rudolf Diesel, drawing on his experience in refrigeration, managed to convince Maschinenfabrik Augsburg-Nürnberg (MAN) to finance his work. But the transition from theory to practice proved arduous and would take four years.

Many concessions were necessary: the initially planned maximum pressure was lowered, and pulverized coal was replaced with a less refined oil, which was easier to handle. The envisaged isothermal combustion was ultimately replaced by isobaric combustion, due to the mechanical constraints of the engine.

Fig.26. *The second prototype developed at MAN by Rudolf Diesel,*

The second prototype developed at MAN by Rudolf Diesel and the first to operate autonomously, in February 1894. It has a single cylinder, 22 cm in diameter, and direct fuel injection is achieved through a compressed air circuit. The engine is now on display at MAN headquarters.

The second prototype, an impressive single-cylinder engine nearly three meters tall, operated autonomously for eight minutes in February 1894. In 1897, the performance of the third prototype was officially measured: it delivered 17 horsepower at 154 revolutions per minute, with a remarkable efficiency of 26.2%. This figure far surpassed contemporary internal combustion engines (by a factor of two) and even exceeded the efficiency of the best steam engines by four times.

MAN quickly marketed this new engine, now known as the Diesel. Although its purchase price was high—due to the high-quality materials and precision machining required—it enjoyed growing success in Europe. Its robustness, consistency, and, above all, low fuel consumption justified its adoption. The patents held by Diesel ensured it a comfortable income.

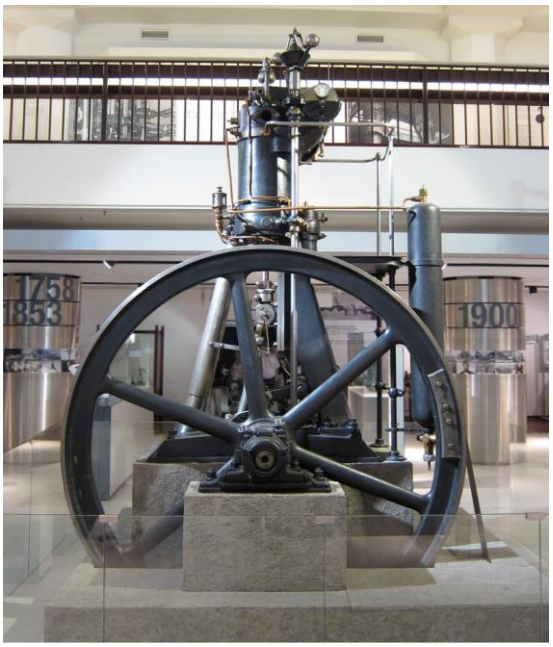


Fig.27. *The third Diesel prototype and the first operational engine.*

The third Diesel prototype and the first operational engine. The stroke of the 25 cm diameter cylinder reached 40 cm. It was tested at the Technical University of Munich, where it achieved 26.2% efficiency in 1897. It is on display at the Deutsches Museum.

The numerous documents left behind make Diesel an endearing character: cultured, diligent, and intelligent (he topped all his classes), he had a keen appreciation for the economic and social upheavals caused by the rapid mechanization of industry and transportation at the end of the 19th century. After a harsh and miserable childhood, expelled from France and then England, he nurtured a strong social ideal that led him to write Solidarismus ("the rational and economic salvation of humanity,"). For him, the decentralization of mechanical power production, for small businesses or collectives, for example, would constitute a decisive social advance. Despite the remarkable success achieved over fifteen years, Rudolf Diesel struggled to find fulfillment. He was constantly the target of legal disputes, with his critics and competitors arguing—not entirely wrong—that the engines he marketed were ultimately very different from the machine described in his patent. The nationalist upsurges preceding the

outbreak of the First World War shook him. A poor financial manager, he multiplied unreasonable expenses and ruinous investments and, above all, he was burdened with severe migraines and medical problems. In 1913, the man seemed tortured by his own ethical and philosophical questions. His engines produced exclusively power in factories and power plants: did they ultimately contribute to the emancipation or the maintenance of the working classes? He took his own life in September.

Fig.28. A nine-cylinder Sulzer RTA76 diesel engine producing 25 MW of power at 95 rpm.

This example is installed here in a factory, but the model is commonly used to power merchant ships.

Despite the untimely death of its inventor, the diesel engine has continued to improve and gain ground. Technological challenges, particularly those related to fuel injection—a key aspect of its operation—have gradually been overcome. Today, this type of engine is favored wherever robustness, fuel economy, and durability are essential criteria, to the detriment of weight or responsiveness.

In the maritime sector, particularly on commercial vessels, gigantic diesel engines are used, sometimes several stories high, operating on two-stroke cycles with high supercharging. These mechanical monsters, which can weigh over 2,000 tons and deliver up to 18,000 horsepower , perform long piston strokes of over two meters at a slow rate of approximately 80 revolutions per minute. This operation promotes near-isothermal combustion and offers an efficiency greater than 50%. In contrast, small diesel engines designed for light commercial vehicles incorporate sophisticated technologies to improve their performance and responsiveness. These compact engines, often limited to 80 horsepower but running at over 2,000 rpm, use very high-pressure direct injection systems—up to 2,000 bars—allowing up to four injections per cycle, to optimize combustion in real time according to power demand.

Ultimately, there are few modern industrial objects whose production, assembly, or transportation do not depend, at some point, on the energy provided by a diesel engine. An impressive achievement for an invention born from the curiosity of a visionary student.

VII.5 The thermodynamic advantages of piston engines

Thermodynamically, piston engines offer several advantages. Operating on a fixed air mass makes it easier to achieve constant-temperature combustion, in accordance with Carnot's recommendations. Conversely, in a continuous operation, such combustion would involve internal combustion in a turbine, which remains technologically unattainable on a large scale .

Another advantage is that the maximum cycle temperature in piston engines is only reached at brief and periodic moments. This allows for temperature peaks exceeding the metallurgical limits of the materials, significantly improving thermal efficiency (see Chapter 7 on the second law of thermodynamics).

However, their complex mechanical structure—including connecting rods, crankshafts, valves, and multiple circuits—limits their use when very high power and high rotational speeds are required. The result of the patient and careful work of its inventor, German engineer Rudolf Diesel, the diesel engine now powers the vast majority of commercial vehicles on road and sea.

From a strictly thermodynamic point of view, the theoretical Diesel cycle differs from Otto's only in its combustion mode: heat input occurs at constant pressure and not at constant volume, as shown in Figure .

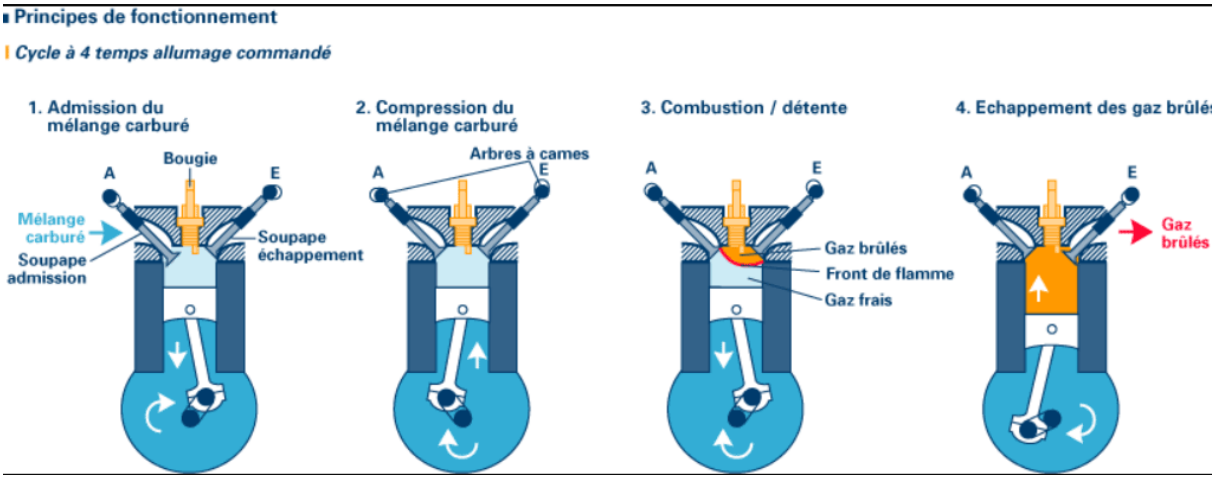


Fig.29. *Operating principle of four-stroke engines*

To understand the significance of this cycle and the true difference between a diesel engine and a gasoline engine, a little historical context is needed. In 1892, Rudolf Diesel designed a "rational" engine to implement the Carnot cycle. He therefore sought two characteristics:

— a high compression ratio, to increase the air temperature before combustion;

— combustion at a constant temperature.

To achieve this, Diesel must wait until the end of compression to inject the fuel, to avoid premature ignition. Isothermal heat transfer, in turn, requires gradual combustion. Thus, the original Diesel engine is inherently equipped with direct fuel injection, independent of air

intake. The Diesel cycle is therefore interesting because it allows for a higher compression ratio and combustion quality than the Otto cycle. Diesel's engine continued to evolve from the impractical concept described in Theory and Construction of a Rational Heat Engine to Replace Steam and Combustion Engines Known to Date in 1893 (400 bar and isothermal combustion of coal powder) to the first production models he developed at the engine manufacturer (MAN) (40 bar and isobaric combustion of petroleum). Like Otto, Diesel was initially interested in stationary engines (his first prototypes were single-cylinder and exceeded three meters in height), but it was applications in commercial transport, where the absence of spark plugs and its excellent efficiency gave it an advantage over spark-ignition engines, that would make his reputation.

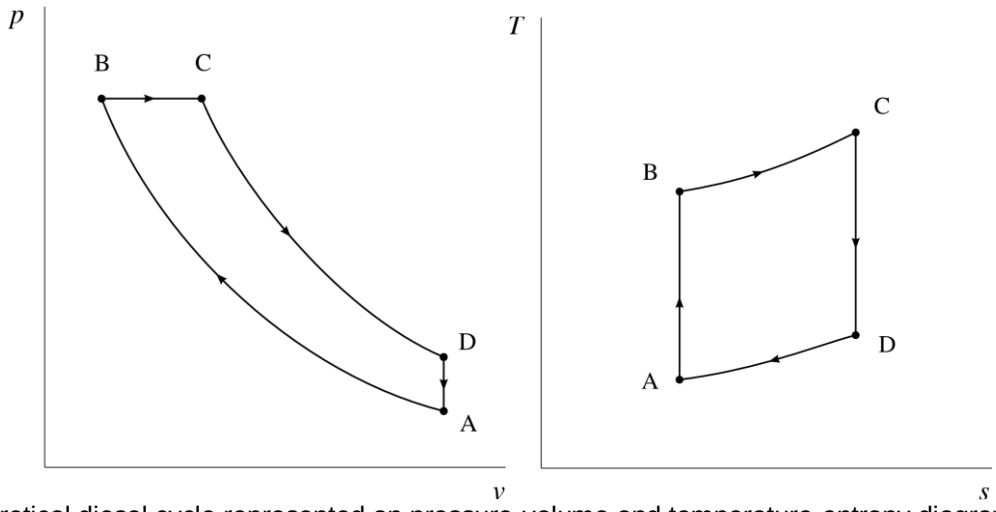


Fig Theoretical diesel cycle represented on pressure-volume and temperature-entropy diagrams.

These graphs represent the ideal path, without irreversible compression or expansion.

VII.6 Practical Application of the Cycles

The two cycles described above are only ideal cycles—they serve as conceptual benchmarks for comparing real engines with each other. Transposing them to a real engine requires taking into account many factors, including:

— The need to bleed the air and combustion products inside the cylinder after the cycle, and the impossibility of doing so completely;

— The fact that the volume occupied by the gas is linked to the rotation of the engine shaft, and therefore cannot be controlled independently of the engine's operating speed;

— Irreversibilities during compression and expansion caused by the rapid movements of the pistons;

— Heat transfer to and from the cylinders during the cycle;

— Gas leakage in the gaps between the pistons and cylinders.

Taking these factors into account, along with the pursuit of objectives related to user comfort and air pollution control, mean that the cycle obtained inside a practical engine cylinder could, for example, resemble that shown in Figure 10.5. In the automotive sector in particular, the adoption of direct injection and the increase in compression ratios on gasoline engines to reduce their consumption and emissions has blurred the distinction between gasoline and diesel—gasoline engines are now closer to the concept of Rudolf Diesel than to that of Nikolaus Otto.

VII.8 Stirling and Ericsson cycles

The ideal Otto and Diesel cycles discussed in the preceding sections are composed entirely of internally reversible processes and thus are internally reversible cycles. These cycles are not totally reversible, however, since they involve heat transfer through a finite temperature difference during the nonisothermal heat-addition and heat-rejection processes, which are irreversible.

Therefore, the thermal efficiency of an Otto or Diesel engine will be less than that of a Carnot engine operating between the same temperature limits.

Consider a heat engine operating between a heat source at *TH* and a heat sink at *TL*. For the heat-engine cycle to be totally reversible, the temperature difference between the working fluid and the heat source (or sink) should never exceed a differential amount *dT* during any heat-transfer process. That is, both the heat-addition and heat-rejection processes during the cycle must take place isothermally, one at a temperature of *TH* and the other at a temperature of *TL*. This is precisely what happens in a Carnot cycle.

There are two other cycles that involve an isothermal heat-addition process at *TH* and an isothermal heat-rejection process at *TL*: the *Stirling cycle* and the *Ericsson cycle.* They differ from the Carnot cycle in that the two isentropic processes are replaced by two constant-volume regeneration processes in the Stirling cycle and by two constant-pressure regeneration processes in the Ericsson cycle. Both cycles utilize **regeneration,** a process during which heat is transferred to a thermal energy storage device (called a *regenerator*) during one part of the cycle and is transferred back to the working fluid during another part of the cycle

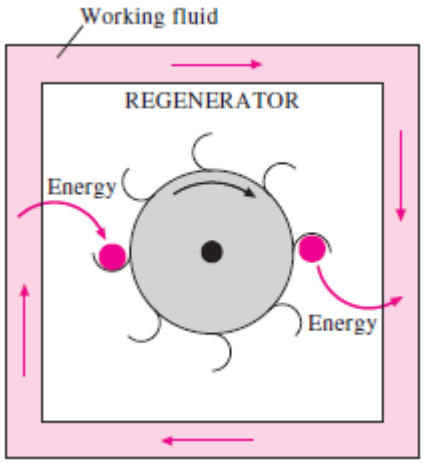


Fig.30. *A regenerator is a device that borrows energy from the working fluid during one part of the cycle and pays it back (without interest) during another part.*

Figure shows the *T-s* and *P-v* diagrams of the **Stirling cycle,** which is made up of four totally reversible processes:

1-2 *T constant* expansion (heat addition from the external source)

2-3 *v constant* regeneration (internal heat transfer from the working fluid to the regenerator)

3-4 *T constant* compression (heat rejection to the external sink)

4-1 *v constant* regeneration (internal heat transfer from the regenerator back to the working fluid)

The execution of the Stirling cycle requires rather innovative hardware. The actual Stirling engines, including the original one patented by Robert Stirling, are heavy and complicated. To spare the reader the complexities, the execution of the Stirling cycle in a closed system is explained with the help of the hypothetical engine shown in Fig..

This system consists of a cylinder with two pistons on each side and a regenerator in the middle. The regenerator can be a wire or a ceramic mesh

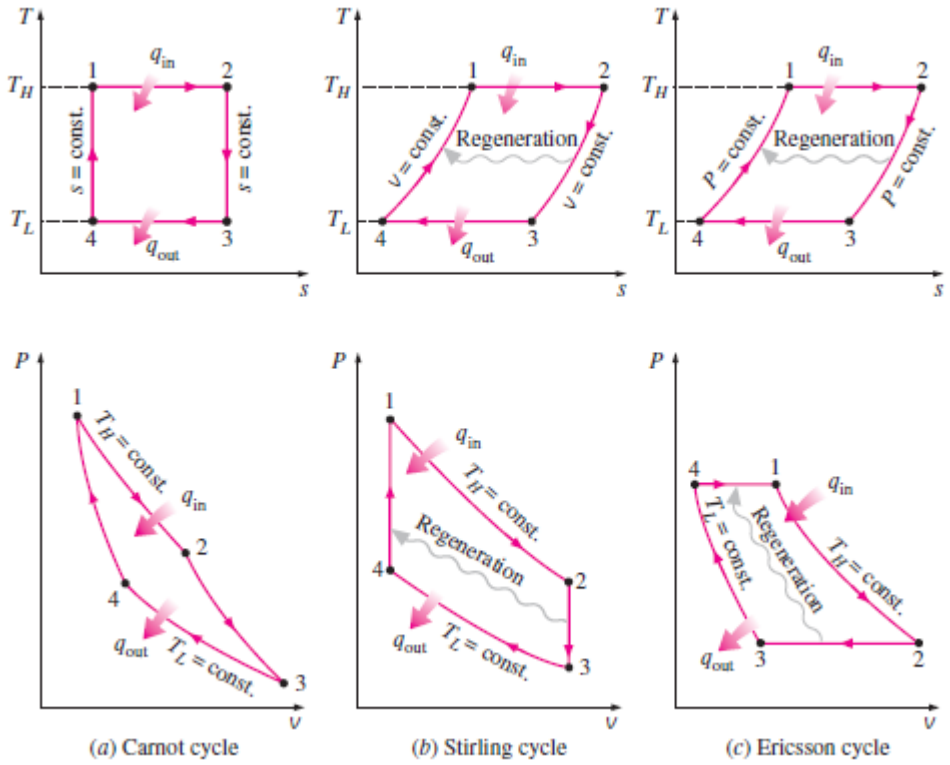


Fig.31. *The T-s and P-v diagrams*

or any kind of porous plug with a high thermal mass (mass times specific heat). It is used for the temporary storage of thermal energy. The mass of the working fluid contained within the regenerator at any instant is considered negligible.

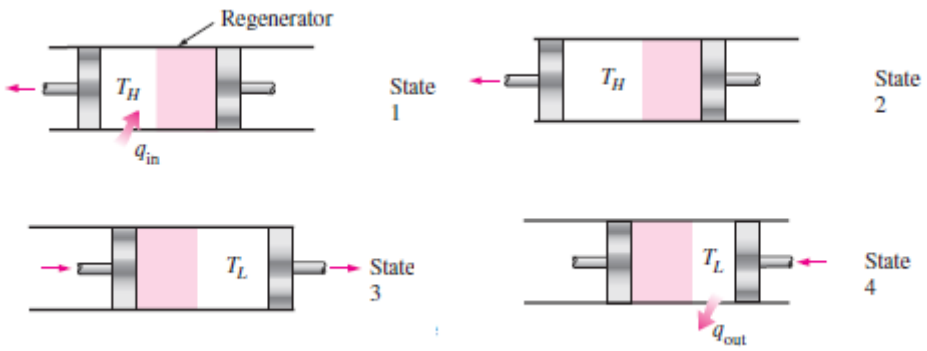


Fig.32. *The execution of the Stirling cycle.*

Initially, the left chamber houses the entire working fluid (a gas), which is at a high temperature and pressure. During process 1-2, heat is transferred to the gas at *TH* from a source at *TH*. As the gas expands isothermally, the left piston moves outward, doing work, and the gas pressure drops. During process 2-3, both pistons are moved to the right at the

same rate (to keep the volume constant) until the entire gas is forced into the right chamber. As the gas passes through the regenerator, heat is transferred to the regenerator and the gas temperature drops from *TH* to *TL*. For this heat transfer process to be reversible, the temperature difference between the gas and the regenerator should not exceed a differential amount *dT* at any point. Thus, the temperature of the regenerator will be *TH* at the left end and *TL* at the right end of the regenerator when state 3 is reached. During process 3-4, the right piston is moved inward, compressing the gas. Heat is transferred from the gas to a sink at temperature *TL* so that the gas temperature remains constant at *TL* while the pressure rises. Finally, during process 4-1, both pistons are moved to the left at the same rate (to keep the volume constant), forcing the entire gas into the left chamber. The gas temperature rises from *TL* to *TH* as it passes through the regenerator and picks up the thermal energy stored there during process 2-3. This completes the cycle.

Steady-flow system operating on an Ericsson cycle is shown in Fig. 9–28. Here the isothermal expansion and compression processes are executed in a compressor and a turbine, respectively, and a counter-flow heat exchanger serves as a regenerator. Hot and cold fluid streams enter the heat exchanger from opposite ends, and heat transfer takes place between the two streams. In the ideal case, the temperature difference between the two fluid streams does not exceed a differential amount at any point, and the cold fluid stream leaves the heat exchanger at the inlet temperature of the hot stream.

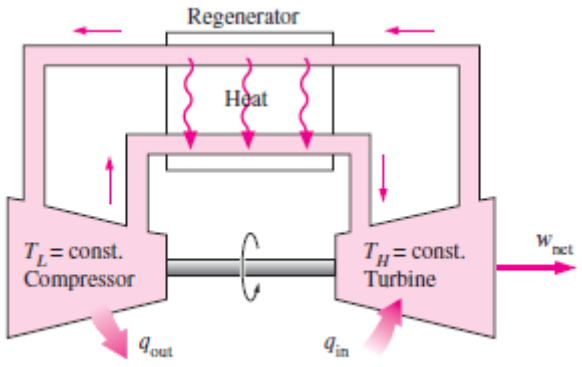


Fig.33. A steady-flow Ericsson engine.

Both the Stirling and Ericsson cycles are totally reversible, as is the Carnot cycle, and thus according to the Carnot principle, all three cycles must have the same thermal efficiency when operating between the same temperature limits:

$$\eta \text{ Stirling} = \eta \text{ Ericsson} = \eta \text{ Carnot} = 1 + \frac{Q2}{Q1} = 1 - \frac{Tc}{TH}$$

VII.9 Brayton cycle: the ideal cycle for gas-turbine engines

Fig.34. *George Brayton 1830 - 1892*

The Brayton cycle was first proposed by George Brayton for use in the reciprocating oil-burning engine that he developed around 1870. Today, it is used for gas turbines only where both the compression and expansion processes take place in rotating machinery. Gas turbines usually operate on an *open cycl.,* Fresh air at ambient conditions is drawn into the compressor, where its temperature and pressure are raised. The high pressure air proceeds into the combustion chamber, where the fuel is burned at constant pressure. The resulting high-temperature gases then enter the turbine, where they expand to the atmospheric pressure while producing power. The exhaust gases leaving the turbine are thrown out (not recirculated), causing the cycle to be classified as an open cycle. The open gas-turbine cycle described above can be modeled as a *closed cycle,* as shown in Fig. 9–30, by utilizing the air-standard assumptions. Here the compression and expansion processes remain the same, but the

combustion process is replaced by a constant-pressure heat-addition process from an external source, and the exhaust process is replaced by a constantpressure heat-rejection process to the ambient air. The ideal cycle that the working fluid undergoes in this closed loop is the **Brayton cycle,** which is made up of four internally reversible processes:

1-2 Isentropic compression (in a compressor)

2-3 Constant-pressure heat addition

3-4 Isentropic expansion (in a turbine)

4-1 Constant-pressure heat rejection

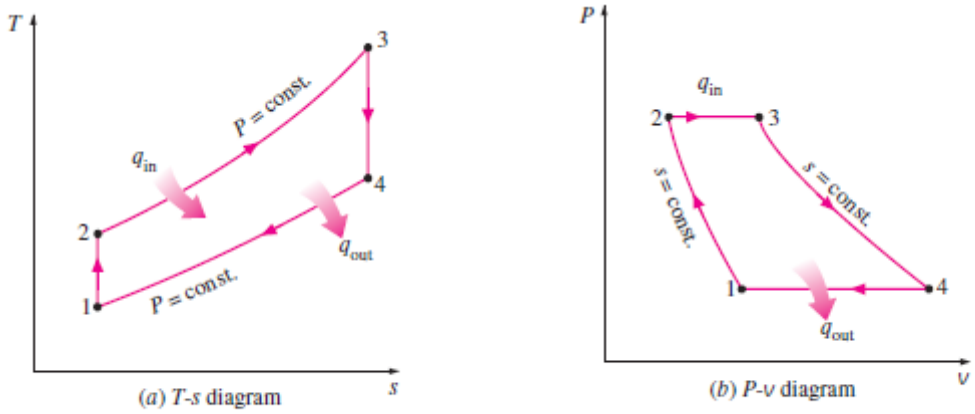


Fig.35. *T-s and P-v diagrams for the ideal Brayton cycle.*

VII.10 The Robert Stirling Engine

Fig.36. *Robert Stirling 1790 - 1878*

At the beginning of the 19th century, frequent steam boiler explosions prompted Robert Stirling to design a high-pressure boilerless engine in 1816. This hot-air engine operated using an external heat source, such as combustion, and was distinguished by the addition of a regenerator. This device, located in the piping, recovered some of the heat to improve energy efficiency.

His brother James attempted to apply it to industry in 1843, but the engine suffered from modest performance compared to the steam engine or the combustion engine. It then fell into oblivion, remaining only a subject of theoretical study until the development of thermodynamics, which allowed Gustav Schmidt to model his cycle in 1871.

Subsequently, John Ericsson designed an engine based on this cycle, which was mass-produced in the United States until around 1914. In 1889, the Rider-Ericsson company marketed hot-air hydraulic pumps that were exported internationally.

In the 1930s, the Philips company resumed research on the Stirling engine. In 1938, it developed a high-performance engine with over 200 horsepower. In 1953, it designed a 180 W generator based on this principle. Despite these advances, its use remained limited, especially in applications such as cryogenics.

It is only in recent decades, with the rise of environmental concerns, that the Stirling engine has attracted renewed interest. It can operate with any heat source: solar, geothermal, nuclear, or even industrial waste heat. Thanks to modern materials capable of withstanding large temperature differences, its efficiency is now much higher.

A notable example: Stirling engines coupled with solar concentrators achieved a solar conversion efficiency of 31.25% in 2008, surpassing that of photovoltaic panels, although their cost remains high.

How the Stirling Engine Works

The Stirling engine is based on a four-phase thermodynamic cycle:

Isochoric heating: the gas is heated to a constant volume;

Isothermal expansion: the gas expands, producing work;

Isochoric cooling: the gas is cooled without changing volume;

Isothermal compression: the gas is compressed while receiving work.

The gas (often air, helium, or hydrogen) circulates between two chambers: one heated, the other cooled. The alternating heating and cooling causes piston movements, converting thermal energy into mechanical energy. The regenerator, by preheating or precooling the gas, further improves the system's efficiency.

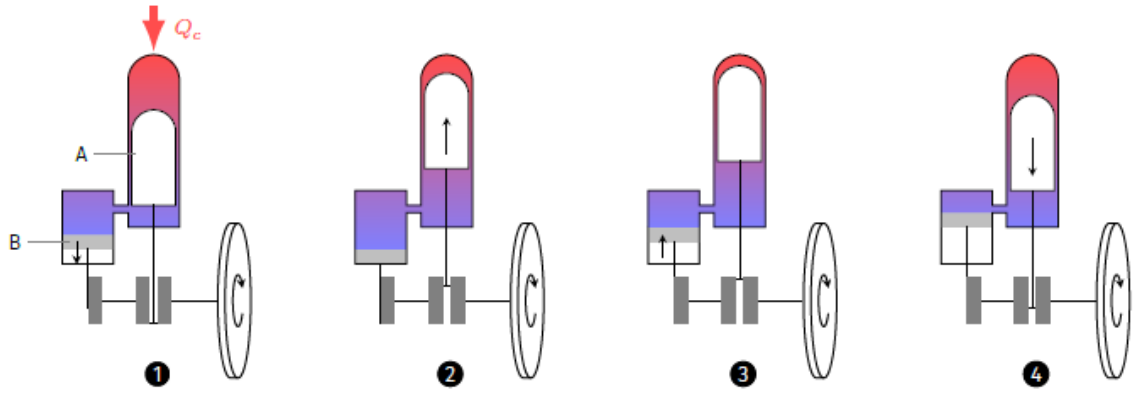


Fig.37. *The different phases of the Stirling cycle (A: delivery piston, B: engine piston).*

▸ The driving piston (MP) drives a flywheel, which is connected via a belt to an electric generator, converting mechanical energy into electrical energy.

▸ The discharge piston (DP) simply moves the air by bringing it into contact with the heat source or moving it away from it.

The air undergoes a cycle that can be broken down into four phases:

1. DP at the bottom. The air is heated by the heat source, causing it to expand, which pushes the driving piston downward. Thus, hot air enters the cold compartment. This air expansion occurs at a virtually constant temperature.
2. DP at the bottom. The movement of the wheel drives the discharge piston upward. Here, the volume does not change, but as the hot air is displaced downward, there is cooling.
3. DP at the top. The driving piston rises, aided by the drop in pressure. The air undergoes quasi-isothermal compression.
4. PM above. The discharge piston descends, bringing cold air into the compartment heated by the heat source. The pressure increases isochorically.

This cycle is called regenerative because a regenerator stores heat as the hot gas passes through the cold compartment (phase 2), then restores it to the cold gas during phase 4. This invention is due to Robert Stirling and makes his engine efficient.

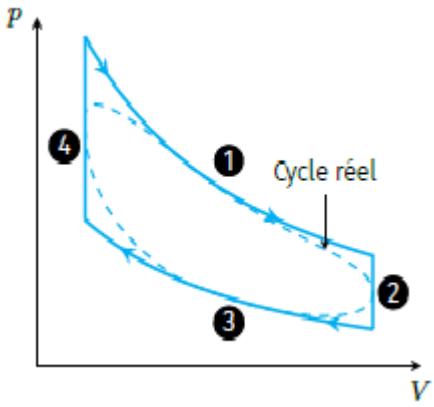


Fig.38. *Robert*: Stirling cycle described in the Watt diagram (solid line the idealized cycle, dotted line the real cycle).

Calculating Efficiency

Let's calculate the engine's efficiency based on the idealized cycle described above and treating air as a perfect gas with an adiabatic exponent γ = 1.4. We'll assume the cycle is described in a quasi-static manner.

First, let's ignore the role played by the regenerator. By definition, the efficiency is written as

$$\eta = \frac{Wnet}{Qin} = \frac{-Wnet}{Q1+Q4}$$

VII.11 Steam Engine Cycles

Steam engines are used in static applications. Many modifications have been made to ideal cycles to reduce cost and increase machine power.

VII.11.1 Exemple:

A steam locomotive is a type of locomotive; it is a railway motive power unit powered by a steam engine. This type of internal combustion engine was the most commonly used, from the dawn of railways until the 1950s. It is still used very locally in some countries in the 21st century, particularly for tourist trains or in the mining industry.

Nowadays, however, most trains are hauled by electric or internal combustion (diesel) locomotives, or consist of multiple units or railcars, sometimes indivisible, with the power distributed under the vehicles and/or inside the bodies.

Fig.39. *Robert steam locomotive*

VII.11.2 Why use a steam engine?

Using water as the working fluid in a heat engine has several notable drawbacks. Unlike internal combustion engines, a system must be provided to cool and recycle the water used, or a constant supply of pure water must be available. Furthermore, some of the heat supplied to the engine is inevitably lost, particularly in the boiler.

So why continue to be interested in steam engines? The main reason is that some heat sources cannot be directly used inside a heat engine. For example, the combustion of coal, wood, or organic waste generates solid residues that cannot circulate through a turbine. Similarly, nuclear reactions cannot take place directly in an airflow. Harnessing these energy sources—which represent a significant portion of global energy production—requires capturing heat outside the engine.

Liquids, particularly water, are highly effective for this type of heat transfer, thanks to their high volumetric heat capacity, much greater than that of air (about a thousand times greater for water). Among the available fluids, water stands out for its abundance and ease of handling.

This is why the majority of engines designed to operate with an external heat source use water as the heat transfer fluid. Since these sources are difficult to exploit in mobile applications, these engines are generally integrated into stationary power generation facilities. This configuration optimizes the costs associated with energy storage and transmission.

Thus, steam power plants reach power outputs of several gigawatts (1 GW = 10^9 W), making them the most powerful thermal systems in the world.

VII.11.3 Engine Evaluation Criteria

Several parameters are taken into account when evaluating the performance and value of steam engines.

VII.11.4 Thermal Efficiency and Overall Efficiency.

The parameter we have learned to quantify so far is, of course, the engine's thermal efficiency. $\eta = \frac{Wnet}{Qin}$ which we always seek to make tend towards its theoretical maximum, $\eta = 1 - \frac{Tmin}{Tmax}$.

VII.11.5 Environmental Impact of Thermodynamic Engines

The heat production required to operate thermodynamic engines raises significant environmental issues. Three main categories of impact can be distinguished:

• Air pollution: The combustion of solid fuels (coal, agricultural or household waste) releases toxic particles. However, the use of filtration systems can significantly limit these emissions.

• Greenhouse gases: Carbon dioxide (CO2), an unavoidable product of hydrocarbon combustion, contributes significantly to global climate change.

• Radioactive waste: Produced by nuclear processes, this waste is small in volume but remains hazardous over very long periods of time

Aside from a few limited alternatives such as geothermal or concentrated solar power, available heat sources all have significant limitations. Despite this, thermodynamic engines remain essential for the production of mechanical and electrical energy, the foundation of our economic and social progress. It is therefore up to engineers and society to evaluate these technologies wisely.

VII.11.6 Steam Engine Cycles

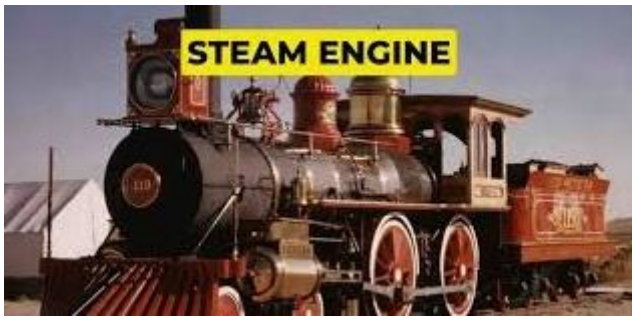


Fig.40.*Steam engine*

VII.12 The Carnot Cycle

Fig.41. *Nicolas Léonard Sadi Carnot* ***1796- 1832***

Since the Carnot cycle we have studied serves as a reference in engine design, we begin our study with it. The temperature of a liquid-vapor mixture remains constant when heated at constant pressure, so achieving isothermal heat transfer (an important characteristic of the Carnot cycle) is relatively easy with steam. A steam engine based on a Carnot cycle is shown schematically in Figures .

The efficiency of the Carnot engine cycle is only achieved when the turbine and compressor operate isentropically. In practice, as we have seen, the turbine power is always lower and the compressor power is always higher than they could be.

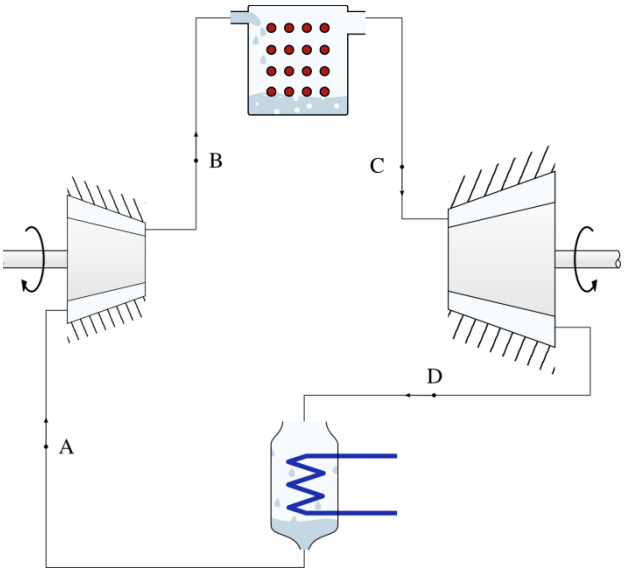


Fig.42. – *Circuit of a steam power station operating on a Carnot cycle.*

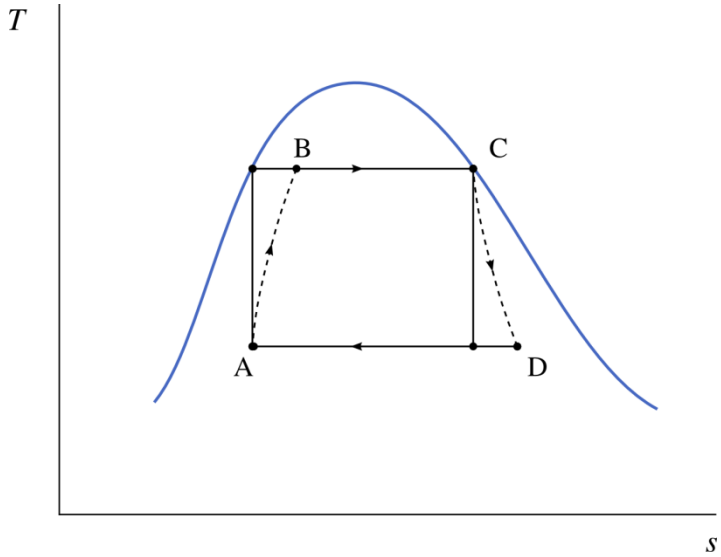


Fig.43. *Temperature-entropy diagram of a steam power plant operating on a Carnot cycle.*

The dotted lines represent the actual (irreversible) changes in the W during compression and expansion.

VII.13 The Rankine Cycle

The Rankine cycle is an endoreversible thermodynamic cycle that includes two isobars and two adiabatics.

It is the cycle that most closely resembles the Carnot cycle. It differs from the latter by substituting two isobaric transformations for the two isothermal transformations, which makes its technical implementation possible.

Fig.44. *William John Macquorn Rankine, 1820 - 1872*

In industrial realities, the direct application of the Carnot cycle faces several obstacles:

– Compressing a mixed-phase fluid (liquid/vapor) represents a major technical challenge.

– It is also complex to precisely stop condensation in a condenser, particularly at point i, where the vapor is not completely condensed.

To overcome these difficulties, the British engineer William Rankine introduced a variant of the thermal cycle in 1859. This modified version consists of allowing the vapor to condense completely, until it reaches a saturated liquid, then compressing only the liquid. The operation of this cycle is illustrated in the figures Thus, unlike the Carnot cycle, the Rankine cycle uses a hydraulic pump to compress the fluid to the liquid state, which has several advantages. On the one hand, a pump is easier to design, manufacture and use than a compressor intended for liquid/vapor mixture. On the other hand, compressing a liquid requires much less energy than compressing a two-phase mixture,

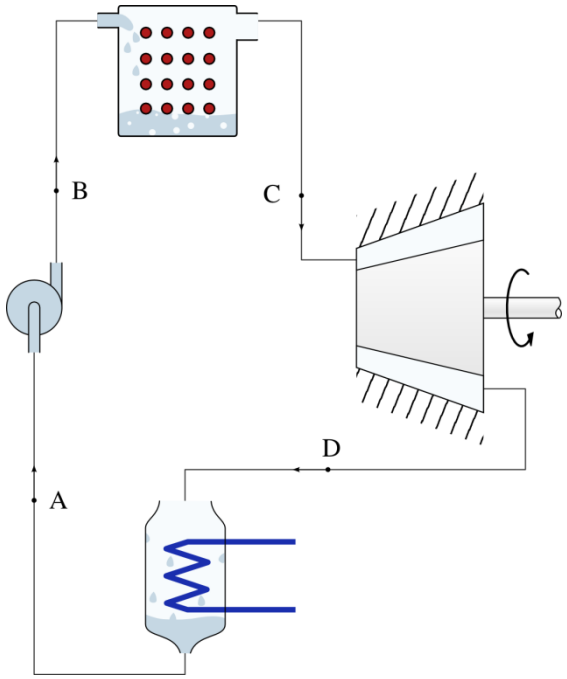


Fig.45. *Circuit of a steam power plant operating on a Rankine cycle.*

The water leaving the condenser is in the form of a saturated liquid; it enters the boiler at a lower temperature..

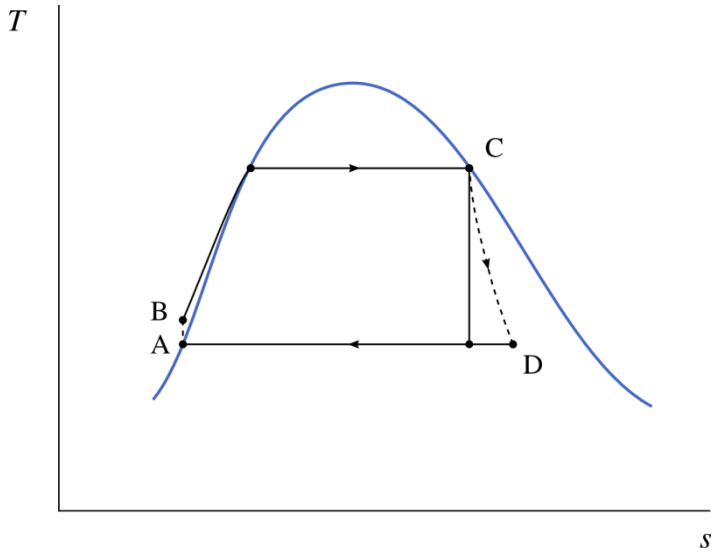


Fig.46. *Temperature-entropy diagram of a steam power plant operating on a Rankine cycle*.

Although this configuration allows for energy savings, it results in a significant drop in the water temperature at the pump outlet compared to that at the compressor outlet. The boiler must then provide more heat to return the water to a saturated liquid state, which implies

additional energy costs. Much of this heat is no longer supplied at the maximum temperature of the cycle, reducing overall efficiency, as explained above.

However, this disadvantage has a practical advantage: it becomes possible to exploit low-temperature heat sources, such as exhaust gases. This can, in some cases, offset the reduced thermodynamic efficiency of the engine by improving the boiler's efficiency, which better utilizes the fuel's energy.

By deliberately moving away from the Carnot cycle, Rankine accepted a lower thermodynamic efficiency, but simplified the installation by removing the compressor, which lightened the overall system.

Dithermal Receiver

The equations are the same as for a dithermal engine, except that W > 0 is assumed. There are two types of receiver:

▶ the refrigeration machine, whose role is to cool a cold source (Qc > 0);

▶ the heat pump, whose role is to heat a hot source (QH < 0).

Dithermal Refrigeration Machine – The fluid exchanges heat with

a cold source (the room to be refrigerated) and a hot source (the outside).

The energy and entropy balance gives

$$Q_c + Q_H = -W < 0 \text{ et } \frac{Qc}{Tc} + \frac{QH}{TH} \leq 0$$

By definition, Qc > 0 (the cold source gives energy to the fluid).

Therefore, QH < 0: the fluid gives off thermal energy to the outside.

The efficiency of a refrigeration machine is defined by $\eta = \frac{Qc}{w}$

VII.14 Study of a Refrigeration Machine

Changes of state are used in refrigeration machines and heat pumps. The use of a liquid/gas mixture is particularly interesting since evaporation or liquefaction can occur at a constant temperature, allowing for efficiencies close to maximum.

Here, we detail the simplified cycle of a refrigeration machine.

VII.14.1 Principle

A fluid (ammonia, isobutane, freons, etc.) undergoes a cycle during which it changes state. During vaporization in the evaporator, the fluid absorbs thermal energy from the room to be refrigerated, which keeps it cold. Let's describe the thermodynamic cycle described by the fluid

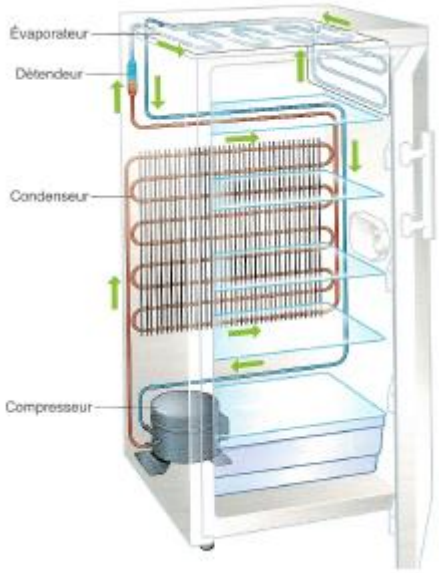


Fig.47. *: Diagram of a refrigerator.*

AB transformation: the fluid in the dry vapor state passes through a compressor, which increases the fluid pressure. This compression can be likened to a reversible adiabatic compression, as a first approximation. The temperature therefore increases.

▸ BC transformation: the dry vapor passes through the condenser and releases heat to the outside by liquefying (QBC). Assume that C is on the saturation curve (boiling point curve).

▸ CD transformation: the liquid passes through an expansion valve. This expansion is likened to a Joule-Thomson expansion, which conserves enthalpy. This expansion produces partial vaporization and cooling.

▸ DA transformation: finally, the liquid/vapor mixture is enriched with vapor in the evaporator until it reaches the dry vapor state, which absorbs the amount of thermal energy QDA. The cycle then repeats.

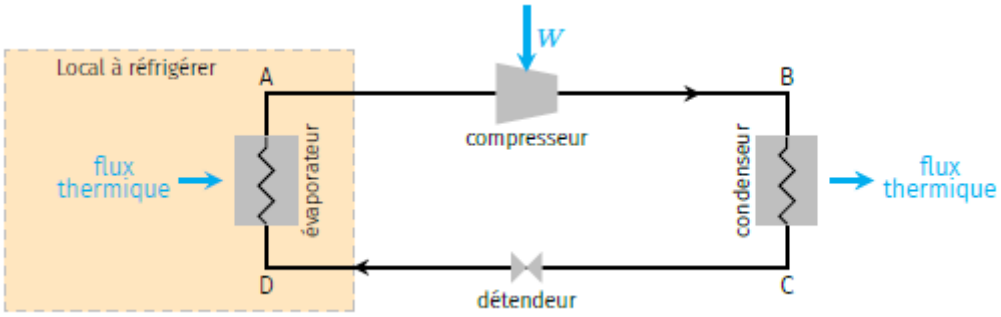


Fig.48. *Principle of a refrigerating machine.*

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