UNIVERSITE
Abdelhamid Ibn Badis
MOSTAGANEM

THERMODYNAMICS HANDOUT
KEY CONCEPTS AND SOLVED EXERCISES
PRESENTED BY: DR. BESBES ANISSA

Carnot efficiency
$$\frac{T_H - T_C}{T_H} \times 100\%$$
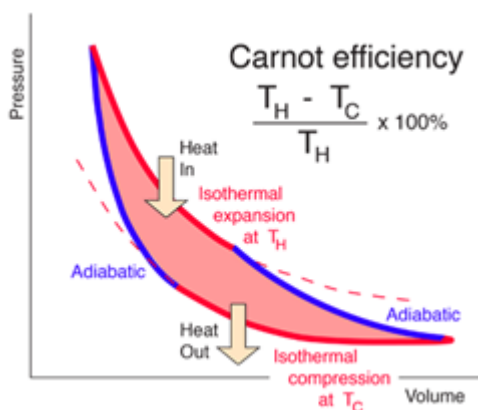
$$\Delta G = \Delta H - T\Delta S$$

$$PV = nRT$$

$$\Delta S_T^\circ = \int_{T_1}^{T} \frac{C_P}{T} dT$$

$$dU = \delta Q - \delta W$$

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Thermodynamics is an essential discipline of physics that studies energy exchanges in the form of heat and work, as well as the laws governing these transformations. It plays a fundamental role in several fields, such as mechanics, chemistry, and engineering, by providing indispensable tools for understanding and modeling the energy processes crucial to these sectors.

The present handout is primarily intended for students in the early years of scientific and technological studies. It briefly brings together all the key elements of thermodynamics.

The content of this handout is structured into seven chapters, each addressing the fundamental concepts of thermodynamics in a detailed and rigorous manner. Each concept is presented with remarkable clarity, thus facilitating the understanding of key principles. To help students thoroughly grasp the topics covered, each chapter is accompanied by a series of solved exercises. These practical applications allow the theoretical concepts to be put into practice, offering a progressive and effective educational approach to understanding the basics of thermodynamics.

This book, which is the result of a subject taught since 2005, has been designed with the aim of making the concepts of thermodynamics accessible to everyone.

Dr A.BESBES

CHAPTER I

GENERAL PRINCIPLES OF THERMODYNAMICS

I.1 Introduction

The term **"thermodynamics"** comes from Greek and consists of two elements: **"thermo,"** meaning heat, and **"dynamics,"** referring to work or movement. This implies movement generated by heat. Thermodynamics developed as a science in the 18th century, following the invention of the steam engine, which led to an in-depth exploration of the relationships between thermal and mechanical phenomena, hence its name.

Thermodynamics can be approached in two ways :

- **Classical thermodynamics :** is a macroscopic approach that relies on measuring a limited number of quantities (pressure, temperature, volume, ...) characterizing the system under study, which is composed of a very large number of particles (atoms or molecules, approximately 6.0225×10^{23}). This approach focuses solely on the initial and final states of evolving systems, providing an energy balance of the system taking into account the path followed, without attempting to understand the mechanisms of the transformation.

- **Statistical thermodynamics:** is based on a microscopic description of matter and phenomena. It takes into account the constituents of matter, such as atoms, molecules, ions, and electrons, as well as the fundamental laws of mechanics that govern the motion of these particles.

Thermodynamics is a branch of physics that examines the thermal behavior of bodies, specifically the movement of heat. Its goal is to analyze the different forms of energy and the possibilities for conversion between them. It also enables the description of system behavior using concepts such as temperature (T), energy (heat Q, work W.), and entropy (S).

I.2 Definitions of thermodynamic systems and the external environment

The system is defined as a portion of matter (of a specific mass) separated from the external environment by a boundary, whether real or imaginary **(Fig I.1),** allowing for exchanges of energy and matter with this environment.

The entirety of **the system** and the **external environment** (the rest of the space surrounding the system) constitutes **the universe.**

There are three types of thermodynamic systems :

- ✓ Open system can exchange energy and matter with the external environment.
  Example**:** Car engine, thermal machine.

- ✓ Closed system can exchange energy but not matter with the external environment.
  Example**:** The cooling circuit of a refrigerator.

- ✓ Isolated system can't exchange either energy or matter with the external

External environment

Universe

System

(S)

Energy and/or matter

Wall separating the system from the external environment
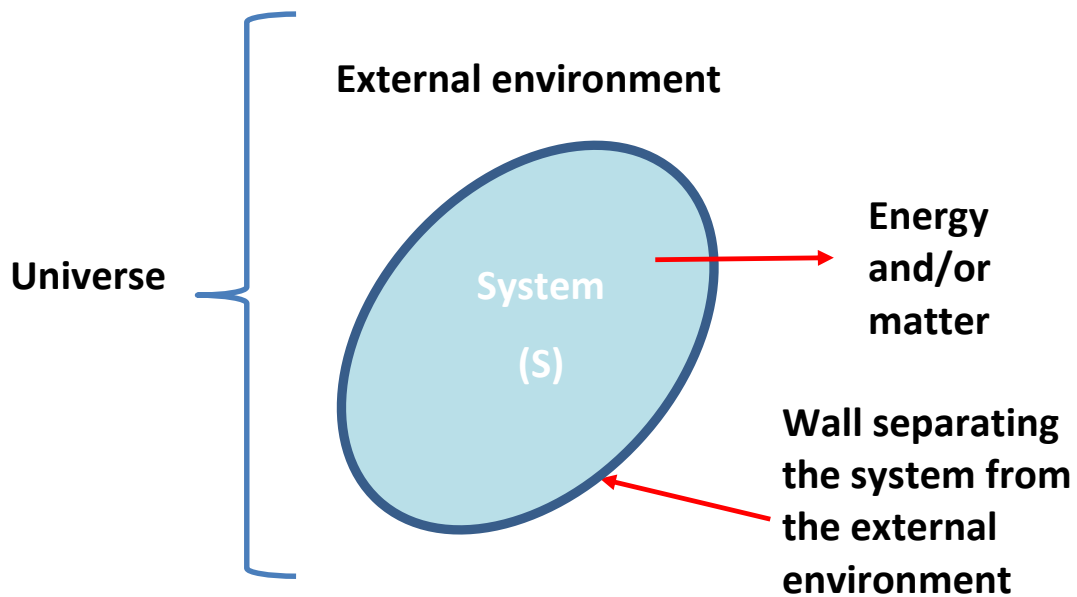
Figure I.1: *Delimitation of the system*

I.3 Description of thermodynamic system

I.3.1 State of thermodynamic system

A thermodynamic system can be characterized by macroscopic quantities known as state variables (mass, volume, pressure, temperature, number of moles, ...), which can be measured directly or indirectly.

I.3.2 State variables

The variables that determine the state of a system are divided into two types :

✓ Intensive variables: are non additive properties and don't depend on the mass or the amount of matter in a system.

   Example**:** Temperature, pressure, mole fraction and mass volume. With the exception of temperature, these variables are generally denoted with lowercase letters.

✓ Extensive variables**:** are additive properties that are proportional to the amount of matter.

   Example: mass, volume, number of moles….

Note: It can be observed that the ratio of two extensive variables is an intensive variable.

Example:

$$\rho = \frac{mass}{Volume} \qquad\qquad C_M = \frac{number\ of\ mole}{Volume}$$

I.3.3 State functions

State functions characterize the system and allow for predicting its evolution from the initial state to the final state. They are independent of the path taken during a transformation and

are expressed in terms of state variables. It is therefore noted that $\Delta F = F_1 - F_2$, regardless of the path taken.

Example: Internal energy **U**, enthalpy **H**, entropy **S** and free enthalpy G.

Work and heat Q aren't state function.

I.3.3.1 State equation for ideal gases

➢ Definition of an ideal gas**:** is defined as a collection of molecules don't interact with each other, except during collisions, and whose volume is negligible compared to the volume occupied by the gas. It never liquefies due to the absence of interaction forces between the particles. The state variables aren't all independent; they are related by equations of state, which allow for a complete description of a system without needing to know all the variables. For example, the state equation for an ideal gas is:

$$PV = nRT \qquad\qquad I.1$$

Where:

P : Gas pressure.

V : Gas volume.

n : Mole number of gas.

R : Ideal pas constant.

T : Gas temperature.

In this equation, known as the state equation for ideal gases, each state variable (pressure, volume, or temperature) depends on the other two variables:

$P = \dfrac{nRT}{V}$	$V = \dfrac{nRT}{P}$	$T = \dfrac{PV}{nR}$	$R = \dfrac{PV}{nT}$	$m = \dfrac{MPV}{RT}$	$\rho = \dfrac{MP}{RT}$

Application I.1

For one mole of a gas under normal condition (P= 1atm, T= 0°C, V=22.4 L), calculate the ideal gas constant R in the following units:

L. atm. mol^{-1}.K^{-1}, J .mol^{-1}.K^{-1}, l.Torr. mole^{-1}.K^{-1} , cal .mol^{-1}.K^{-1}

Solution The value of the ideal gas constant (R) under standard conditions (STP) :

$$PV = nRT \Rightarrow R = \frac{PV}{nT}$$

- **l.atm.mol^{-1}.K^{-1}**   R = (1.22,4) / (1.273) = **0,082 l.atm.mol^{-1}.K^{-1}**

- **J. mol^{-1}.K^{-1}**   1atm=1.013 10^5 Pa and 1L=10^{-3} m^3

                         R = (1,013.10^5.22,4.10^{-3}) / (1.273) = **8,31 J. mol^{-1}.K^{-1}**

- **cal.mol^{-1}.K^{-1}**   1 cal=4.185 J

                         R = 8,31 / 4,185 = 1,98   **R≈2 cal. mol^{-1}.K^{-1}**

- **l.torr.mol^{-1}.K^{-1}**   **760 torr= 1atm**

                 R = 0,082×760 **= 62.32 l.torr.mol^{-1}.K^{-1}**

I.3.3.2 State equation for real gases (Vander Waals, Berthelot)

➤ Definition of real gas**:** A real gas differs from an ideal gas in that its molecules occupy a volume and interact through van der Waals forces. By definition, any gas found in nature or synthesized is considered a real gas.

The Van der Waals model takes into account the repulsive interactions between particles at very short distances, as well as the attractive interactions between particles at greater distances. The equation of state for 'n' moles of gas is then expressed in the following form:

$$(P + \frac{a}{V^2})(V - b) = RT \qquad\qquad I.2$$

With:

a : Cohesion term (constant).

b : Molar covolume (constant).

n : Number of moles

P : Pressure.

R : Ideal gas constant.

T : Temperature.

V : Volume.

I.4 Evolution and thermodynamic equilibrium states of a system

I.4.1 Mechanical equilibrium state

Under the influence of energy exchanges or transfers between the system and its environment, the system evolves, and its state variables are modified. This process is referred to as transformation or change of state, transitioning from an initial state (which describes the system before the transformation) to a final state (which describes the system after the transformation). During this process, the system passes through an infinite number of intermediate states, forming the path followed. The initial and final states are generally equilibrium states, where the system's variables remain constant. A system is in thermodynamic equilibrium when it is simultaneously in thermal, mechanical, and chemical equilibrium.

✓ Mechanical equilibrium is achieved in the presence of a movable or deformable wall, with equal pressures inside and at the outer surface of the system.

✓ Thermal equilibrium is achieved when a body at a higher temperature transfers thermal energy to a body at a lower temperature.

✓ Chemical equilibrium results from two simultaneous chemical reactions whose effects cancel each other out.

<u>Example</u>: The combustion reaction of propane with oxygen stops when one of the reactants is completely exhausted; it is described as a total, complete, or irreversible reaction.

I.5 <u>Possible transfers between the system and the external environment</u>

The system can exchange energy and/or matter with the external environment, and three cases can be distinguished:

✓ <u>Closed system</u>: there is no transfer of matter with the external environment. Only energy exchanges are possible.

✓ <u>Open system</u>: there are possible transfers of matter and energy with the external environment.

✓ <u>Isolated system</u>: there is no transfer (neither matter nor energy) possible with the external environment.

a) <u>Transfers or exchanges of energy (work, heat)</u>

Energy transfer refers to the movement of energy from one environment to another while maintaining its form. During this exchange with the external environment, the system either gives or receives energy.

b) <u>Transfers or exchanges of matter</u>

The matter transfer occurs from the system to the external environment (case of an open system).

I.6 <u>Transformations of a system's state</u>

I.6.1 <u>Ideal gas transformations</u>

It is the evolution of the gas from an initial state to a final state in response to a change in the external constraints applied to it.

$$P_1, V_1, T_1 \xrightarrow{\text{Transformation}} P_2, V_2, T_2$$

Different types of transformations are recognized based on the evolution of state parameters, such as temperature, pressure, volume, and exchanged heat.

a) <u>Isochoric transformations of an ideal gas</u> is a thermodynamic process that occurs at constant volume $\left(\frac{T}{P} = constant\right)$

b) <u>Isobaric transformations of an ideal gas</u> is a thermodynamic process that occurs at constant pressure $\left(\frac{T}{V} = constant\right)$

c) <u>Isothermal transformations of an ideal gas</u> is a thermodynamic process that occurs at constant temperature $(\mathrm{PV=Cte})$

d) <u>Adiabatic transformations of an ideal gas</u> is a thermodynamic process that occurs without the exchange of heat with the external environment.

e) Open, closed, or cyclic transformations: An **open transformation** refers to a series of transformations of a system where the final state is different from the initial state. A **closed or cyclic transformation** is one in which, at the end of the process, the system returns to its initial state.

f) Monothermal transformations are a thermodynamic process in which the initial temperature is equal to the final temperature.

g) Infinitesimal transformations are those in which the initial and final states are extremely close to each other. In contrast, a transformation that isn't infinitesimal is referred to as a finite transformation.

h) Quasi-static transformations are thermodynamic processes in which all the intermediate states of the system are well-defined and close to equilibrium states. For a transformation to be considered quasi-static, it must occur very slowly, so that it can be viewed as a succession of equilibrium states.

i) Reversible and irreversible transformations: **A transformation is reversible** if it occurs slowly, following a continuous series of mechanical or thermal equilibrium states at each stage of the thermodynamic system's evolution. The direction of this transformation can be reversed at any time by an infinitesimal change in a variable. **A transformation is irreversible** if the transition of the system from the initial state to the final state occurs in one or more steps, without the possibility of returning to the initial state. It is a spontaneous transformation that can't be stopped or reversed.

I.6.2 Physical transformations

A physical transformation (melting, solidification, vaporization, liquefaction, sublimation) occurs when a substance changes its physical state depending on the temperature and pressure to which it is subjected **(see figure I.2).** These state changes often happen during heat exchanges with the environment, referred to as **latent heat of transformation (L).**

Figure I.2 *Diagram of changes in state of matter*

I.6.3 Chemical transformations or chemical reactions

A chemical transformation occurs when one or more substances, called **reactants,** interact to create one or more new substances, referred to as **products**. Unlike physical transformations, a chemical reaction alters the nature of the substances involved, so the reactants don't have the same properties as the products formed. A chemical transformation is represented by a **chemical equation.**

Example

    Combustion reaction: $CH_4 + O_2 \rightarrow CO_2 + 2H_2O$

    Synthesis reaction : $C_2H_4 + H_2 \rightarrow C_2H_6$

Esterification reaction :
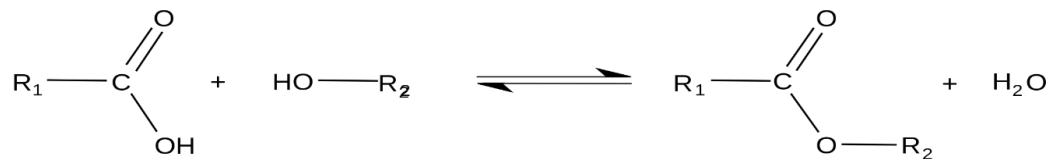
Explosion reaction: is characterized by a rapid oxidation or decomposition reaction, resulting in an increase in temperature, pressure, or both simultaneously.

Corrosion reaction : The corrosion of a metal refers to the gradual deterioration of the material due to a chemical and/or electrochemical reaction with its environment. It is a natural process that converts the metal into a stable chemical form.

I.6.4 Graphical representation of ideal gas transformations

To analyze the transformations of a gas, we use the parameters P, V, and T, which are related by the state equation **f (P,V,T) = 0**. Two of these parameters are sufficient to study the system and represent it on a diagram.

a) Clapeyron diagram

It is the equation representing the transformation curve in the P(V) plane. **P =f (V) => P = constant / V (figure I.3)**.
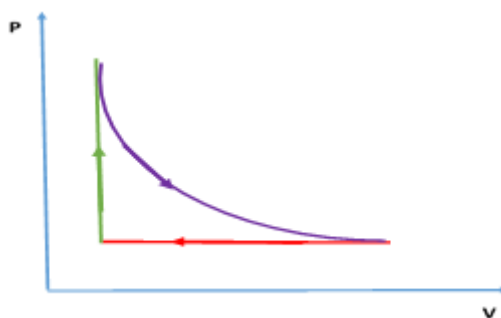
Figure I.-3*: Clapeyron diagram*

b) Amagat diagram

It is the equation of the transformation curve in the PV (V) plane or **PV =f (V) (figure I.4).**
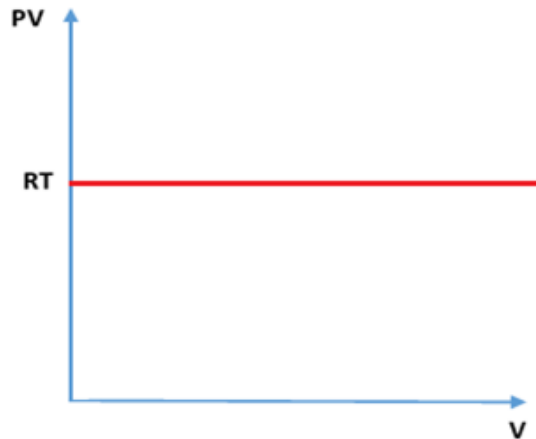
Figure I.4 *Amagat diagram*

I.7 Reminder of the ideal gases laws

A gas is referred to as ideal if it adheres to a certain number of laws, namely:

a) Boyle-Marriott law: For a certain number of moles **n** of ideal gas at constant temperature, the product **PV** is constant

$$\begin{cases} P_1 V_1 = nRT_1 \\ P_2 V_2 = nRT_2 \end{cases}$$

$$For \ \ T = C^{ste} \ \ \rightarrow \ \ \ P_1 V_1 = P_2 V_2 \qquad\qquad\qquad I.3$$

Application I.2 A cylinder with a movable piston contains 10 liters of hydrogen at a pressure of 1 atm. By moving the piston, the gas occupies a volume of 2 liters at the same temperature. What is the pressure in the cylinder?

Solution

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{V_1}{V_2} P_1 = \frac{10}{2} \times 1 = 5 \ atm$$

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b) Gay-Lussac law**:** for a certain number of moles nnn of ideal gas at constant volume, the ratio **T/P** is constant.

$$\begin{cases} P_1 V_1 = nRT_1 \\ P_2 V_2 = nRT_2 \end{cases}$$

$$For \ \ V = C^{ste} \ \ \rightarrow \ \ \frac{T_1}{P_1} = \frac{T_2}{P_2} \qquad\qquad\qquad I.4$$

Application I.3 In a 30 liter container, a gas is at a pressure of 346 mmHg and at a temperature of 23.7 °C. If the temperature increases to 107.5 °C, what will the pressure be in kPa in the container ?"

Solution

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{346}{296} = \frac{P_2}{380}$$

$$P_2 = 444.18 \; mmHg$$

Let 760 mmHg= 101.3 kPa

So

$$P_2 = \frac{444.18 \times 101.3}{760} = \mathbf{59.20 \; kPa}$$

c) <u>Charles law:</u> for a certain number of moles n of ideal gas at constant pressure, the ratio V/T remains constant.

$$\begin{cases} P_1 V_1 = nRT_1 \\ P_2 V_2 = nRT_2 \end{cases}$$

$$\boldsymbol{For \;\; P = C^{ste}} \;\; \rightarrow \;\; \boldsymbol{\frac{V_1}{T_1} = \frac{V_2}{T_2}} \qquad\qquad \textbf{I.5}$$

Application I.4 A quantity of chlorine occupies a volume of 38 cm³ at a temperature of 20°C. Calculate its volume at 45 °C, while keeping the pressure constant.

Solution

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{T_2}{T_1} \times V_1 = \frac{318}{293} \times 38 = \mathbf{41.2 \; cm^3}.$$

d) <u>Dalton law</u>

For a mixture of chemically inert gases (which don't react with each other) occupying a volume V, each gas occupies this volume as if it was alone, under a pressure **P$_i$,** referred to as the partial pressure. The total pressure of the mixture is equal to the sum of the partial pressures of the gases that make it up.

$$P_i V = n_i RT$$

$$P_{tot} V = n_{tot} RT \rightarrow \frac{P_{tot}}{n_{tot}} = \frac{RT}{V}$$

$$P_i = n_i \frac{RT}{V} = \frac{n_i}{n_{tot}} P_{tot}$$

$$P_i = x_i P_{tot} \qquad\qquad\qquad\qquad\qquad\qquad\qquad I.6$$

$$P_{tot} = \sum P_i \qquad\qquad\qquad\qquad\qquad\qquad\qquad I.7$$

Application I.5 A balloon contains a mixture of 36 g of carbon dioxide (CO_2) and 6 moles of nitrogen (N_2). The total pressure of the system is 253 kPa. What is the partial pressure of each gas?

Solution

n $(CO_2)=(CO_2)/M(CO_2) =36 /44=0.82\ mole$ and $n(N_2)= 6\ moles$

$n_{(tot)}=0.82+6=6.82\ moles$ $\qquad$ $P_{(tot)}=253\ Kpa$

Calculation of the partial pressure of CO_2 :

$$P_{CO2} = x_{co2} \times P_{tot} = \frac{n_{Co2}}{n_{tot}} \times P_{tot} = \frac{0.82}{6.82} \times 253 = \mathbf{30.4\ Kpa}$$

Calculation of the partial pressure of N_2 :

$$P_{N2} = x_{N2} \times P_{tot} = \frac{n_{N2}}{n_{tot}} \times P_{tot} = \frac{6}{6.82} \times 253 = \mathbf{222.58\ Kpa}$$

CHAPTER II

HEAT, WORK AND CALORIMETRY

II.1 Concept of temperature

II.1.1 Thermometry: is a branch of physics that focuses on the measurement of temperature. Its name comes forme Greek, where **thermós** means **"hot"** and **métron** means **"measure."**

Temperature: is an intensive quantity that is identifiable and measurable; it characterizes the state of a body (cold – hot).

II.1.2 Temperature scale: the unit of temperature in the International System is the **kelvin**, symbolized by **K**. There are also other measurement systems, such as the Celsius (centigrade) and Fahrenheit scales. The boiling and freezing temperatures of water are used to establish a temperature scale on a thermometer, as they represent the upper and lower fixed points. The interval between these two points is then divided into a certain number of equal parts, called **degrees**.

a) Celsius or Centigrade scale: it was invented by the Swedish physicist Anders Celsius (1701-1744) in 1742. Its symbol is °C (degree Celsius or centigrade).

   Example:

   - The thermometer displays **t = 0°C** when it is immersed in melting ice at atmospheric pressure.

   - The thermometer displays **t = 100°C** when it is immersed in boiling water at atmospheric pressure.

b) Fahrenheit scale it was proposed by the German physicist Daniel Gabriel Fahrenheit (1686-1736) in 1724 and is used in Anglo-Saxon countries. Its symbol is **°F** (degree Fahrenheit).

$$[\theta^0 F] = \frac{9}{5} t(°C) + 32 \qquad\qquad II.1$$

   Example

   The temperature of melting ice corresponds to **32°F**, while that of boiling water is **212°F.**

c) Absolute or Kelvin scale in 1702, the French physicist Guillaume Amontons (1663-1705) first proposed the idea of absolute zero. **Absolute temperature** is measured on the Kelvin scale starting from this zero point (0 K). Unlike other scales (Celsius, Fahrenheit, Rankine), this temperature scale doesn't have a degree symbol. The Kelvin scale (K) is the only officially recognized absolute scale.

$$\mathbf{T\ (K) =\ t\ (°c) +\ 273,15} \qquad (273K = 0°C) \qquad II.2$$

   Example

   The melting point of ice is **273.15 K** or 0°C, and the boiling point of water is **373.15 K** or 100°C.

II.1.3 Design of a Mercury thermometer

To measure or determine temperature, we use instruments called thermometers, which differ in the measurement principles they employ. Among the most well-known is the **mercury thermometer**, invented in 1724 by the German physicist Daniel Gabriel Fahrenheit. This instrument consists of a glass tube filled with mercury, a liquid chemical element whose length varies with temperature. To read the temperature, one simply consults the graduations marked along the tube. At its ends, the tube is capped by a bulb filled with mercury on one side and a gas composed of nitrogen on the other, at a pressure lower than atmospheric pressure.

II.1.4 The different types of thermometers: there are different types of thermometers:

a) Gas thermometers: Based on the principle of the variation in the volume of a gas at constant pressure and mass, or the change in pressure at constant volume and mass, it is used as a regulator due to its sensitivity to temperature variations.

Figure II.1 Gas thermometer

b) Liquid or needle thermometers have a graduated scale that allows for reading the temperature. They consist of a reservoir containing a colored liquid, topped with a thin tube attached to a graduated support. As the temperature rises, the liquid or the needle moves up the tube. Among the most common are :

- *Alcohol thermometer:* Due to its very low melting point, which ranges from −130 °C to 78 °C, it is commonly used in the medical field for measuring body temperature, air temperature, and at very low freezing temperatures.

- *Mercury thermometer:* Often used in wall thermometers to measure air temperature.

Figure II.2 Liquid thermometer (alcohol)

c) Needle thermometers these instruments consist of a pair of strips made of different materials with varying coefficients of expansion.

Figure II.3 *Needle thermometer*

d) Electronic thermometers**:** the temperature is displayed in numerical form on these instruments. They can be used in all conditions and measure body temperature, air temperature, room temperature, etc. They are very easy to use, as they show the exact value on their screens with just a click.

Figure II.4 *Electronic thermometer*

II.1.5 The zeroth principle of thermodynamics

The zeroth principle of thermodynamics was established to address issues related to the measurement and comparison of temperatures. Previously, temperature scales were arbitrary and depended on specific measurement methods. The need for a more reliable foundation for comparing temperatures was a significant concern in the scientific community of the 19th century. It was the German physicist Gustav H. Johannsen (1840-1901) who first proposed the central idea of the zeroth law in the 1860s.

The zeroth law is so named because it serves as the foundation for the creation of temperature scales and establishes a fundamental principle for measuring temperature. The zeroth principle of thermodynamics states that:

« If two systems are in thermal equilibrium with a third system, they are also in equilibrium with each other».
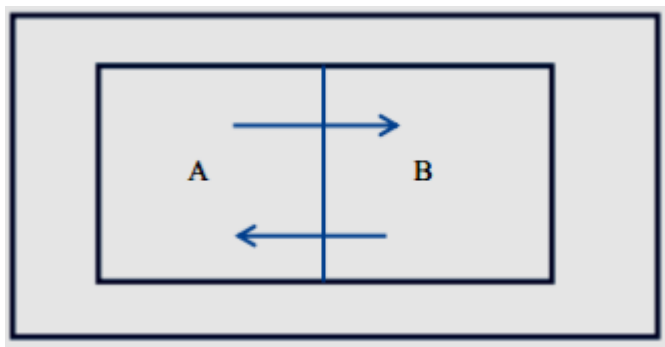
Figure II.5 *Heat exchange between two bodies A and B*

<u>Example</u>

- A piece of ice is placed in a glass filled with water at room temperature. In this experiment, three elements are present: the ice, the water, and the glass. Initially, these three elements will exchange heat and energy until they reach thermal equilibrium. After some time, they will all reach the same temperature.

- Two cups of coffee, one hot and the other cold. When they come into contact, heat flows from the hot cup to the cold cup until both reach the same temperature and establish thermal equilibrium.

II.2 <u>Concept of heat or quantity of heat Q</u>

II.2.1 <u>General Expression of the quantity of heat Q</u>

The quantity of heat, or thermal transfer, is a form of energy measured in joules or calories, denoted as **Q**. When two bodies at different temperatures come into thermal contact, heat is transferred from the hotter body to the colder body until they reach thermal equilibrium

II.2.2 <u>Different expressions of heat for the systems f (P, V, T) = 0</u>

We can distinguish two types of heat:

a) <u>Sensible heat</u>

This heat transfer depends on the initial temperatures of the two bodies, their equilibrium temperature, as well as their mass and nature (iron, aluminum, leather,...). The quantity of heat Q absorbed or released by a body is expressed by the following relationship:

$$Q = mc(T_f - T_i) = C(T_f - T_i) \qquad\qquad II.3$$

$$Q = nc(T_f - T_i) = C(T_f - T_i) \qquad\qquad II.4$$

m: Mass of the body in kilograms (kg).

n: Number of mole

c: Specific heat capacity in $J.kg^{-1}.K^{-1}$ or molar specific heat capacity in $J.mol^{-1}.K^{-1}$, it is a constant that depends on the body.

C: Thermal capacity **C = mxc** in J.K^{-1}

T$_f$: Final temperature or equilibrium temperature in K.

T$_i$: Initial temperature in K.

- **Q ≤ 0:** The quantity of heat Q is **released** by the body.
- **Q ≥ 0:** The quantity of heat Q is **absorbed** by the body.

The heat exchanged by a system with the surroundings during a transformation depends on the path taken. Therefore, it is not a state function.

<u>Case of an isochoric transformation</u>**:** During an isochoric transformation of a gas, we have **$dV = 0$**, Therefore, the elementary quantity of heat involved is:

➢ **For an infinitesimal transformation :**

$$\delta Q = C_v dT + I dV \ \ (dV = 0 \Rightarrow I dV = 0)$$

We will therefore have: $\delta Q = C_v dT$

➢ **For a finite transformation :**

The heat Q exchanged during a finite transformation between state **(1)** and state **(2)** is:

$$\int_1^2 \delta Q = \int_{T1}^{T2} C_v \, dT = \int_{T1}^{T2} mc_v dT = \int_{T1}^{T2} nc_v dT$$

If "C_V" is constant between T$_1$ and T$_2$:

$$Q = Q_v = C_v(T_2 - T_1) = mc_v(T_2 - T_1) == nc_v(T_2 - T_1) \qquad II.5$$

<u>Case of an isobaric transformation</u>**:** For an isobaric transformation of a gas, the quantity of heat involved is:

$$\delta Q = C_p dT + h dP \ \ (dP = 0 \Rightarrow h dP = 0)$$

$$\int_1^2 \delta Q = \int_{T1}^{T2} C_P \, dT = \int_{T1}^{T2} mc_P dT = \int_{T1}^{T2} nc_P dT$$

If "C_P" is constant between T$_1$ et T$_2$:

$$Q = Q_P = C_P(T_2 - T_1) = mc_P(T_2 - T_1) = nc_P(T_2 - T_1) \qquad II.6$$

b) <u>Latent heat</u>

Latent heat is the amount of heat required for a certain quantity of matter to change its physical state at constant temperature and pressure. It is proportional to the quantity of matter (mass or number of moles) as well as the value of the latent heat associated with this change of state.

$$Q = mL = nL \qquad\qquad\qquad II.7$$

For each type of matter, there are three forms of latent heat associated with the six physical state changes **(L$_s$, L$_v$, and L$_f$).** were, L$_s$, L$_v$, or L$_f$ represent the mass or molar heat associated with sublimation, vaporization, or fusion, respectively.

Note: The heat required for a phase change is much greater compared to the heat needed to raise temperatures (sensible heat).

Example:

Vaporization - condensation

At sea level, at 100 °C and under atmospheric pressure, the latent heat of vaporization-condensation is generally considered to be: **Lᵥ = 2250 kJ/ kg.**

Solidification-fusion

At sea level, at 0 °C and under atmospheric pressure, the latent heat of solidification-fusion is generally estimated to be: **L_f = 334 kJ /kg.**

II.2.3 The thermal heat capacity C

It is the amount of heat (in joules or calories) required to raise the temperature of a system by 1 K

II.2.4 Different types of thermal heat capacity

- **The molar heat capacity**, or molar specific heat, expressed in J·mol⁻¹·K⁻¹, corresponds to the amount of heat required to raise the temperature of one mole of a system by 1 K.

- **Mass heat capacity**, or specific mass heat, expressed in J·kg⁻¹·K⁻¹ or J·g⁻¹·K⁻¹, represents the amount of heat required to raise the temperature of a mass of a system by 1 K.

- **The molar or mass heat capacity at constant pressure** C_P is the ratio of the amount of energy transmitted by heat **Qp** to the increase in temperature of one mole of a pure substance for a small change **(T' - T)**.

$$C_p = \frac{\partial Q}{\partial T} \qquad\qquad II.7$$

- **The molar or mass heat capacity at constant volume** is the ratio of the amount of energy transmitted by heat **Qv** to the increase in temperature of one mole of a pure substance for a small change **(T' - T)**.

$$C_v = \frac{\partial Q}{\partial T} \qquad\qquad II.8$$

a) Heat capacity for ideal gases

For a substance considered as an ideal gas, there is a clearly established relationship between **Cp** and **Cv**. Joule's experiment shows that, for an ideal gas, the change in internal energy depends solely on the change in temperature. Thus, for a given temperature change, it is possible to achieve the same change in internal energy either through a transformation at constant volume or through a transformation at constant pressure. By applying the first principle of thermodynamics to both types of transformation, we obtain:

$$V = C^{ste} \quad \rightarrow \quad dU = \delta Q_v \qquad\qquad II.9$$

$$P = C^{ste} \quad \rightarrow \quad dU = \delta Q_p - PdV \qquad\qquad II.10$$

From which $\qquad \delta Q_v = \delta Q_p - PdV \qquad\qquad II.11$

With $$\delta Q_v = C_v dT \qquad\qquad\qquad II.12$$

$$\delta Q_p = C_p dT \qquad\qquad\qquad II.13$$

Therefore $$C_v dT = C_p dT - PdV$$

For an ideal gas, at constant pressure: $PdV = nRdT$

Where **n** is the number of moles contained in one unit of mass of the gas substance. Thus, we obtain: $C_v dT = C_p dT - nRdT$

Consequently $C_v = C_p - nR$ $\qquad\qquad\qquad II.14$

This relationship was established and experimentally verified by Mayer.

➢ Monatomic ideal gas

A monatomic gas is a gas whose constituents are isolated atoms, such as Helium (He) or Neon (Ne).

The values of the molar heat capacities for this type of gas are:

$$C_v = \frac{3nR}{2} \qquad\qquad\qquad II.15$$

$$C_p = \frac{5nR}{2} \qquad\qquad\qquad II.16$$

➢ Diatomic ideal gas

A diatomic gas is a gas whose constituents consist of two identical or different atoms, such as O_2, N_2, CO, HCl, NO, ….

The values of the molar heat capacities for this type of gas are:

$$C_v = \frac{5nR}{2} \qquad\qquad\qquad II.17$$

$$C_p = \frac{7nR}{2} \qquad\qquad\qquad II.18$$

➢ Relationship between Cp and Cv for an ideal gas, Mayer's relation

The Mayer relation, formulated in the 19th century by Julius Robert Mayer, establishes a link between the heat capacities at constant pressure Cp and at constant volume Cv of an ideal gas, according to the following formula:

$$C_p - C_v = nR \qquad\qquad\qquad II.19$$

$$\gamma = \frac{C_p}{C_v} \qquad\qquad\qquad II.20$$

For monatomic gases :

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.6$$

and diatomic gases:

$$\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.4$$

➢ Cp and Cv for a mixture of ideal gases

For a mixture of chemically inert ideal gases (a mixture that doesn't undergo a chemical reaction), the following law allows for the determination of Cp and Cv of the mixture.

$$C_p = \sum x_i C_{pi} \qquad\qquad II.21$$

$$C_v = \sum x_i C_{vi} \qquad\qquad II.22$$

➢ Thermal heat capacity for liquids and solids

For negligible volume changes of a solid, the enthalpy is practically equivalent to its internal energy, which is given by: $U \approx 3nRT$ from which $C_v = 3nR.$

The mass heat capacity of a solid is calculated by measuring, at constant pressure the heat transferred to the water of a calorimeter by a mass of solid that has been previously heated.

In the case of copper, this measurement yielded: **C_p= 385 J.kg^{-1}.K^{-1}**

From which **C_{pm}= 385 ×0.063=24.44 J.mol^{-1}.K^{-1} ≈ 3R**

The thermal heat capacity for liquids and solids is not constant and depends on:

a) **The allotropic state of the body:** For example, the heat capacity is higher for carbon in the graphite form than in the diamond form (0.6 cal.g^{-1}.K^{-1} compared to 0.113 cal.g^{-1}.K^{-1} between 0 and 100 °C).

b) **The temperature:** The true specific heat of a solid or liquid generally increases with temperature.

II.2.5 Calculation of the amount of heat for different transformations

Application II.1 Calculate the amount of heat for one mole of iodine as it goes from 300 K to 500 K at a pressure of one atmosphere.

Data: The molar heat capacities of iodine: C_p (I_2, solid) = 5, 4 cal. $mol^{-1}K^{-1}$

C_p (I_2, liquid) = 19, 5 cal. $mol^{-1}K^{-1}$

C_p (I_2, gas) = 9, 0 cal. $mol^{-1}K^{-1}$

The latent heats of phase changes are $L_{vaporisation,\ 475K}$ = 6, 10 $kcal.mol^{-1}$

$L_{fusion,\ 387K}$ = 3, 74 $kcal.mol^{-1}$

Solution

The amount of heat when one mole of iodine goes from 300 K to 500 K at a pressure of one atmosphere.

$$I_2(s) \rightarrow I_2(s) \rightarrow I_2(l)\ \rightarrow I_2(l) \rightarrow\ I_2(g)\ \rightarrow\ I_2(g)$$

$$\textcolor{red}{Q_1 \qquad Q_2 \qquad Q_3 \qquad Q_4 \qquad Q_5}$$

$$T_1{=}300K \qquad 387K \quad 387K \qquad 457K \quad 457K \qquad T_4{=}500K$$
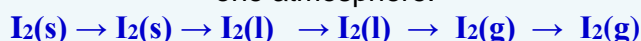
The amount of heat for warming solid iodine is:

$$Q_1 = \int_{300}^{387} nC_{p(I2,s)}\, dT = nC_{p(I2,s)}(387 - 300) = 469.8\ cal \qquad \textcolor{red}{Q_1= 0.4698\ kcal}$$

The amount of heat for fusion is :

$$Q_2 = nL_f = 3.74\ k\text{cal} \qquad\qquad \textcolor{red}{Q_2= 3.74\ kcal}$$

The amount of heat for warming liquid iodine is :

$$Q_3 = \int_{387}^{457} nC_{p(I2,l)}\, dT = nC_{p(I2,l)}(457 - 387) = 1365\ cal \qquad \textcolor{red}{Q_3 = 1.365\ kcal}$$

The amount of heat for vaporization is :

$$Q_4 = nL_v = 6.10\ k\text{cal} \qquad\qquad \textcolor{red}{Q_4= 6.10\ kcal}$$

The amount of heat for warming gaseous iodine is:

$$Q_5 = \int_{457}^{500} nC_{p(I2,g)}\, dT = nC_{p(I2,g)}(500 - 457) = 387\ cal \qquad \textcolor{red}{Q_5 = 0.387\ kcal}$$

The amount of heat for transforming iodine from the initial state to the final state is :

II.3 Calorimetry

Calorimetry is a technique that involves carrying out a transformation in an adiabatic system and measuring the resulting temperature changes. By analyzing these temperature variations, it is possible to détermine the heat produced or absorbed during the reaction associated with this transformation.

II.3.1 The calorimeter is a laboratory device designed to measure heat exchanges, thermal capacities, latent heats, and heat of reactions. It operates as an isolated system,

ensuring that there are no thermal exchanges with the outside, resulting in a net thermal balance of zero for the transformations taking place. The heat exchanges are associated with chemical reactions or phase changes of the substances within the calorimeter and occur at constant pressure (isobaric). The principle is straightforward: when one body releases heat, another body absorbs it completely, illustrating the equality of heat exchanges.

$$\sum Q_i = 0 \qquad\qquad II.23$$

A calorimeter includes a calorimetric vessel where the heat to be measured is manifested, as well as a stirrer, a thermometer, and an insulating jacket designed to minimize heat losses to the outside **(Fig. II.6).**
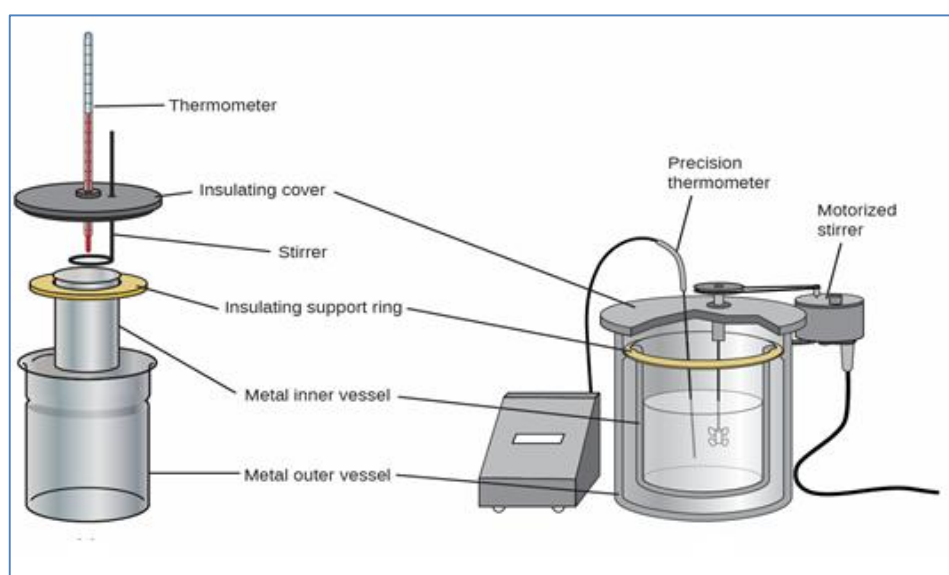
Figure II.6 Berthelot calorimeter

II.3.2 Different types of calorimeters

Depending on the nature of the compounds and the transformations studied, the suitable calorimeters are:

- **Constant pressure calorimeter**, suitable for transformations involving only condensed phases **(liquids or solids).** In this case, the heat exchanges within the calorimeter correspond to the change in the state function enthalpy.

$$\Delta H = Q_p \qquad\qquad II.24$$

- **Constant volume calorimeter bomb,** used for chemical reactions involving gases to prevent the loss of matter (in the form of gas) from the calorimeter. In this case, the heat exchanges within the bomb correspond to the change in the state function of internal energy.

$$\Delta U = Q_v \qquad\qquad II.25$$

II.3.3 Calorimeter water value

The water equivalent (or water value) of a calorimeter corresponds to the mass of water μ that exchanges the same amount of heat with the outside as the calorimeter and its accessories when they undergo the same temperature change.

$$C_{cal} = \mu c_{eau} \qquad\qquad II.26$$

C_{cal} : Calorimetric capacity of the calorimeter (J/K).

c_{eau} : Specific heat of water (J/Kg.K).

μ : water value (kg)

Application II.2 An adiabatic calorimeter contains 0.2 kg of water at 15 °C. 0.2 kg of water at 45.9 °C is added, and the final temperature reaches 30 °C. Calculate the mass of water μ in the calorimeter.

Data: *The specific heat of water c=4185 J/kg. °C*

Solution

We mix m_2 = 0.2 kg of **"Hot"** water (T_2 = 45.9°C), with a **"Cold"** system, at the temperature of: T_1 = 15°C, having a mass m_1 = 0.2 kg of water and a calorimeter whose "water mass" is μ. The final temperature is T_f = 30°C.

- **Heat released Q_c :** $Q_c = m_2 c (T_f - T_2)$.

- **Heat absorbed Q_r :** $Q_r = (m_1 + \mu) c (T_f - T_1)$

We apply the principle of mixtures : $\sum Q_i = 0 \implies Q_c + Q_r = 0$

$$m_2 c (T_f - T_2) + (m_1 + \mu) c (T_f - T_1) = 0$$

$$\mu = \frac{m_2 (T_2 - T_f)}{(T_f - T_1)} - m_1 = 0.012 kg = \textcolor{red}{12g}$$

II.3.4 Calculation of the equilibrium temperature

The thermal equilibrium temperature is reached when a body A, with a higher temperature **(T₁),** transfers thermal energy to a body B, which has a lower temperature **(T₂).** According to the zeroth law of thermodynamics, this transfer continues until both bodies reach the same temperature.

Application II.3 A calorimeter contains 100 g of water at 20 °C. 80 g of water at 50 °C is added. What would the equilibrium temperature T_{eq} be if the capacity of the calorimeter and its accessories is considered negligible?

Data: *The specific heat of water c=4185 J/kg. °C*

Solution

We apply the principle of mixtures $\quad\quad \sum Q_i = 0 \implies Q_{cal} + Q_1 + Q_2 = 0$

- $Q_{cal} = 0$

- $Q_2 = m_2 c (T_{eq} - T_2).$

- $Q_1 = m_1 c (T_{eq} - T_1)$

$$m_1 c (T_{eq} - T_1) + m_2 c (T_{eq} - T_2) = 0$$

$$T_{eq} = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2} = \mathbf{33.3°C}$$

II.3.5 Calculation of the combustion heat at constant pressure Q_P

Application II.4 In a calorimeter, 50 ml of HCl $_{(aq)}$ 1M and 50 ml of NaOH $_{(aq)}$ 1M, both at 22 °C, are added. The temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat generated by this reaction?

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

We assume that the calorimeter absorbs no heat from the reaction and that there is no thermal exchange between the calorimeter and the external environment.

Solution

We have 100 ml of a mixture of HCl and NaOH at 22 °C; this entire 100 ml solution will absorb the heat released by the reaction. The HCl and NaOH then recto until the temperature of the solution reaches 28.9 °C.

$$Q_{reaction} = -Q_{solution}$$

$$Q_{solution} = cm\Delta T$$

Since the solution is aqueous, we can treat it like water in terms of specific heat and mass values. The density of water is about 1 g/mL, and its specific heat is 4.184 J.g^{-1}.°C^{-1}

$$Q_{solution} = 4.84 \times 100 \times (28.9 - 22) = 2900\,J$$

$$Q_{reaction} = -Q_{solution} = \mathbf{2900\,J}$$

The negative sign indicates that the reaction is exothermic. It produces **2900 J** of heat.

II.3.6 Constant Calculation of the combustion heat at constant volume Q_v

Application II.5 3.12 g of glucose ($C_6H_{12}O_6$) are burned in a bomb calorimeter containing 775 g of water, the temperature of the calorimeter rises from 23.8 °C to 35.6 °C. The bomb has a heat capacity of 893 J/°C. What is the amount of heat produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb

$$Q_{reaction} = -(Q_{water} + Q_{Bomb})$$

$$Q_{reaction} = -[4.484 \times 775(35.6 - 23.8) + 893 \times (35.6 - 23.8)]$$

$$Q_{reaction} = -48800 J$$

This reaction released 48.8 kJ of heat when 3.12 g of glucose were burned.

II.3.7 Calculation of latent heats of phase change (L_f, L_{vap}, L_{sub}, ...)

Application II.7 In a calorimeter containing 1 kg of water at 15 °C, 1 kg of water at 65 °C is added, the final temperature reaches 38.8 °C. Calculate the water equivalent of the calorimeter.

Next, take the same calorimeter containing 1 kg of water at 15 °C and add 50 g of ice at 0 °C, resulting in a final temperature of 10.87 °C. Calculate the latent heat of fusion of ice (L_{fus}).

Finally, use the same calorimeter with 1 kg of water at 15 °C and add 50 g of ice at -5 °C, resulting in a final temperature of 10.76 °C. Calculate the specific heat of ice.

Data: The specific heat of water c=4185 J/kg. °C

Solution

We apply the principle of mixtures $\quad \sum Q_i = 0 \implies Q_{cal} + Q_1 + Q_2 = 0$

$$C_{cal}(T_{eq} - T_1) + m_1 c_e(T_{eq} - T_1) + m_2 c_e(T_{eq} - T_2) = 0$$

$$C_{cal} = \frac{-\left(m_1 c_e(T_{eq} - T_1) + m_2 c_e(T_{eq} - T_2)\right)}{(T_{eq} - T_1)} = 422.01 \, J.K^{-1}$$

$$C_{cal} = \mu_e c_{eau} \implies \mu_e = \frac{C_{cal}}{c_{eau}} = 0.1 \, kg$$

$$\sum Q_i = 0 \implies Q_{cal} + Q_{water} + Q_{ice} = 0$$

$$C_{cal}(T_{eq} - T_1) + m_1 c_e(T_{eq} - T_1) + m_2 L_f + m_2 c_e(T_{eq} - T_f) = 0$$

$$L_f = -\frac{[C_{cal}(T_{eq} - T_1) + m_1 c_e(T_{eq} - T_1) + m_2 c_e(T_{eq} - T_f)]}{m_2} = 335048.07 \, J.kg^{-1}$$

$$C_{cal}(T_{eq} - T_1) + m_1 c_e(T_{eq} - T_1) + m_2 c_s(T_f - T_2) + m_2 L_f + m_2 c_e(T_{eq} - T_f) = 0$$

$$c_s = -\frac{[C_{cal}(T_{eq} - T_1) + m_1 c_e(T_{eq} - T_1) + m_2 L_f + m_2 c_e(T_{eq} - T_f)]}{m_2(T_f - T_2)} = 2117.86$$

$$c_s = 2117.86 \, J.kg^{-1}.K^{-1}$$

II.4 Work

The common definition of work is the product of a force F acting on a body and the displacement x of that body in the direction of the force.

$$W = \int_{1}^{2} F.dx \qquad\qquad II.27$$

It represents a variation in energy associated with an ordered displacement of objects such as molecules (volume change work) or electrons (electrical work), under the influence of a force.

II.4. 1 General expression of pressure work

In thermodynamics, the work done by a system corresponds to the energy transferred from the system to its environment. It is essential to distinguish between the work done by the system on its external environment and the work done on the system by the external environment.

An infinitesimal change **dP** in the external pressure P is created on a fluid, for example, an increase. This slight pressure imbalance causes a deformation of the separating surface **dS**, resulting in a displacement **dl** measured perpendicular to the surface at the center of the element **dS (Fig. II.7).**
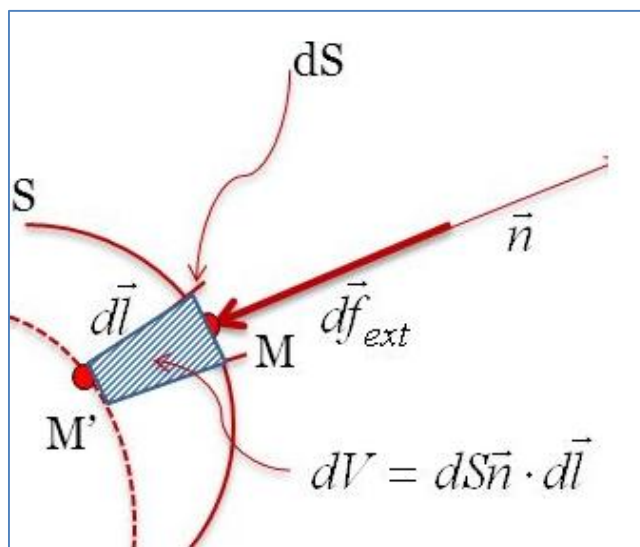
Figure II.7 *Volume change work of a fluid*

The elementary work received by the fluid along the surface element dS is equal to:

$\partial W = \overrightarrow{df_{ext}}.\overrightarrow{dl}$ avec $\overrightarrow{df_{ext}} = -P_{ext}\,dS.l$ let $\partial W = -P_{ext}\partial V$

dS.dl is equal to the decrease in volume **dV**.

A positive value of work indicates that it is absorbed by the system, while a negative value means it is provided by the system to the external environment.

Example:

Let's consider a system whose volume can vary. A typical example is a gas contained in a closed vessel with a piston **(Fig. II.8).**
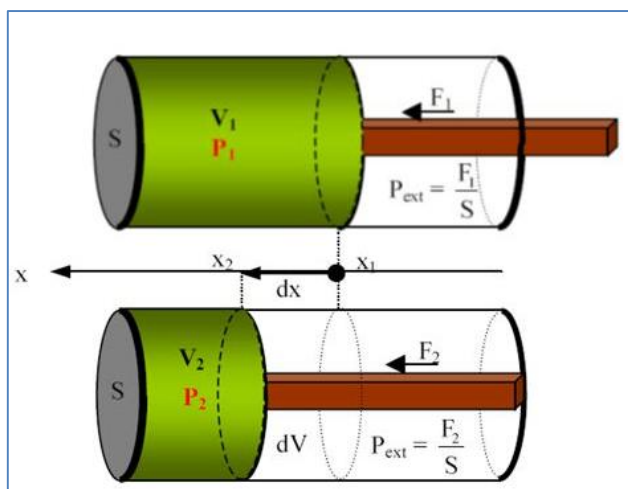
Figure II.8 Work of pressure forces

The system we are examining here consists of the whole (gas + piston). The external force acting on this system is the pressure force coming from outside (the atmosphere). Denoting **P_{ext}** as the external pressure, this force is directed in the increasing **x** direction and has a magnitude of **SP_{ext}**, where **S** is the surface area of the piston. When the position of the piston increases by **dx**, the work done by the pressure force, which also corresponds to the work received by the system, is given by:

$$\delta W = P_{ext}\, S\, dx = -P_{ext}\, dV \qquad\qquad II.28$$

Note: The expression $\delta W = -P_{ext}\, dV$ is applicable to all geometries, not just to a piston. It also applies to a balloon being inflated, to a metal expanding…

II.4. 2 Reversible work W_{rev}

A reversible transformation is a process that is slow enough for mechanical equilibrium to be constantly maintained, so that at every moment **$P_{int}= P_{ext}$** (with **P_{int}** is the pressure of the fluid) and therefore:

$$\delta W = -P_{ext}dV = -P_{int}dV = -\frac{nRT}{V}dV \Rightarrow \int \delta W = \int -nRT\frac{dV}{V} \qquad II.29$$

II.4. 3 Irreversible work W_{irrv}

An irreversible transformation is a sudden process that doesn't pass through equilibrium states (mechanical and thermal equilibria aren't reached). This type of transformation can't be reversed. In this case, **$P_{ext} = P_{final}$** and the elementary work will be :

$$\delta W = -P_{ext}dV = -P_f dV \Rightarrow \int \delta W = -P_f \int dV \qquad II.30$$

Application II.8 2 liters of an ideal gas expand from state 1 (P_1 = 1 atm, V_1 = 2 liters) to state 2 (P_2 = 0.5 atm, V_2 = 4 liters). Calculate the work W done during this expansion, which occurs as follows:

- **Reversible**
- **Irreversible**

Solution

- **Reversible expansion**

$$W = \int_{V1}^{V2} -P_{ext}dV$$

$$P_1V_1 = P_2V_2 = nRT$$

$$W = \int_{V1}^{V2} -P_1V_1dV = -P_1V_1\int_{V1}^{V2}\frac{dV}{V} = P_1V_1 ln\frac{V_1}{V_2} = 10^5 \times 2\ 10^{-3}\ ln(0.5)$$

$$W = -138.62\ J$$

- **Irreversible expansion**

$$W = \int_{V1}^{V2} -P_{ext}dV = -P_2\int_{V1}^{V2}dV = -P_2(V_2 - V_1) = -0.5\ 10^5(4-2)10^{-3}$$

$$W = -100\ J$$

II.4. 4 Application of work calculation for different transformations

- ➢ Isobaric transformation **:** This transformation occurs at constant pressure

$$W = \int_{V1}^{V2} -P_{ext}dV = -P\int_{V1}^{V2}dV = -P(V_2 - V_1) \qquad\qquad II.31$$

- ➢ Isothermal transformation: This transformation occurs at constant temperature

$$T = Cte \implies P_1V_1 = P_2V_2 = nRT \implies P = \frac{nRT}{V}$$

$$W = \int_{V1}^{V2} -P_{ext}dV = \int_{V1}^{V2} -\frac{nRT}{V}dV = -nRT\int_{V1}^{V2}\frac{dV}{V} = nRTln\frac{V_1}{V_2} \qquad II.32$$

- ➢ Isochoric transformation: This transformation occurs at constant volume, which means that the volume change is zero, resulting in **W_{1-2} = 0**; therefore, the work done during this transformation is null.

- ➢ Adiabatic transformation (isentropic): is a process in which there is no heat exchange with the external environment **(Q = 0).** This type of transformation occurs when the thermodynamic system (such as an ideal gas) is contained in a vessel insulated from external influences by adiabatic walls. Additionally, transformations that occur very rapidly, where the system doesn't have time to exchange heat with the outside, can also be considered adiabatic. During an

adiabatic transformation, the variables P and V change simultaneously, but
$$PV^{\gamma} = Cte$$

$$W = \int_{V1}^{V2} -P_{ext}dV = \int_{V1}^{V2} -\frac{Cte}{V^{\gamma}}dV = -Cte\int_{V1}^{V2}\frac{dV}{V^{\gamma}} = -Cte\left(\frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma}\right)$$

$$W = \frac{P_2V_2^{\gamma}V_2^{1-\gamma} - P_1V_1^{\gamma}V_1^{1-\gamma}}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \qquad\qquad II.33$$

Application II.9 One mole of an ideal gas at an initial temperature of 298 K expands from a pressure of 5 atm to a pressure of 1 atm. Calculate the work done by the gas in each of the following cases:

- **Isothermal expansion**
- **Adiabatic expansion**

Data $\gamma = 1.4$ R=.8.31 J.mol^{-1}.K^{-1}

Solution

- **Isothermal expansion**

$$P_1V_1 = P_2V_2 \Longrightarrow \frac{V_1}{V_2} = \frac{P_2}{P_1}$$

$$W = nRTln\frac{V_1}{V_2} = nRTln\frac{P_2}{P_1} = 1 \times 8.31 \times 298\, ln\frac{1}{5}$$

$$W = -3985.57\,J$$

- **Adiabatic expansion**

$$P_1V_1 = nRT_1 \Longrightarrow V_1 = \frac{nRT_1}{P_1} = 4.88\,litres$$

$$P_2V_2^{\gamma} = P_1V_1^{\gamma} \Longrightarrow V_2 = V_1\left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} = 13.23\,litres$$

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{(13.23 - 5 \times 4.88)10^2}{0.6}$$

$$W = -1860.54\,J$$

CHAPETR III

THE FIRST LAW OF THERMODYNAMIC

III.1 Equivalence between heat and work

At the end of the 18th century, many scientists were trying to understand the nature of heat. Several theories and experiments were developed to explain its origin, until James Prescott Joule (1818-1889) conducted an experiment demonstrating that heat was merely a form of energy derived from mechanical energy (work). He showed, through his experiment, that it was possible to raise the temperature of water by transferring mechanical (potential) energy to it. The mechanical energy required to increase the temperature of water from 14.5 ⁰C to 15.5 ⁰C was 4.18 J per gram, which led to the definition of **the calorie.**

Joule's experiment

James Prescott designed the device illustrated in **(Fig III.1).** When a mass fell, it caused a drum to rotate, with an axis equipped with paddles moving inside an insulated container (calorimeter) holding a precise amount of water. Joule observed that the agitation of the water by the paddles resulted in a temperature increase. By calculating the mechanical work done by the mass, he determined that the work required to heat 1 g of water by 1 °C was 4.18 J, leading him to conclude that this work was entirely converted into heat.
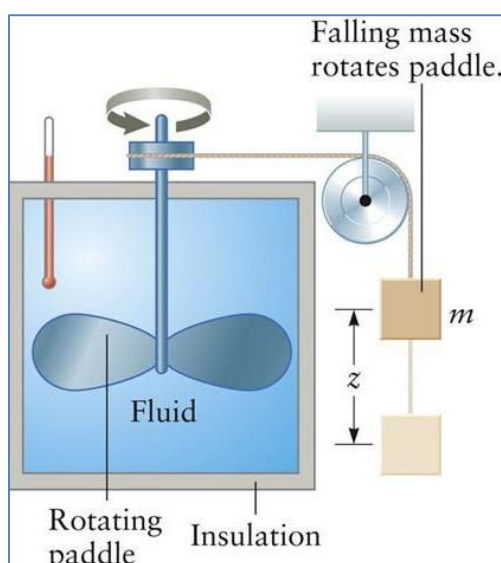
Figure III. 1 Apparatus of Joule's experiment.

The measurement of W and Q reveals that, regardless of the system analyzed, their ratio remains constant and depends solely on the units chosen. When W is expressed in Joules, W and Q represent two manifestations of the same quantity: W corresponds to mechanical energy, while Q refers to thermal energy. Generally, all experiments conducted on transformation cycles between work and heat with the external environment have led to the establishment of the equivalence between heat and work:

$$\frac{|Q|}{|W|} \approx 4.18 \, J.cal^{-1} \qquad\qquad III.1$$

III.2 <u>Statement of the first law of thermodynamics</u>

The first law of thermodynamics, also known as the principle of conservation of energy, states that:

« If, during a cyclic transformation, any system can exchange only work and heat with the external environment, the sum of the work and heat received by the system is zero ».

$$W + Q = 0 \qquad\qquad III.2$$

In this classic statement, the term "exchange" is of great significance. Indeed, "work" does not simply refer to the work done by the forces acting on the system; it actually denotes the mechanical energy exchanged between the system and its environment. These two concepts can sees differ.

In other words:

« The change in internal energy of the system between two equilibrium states, the initial state and the final state, is equal to the sum of the work done by the external forces applied and the amounts of heat received from the external environment ».

We write the change in energy when passage from state 1 to state 2

$$E_2 - E_1 = W_{1-2} + Q_{1-2} \qquad\qquad III.3$$

III.3 <u>General Expression of the first law</u>

When a system transitions from state A to state B, the change in internal energy (ΔU) is equal to the algebraic sum of heat (Q) and work (W):

$$\Delta U = U_2 - U_1 = W + Q \qquad\qquad III.4$$

The change in internal energy (ΔU) depends only on the initial state (A) and the final state (B); it is independent of the path taken (U is a state function).

III.4 <u>Definition of internal energy U</u>

Internal energy is a state variable that allows us to assess the changes in energy during a transformation. The symbol Δ in front of U indicates that ΔU represents the variation of this quantity in the system during the transformation, without needing to know the details of the process. This characteristic is known as the principle of initial and final states. According to the first principle of thermodynamics, which states that the change in total energy (Q + W) is the same regardless of the path taken, we can write:
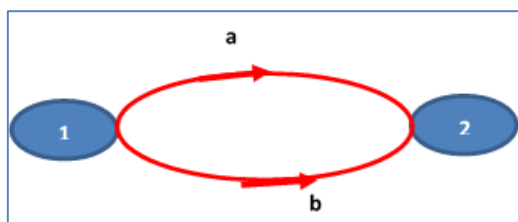
$$\Delta U_{1-2} = U_2 - U_1 = (W_a + Q_a) = (W_b + Q_b) = \text{Cte}$$

III.5 Differential expression of internal energy

For an infinitesimal transformation, we have:

$$dU = dW + dQ$$

Given that U(t) and U(t+dt) exist for a transformation, which means that the system undergoes a continuous series of internal thermodynamic equilibrium states. Therefore, in the case where only pressure forces do work, The differential expression of the first principle corresponds to:

$$dU = \delta W + \delta Q = -P_{ext}dV + \delta Q \qquad\qquad III.5$$

Application III.1 Calculate the variation in internal energy of a system that absorbs Q = 2 kJ and provides external work W = 500 J
Solution :

$$\Delta U = W + Q$$

It absorbs 2000 J ⇒ Q = + 2000J; provides work ⇒ W = - 500J;   **ΔU= +1500 J.**

III.6 Calculation of the change in internal energy ΔU

III.6.1 First law of Joule: the change in internal energy of an ideal gas

The first law of Joule states that, for an ideal gas, internal energy U depends solely on temperature. We define C_V, the heat capacity at constant volume, as the partial derivative of internal energy versus temperature:

$$C_V = \left(\frac{dU}{dT}\right)_V \qquad\qquad III.6$$

For 1 mole of a monatomic ideal gas $\left(C_V = \frac{3}{2}R\right)$, the change in internal energy is given by:

$$\Delta U = U_2 - U_1 = C_V\Delta T = \frac{3}{2}R(T_2 - T_1) = \frac{3}{2}(P_2V_2 - P_1V_1) \qquad III.7$$

Note :

If the transformation is adiabatic (thermally isolated): **Q = 0**, then **ΔU = W**; in this case, W is independent of the path taken.

III.6.2 Isochoric transformation

This transformation occurs at constant volume, which means that the work related to the change in volume of the gas is zero **(W = 0).** According to the first principle of thermodynamics, $\Delta U = U_2 - U_1 = Q_V + W_V$ becomes:

$$\Delta U = Q_V = nC_V\Delta T \qquad\qquad III.8$$

III.6.3 Isobaric transformation

At constant pressure, the work done on the gas is expressed as : $W_P = -P(V_2 - V_1)$

On the other hand, according to the first principle, we have:

$$Q_P = \Delta U - W_P = nC_V\Delta T + P(V_2 - V_1) \qquad\qquad III.9$$

III.6.4 Relationship between Q_P and Q_V

At constant volume, the change in internal energy is equal to the amount of heat exchanged, denoted as Q_V. $\Delta U = Q_V$

And in the case of an isobaric transformation:

$$\Delta U = Q_P - P(V_2 - V_1) \Longrightarrow U_2 - U_1 = Q_P - PV_2 + PV_1$$

$$Q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

➢ For an ideal gas (Mayer's relation)

Knowing that: $dH = dU + d(PV)$

with $dH = Q_P = nC_P dT$ et $dU = Q_V = nC_V dT$

then $nC_P dT = nC_V dT + d(PV)$

and $PV = nRT$

Therefore $nC_P dT = nC_V dT + d(nRT) = nC_V dT + nRdT$

From there, we obtain Mayer's relation:

We will have:

$$C_P - C_V = R \qquad\qquad III.10$$

➢ For chemical reactions

In thermochemistry, Q_P and Q_V correspond to the heat of reaction at constant pressure and constant volume, respectively. We have:

$$Q_P = Q_V + \Delta(PV) = Q_V + \Delta nRT \qquad\qquad III.11$$

Application III.2 Calculate the heat of the methane combustion reaction at constant pressure, knowing that this reaction releases 2000 kJ at 25°C

Solution:

$Q_P = Q_V + \Delta nRT$ with $Q_V = -2000$ kJ

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$\Delta n = \sum n_{(products(g))} - \sum n_{(reactants(g))}$$

$$\Delta n = 1 - 3 = -2 \ moles$$

$$Q_P = -2000 - 2 \times 8.31 \times 298 \times 10^{-3} = -1995.047 \ kJ$$

➢ Reversible adiabatic work W$_{rev}$ (Laplace's equation)

A gas assumed to be ideal undergoes an adiabatic (isentropic) transformation with no change in heat quantity. The change in internal energy for this transformation is:

$dU = dQ + dW = dQ - Pd\,V = nC_V dT$

Then $dQ = nC_V dT + Pd\,V = 0$

$$nC_V dT = -Pd\,V \qquad (\mathbf{1})$$

We also have: $\boldsymbol{d}H = dU + d(PV) = dQ - PdV + PdV + VdP$

Then $dQ = dH - VdP$ avec $dH = nC_P dT$

Therefore $dQ = nC_P dT - VdP = 0$

$$nC_P dT = VdP \qquad (\mathbf{2})$$

We divide equation (1) by (2) :

$$\frac{nC_V dT}{nC_P dT} = \frac{= -Pd\,V}{VdP}$$

$$\left(\frac{dP}{P}\right)\frac{nC_V dT}{nC_P dT} = \frac{= -Pd\,V}{VdP}\left(\frac{dP}{P}\right)$$

$$\left(\frac{C_P}{C_V}\right)\frac{C_V}{C_P}\frac{dP}{P} = \frac{-d\,V}{V}\left(\frac{C_P}{C_V}\right)$$

$$\frac{dP}{P} = -\left(\frac{C_P}{C_V}\right)\frac{d\,V}{V}$$

We define the adiabatic constant

$$\gamma = \frac{C_P}{C_V}$$

So

$$\frac{dP}{P} = -\gamma\frac{d\,V}{V}$$

$$\int_1^2 \frac{dP}{P} = \int_1^2 -\gamma\frac{d\,V}{V}$$

$$\Rightarrow ln\left(\frac{P_2}{P_1}\right) = \gamma ln\left(\frac{V_1}{V_2}\right) = ln\left(\frac{V_1}{V_2}\right)^\gamma$$

$$\Rightarrow \frac{P_2}{P_1} = \frac{V_1^\gamma}{V_2^\gamma}$$

We obtain the formula that describes the equation of state for adiabatic transformations, also known as **Laplace's formula**:

$$P_1 V_1^\gamma = P_2 V_2^\gamma \qquad\qquad III.12$$

The equation of state for adiabatic transformations can be described by temperature as a function of volume and temperature as a function of pressure:

An ideal gas has :

$$PV = nRT \implies P = \frac{nRT}{V}$$

We have:

$$\frac{P_2}{P_1} = \frac{V_1^{\gamma}}{V_2^{\gamma}} \implies \frac{\frac{nRT_2}{V_2}}{\frac{nRT_1}{V_1}} = \frac{V_1^{\gamma}}{V_2^{\gamma}} \implies \frac{nRT_2}{V_2}V_2^{\gamma} = \frac{nRT_1}{V_1}V_1^{\gamma}$$

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \qquad\qquad III.13$$

Otherwise

$$PV = nRT \implies V = \frac{nRT}{P}$$

$$\frac{P_2}{P_1} = \frac{V_1^{\gamma}}{V_2^{\gamma}} \implies \frac{P_2}{P_1} = \frac{\left(\frac{nRT_1}{P_1}\right)^{\gamma}}{\left(\frac{nRT_2}{P_2}\right)^{\gamma}} \implies P_2 (nR)^{\gamma}\left(\frac{T_2}{P_2}\right)^{\gamma} = P_1 (nR)^{\gamma}\left(\frac{T_1}{P_1}\right)^{\gamma}$$

$$P_2^{1-\gamma} T_2^{\gamma} = P_1^{1-\gamma} T_1^{\gamma} \qquad\qquad III.14$$

Calculation of work :

$$W_{1-2} = -\int_1^2 P dV$$

We have $dQ = 0$ so $dU = dQ + dW = dW \implies dW = dU = nC_V dT$

$$W = \int_1^2 dU = \int_1^2 nC_V dT = nC_V \Delta T$$

We have :

$$\begin{cases} \gamma = \dfrac{C_P}{C_V} \\ R = C_P - C_V \end{cases}$$

$$\gamma C_V - C_V = R \implies C_V = \frac{R}{\gamma - 1} \quad et \ C_P = \gamma C_V = \frac{\gamma R}{\gamma - 1}$$

So

$$W = \int_1^2 nC_V dT = \int_1^2 n\frac{R}{\gamma - 1} dT = \frac{nR}{\gamma - 1}(T_2 - T_1) = \frac{nRT_2 - nRT_1}{\gamma - 1}$$

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \qquad\qquad III.15$$

➤ Irreversible adiabatic work W_irrv

There is no exchange of heat or work between the gas and the surroundings in this type of transformation.

$$W_{1-2} = \int_1^2 -PdV = P(V_1 - V_2) \qquad III.16$$

III.7 Concept of enthalpy H

The enthalpy function, denoted by H, represents the total energy of a thermodynamic system. It includes the internal energy (U) of the system, plus the work that the system must perform to oppose the external pressure and occupy its volume. Enthalpy is an extensive state function, meaning it is independent of the path taken to reach that state. It is based solely on the initial and final conditions, without considering the intermediate states.

III.7.1 The enthalpy function

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

$$Q_P = (U_2 + PV_2) - (U_1 + PV_1)$$

Let's assume $\mathbf{H = U + PV}$ the enthalpy function

Then

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

Note :

- Like internal energy U, H is a state function. It is expressed in Joules.
- The change in enthalpy ΔH depends only on the initial and final states.
- For a cycle, we have: $\Delta U = \Delta H = 0$

III.7.2 Differential expression of enthalpy

From the definition of the state function $\mathbf{H = U + PV}$, we deduce the differential:

$$\mathbf{d}H = dU + d(PV) = dU + PdV + VdP$$

Let's apply the first principle:

$$dU = dQ + dW = dQ - Pd\,V$$

$$\mathbf{dH = dU + d(PV) = dQ - Pd\,V + PdV + VdP = dQ + VdP} \qquad III.17$$

III.7.3 Second law of Joule; the variation of enthalpy of ideal gases

The second law of Joule states that the enthalpy of an ideal gas depends only on temperature

$$\mathbf{dH = dU + d(PV)}$$

$$\left(\frac{dH}{dP}\right)_T = \left(\frac{dU}{dP}\right)_T + \left(\frac{d(PV)}{dP}\right)_T$$

At T=Cte :

$$dU = 0 \Rightarrow \left(\frac{dU}{dP}\right)_T = 0$$

At T=Cte :

$$PV = nRT = Cte \Rightarrow d(PV) = 0 \Rightarrow \left(\frac{d(PV)}{dP}\right)_T = 0$$

So:

$$\left(\frac{dH}{dP}\right)_T = 0$$

We have: $H = U + PV \Rightarrow dH = dU + PdV + Vdp$

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

⇒ Hence: $dH = C_P dT = n c_P\, dT$

with:

C_P : Heat capacity of the gas at constant pressure.

c_P : Molar heat of the gas at constant pressure.

- $C_V = n c_V$ and $C_P = n c_P$.

Since the two specific heat capacities are such that: $\gamma = \frac{c_P}{c_V}$

We deduce

$$\Delta H = \gamma \Delta U \qquad\qquad\qquad III.18$$

The same result applies to enthalpy H. The partial derivative of H with respect to temperature is denoted Cp, called the heat capacity at constant pressure:

$$C_P = \left(\frac{dH}{dT}\right)_P$$

Application III.3 One mole of NO (assumed ideal gas) undergoes the following successive transformations:

- State 1 to State 2: A reversible isothermal compression.
- State 2 to State 3: A reversible adiabatic expansion.
- State 3 to State 1 : An isobaric heating that returns it to state 1.

1- Calculate V_1, V_2, V_3, T_2 et T_3
2- Represent the transformation cycle in a Clapeyron diagram (P,V).
3- For each transformation, calculate (in joules) the following quantities: work, heat exchanged, the change in internal energy, and enthalpy.

Data :

P_1= P_3=2atm P_2=10atm T_1=300K   R=8.32 J.mol^{-1}K^{-1} $C_v = \frac{3}{2}R$ $C_p = \frac{5}{2}R$

Solution :

1 Calculation of V_1, V_2, V_3 et T_3

$$V_1 = \frac{nRT}{P_1} = 12.3 \; l$$
$$T = Cte \quad \Rightarrow T_2 = T_1 = 300K$$
$$T = Cte \Rightarrow P_2V_2 = P_1V_1 \quad \Rightarrow V_2 = \frac{P_1V_1}{P_2} = 2.46 \; l$$
$$\gamma = \frac{c_P}{c_v} = \frac{5}{3} = 1.6$$
$$P_2V_2^{\gamma} = P_3V_3^{\gamma} \quad \Rightarrow V_3 = \left(\frac{P_2}{P_3}\right)^{\frac{1}{\gamma}} \quad V_3 = 6.46 \; l$$
$$T_3 = \frac{P_3V_3}{nR} = 157.6 \; K$$

3 Calculation of W, Q, ΔU and ΔH for each transformation.

Transformation (1-2)

$$T = Cte \quad \Rightarrow \qquad \Delta U_{12} = 0 \qquad \Delta H_{12} = 0$$
$$W_{12} = \int_{V1}^{V2} -PdV = \int_{V1}^{V2} -nRTd\frac{dV}{V} = -nRTln\frac{V_2}{V_1} \qquad W_{12} = 4017.15 \; J$$
$$\Delta U_{12} = 0 \Rightarrow Q_{12} = -W_{12} = nRTln\frac{V_2}{V_1} \qquad\qquad Q_{12} = -4017.15 \; J$$

Transformation (2-3)

Adiabatic Transformation $\Rightarrow Q_{23} = 0$
$$\Delta U_{23} = nc_V(T_3 - T_2) = -1777.15 \; J$$
$$W_{23} = \Delta U_{23} = nc_V(T_3 - T_2) = -1777.15 \; J$$
$$\Delta H_{23} = nc_P(T_3 - T_2) = -2961.92 \; J$$

Transformation (3-1)

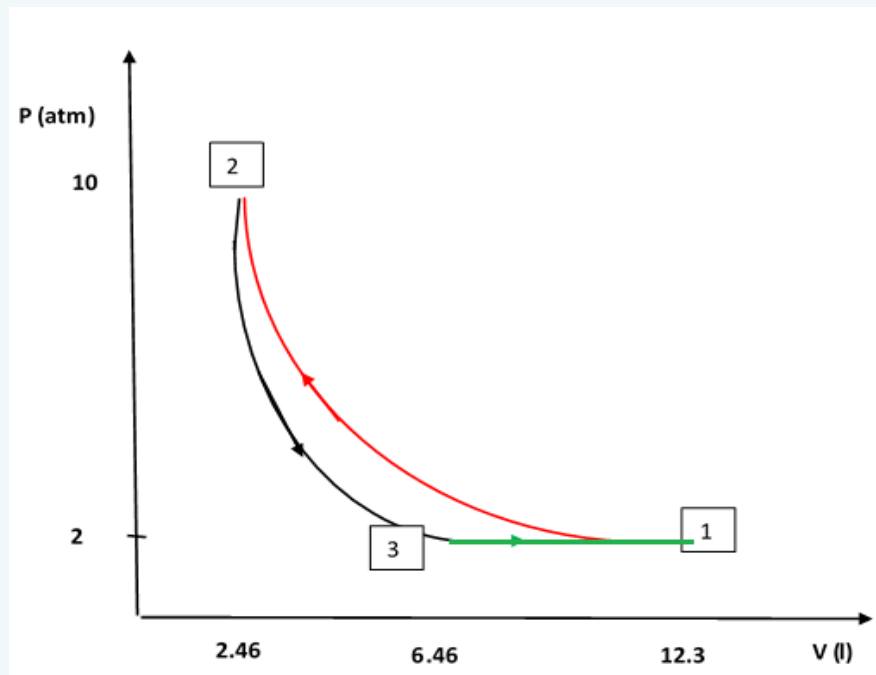$$W_{31} = \int_{V3}^{V1} -PdV = -P_1\int_{V3}^{V1} dV = -P_1(V_1 - V_3) = -1183.2\,J$$

$$\Delta H_{31} = nc_P(T_1 - T_3) = +2961.92\ J$$

Isobaric Transformation $\Rightarrow Q_{31} = \Delta H_{31} = nc_P(T_1 - T_3) = +2961.92\ J$

$$\Delta U_{31} = Q_{31} + W_{31} = +1778.74\ J$$

2 Clapeyron diagram

CHAPTER IV

APPLICATION OF THE FIRST PRINCIPLE OF THERMODYNAMIC TO THERMOCHEMISTY

IV.1 Introduction

Thermochemistry is the study of heat exchanges associated with chemical reactions. When a system undergoes chemical reactions, it can exchange energy with its surroundings, as the bonds between molecules change between the initial state (before the reaction) and the final state (after the reaction). Generally, the sum of the energies of these bonds is different in these two states. As a result of the reaction, there will be either a release or an absorption of heat.

IV.2 Reaction heats

Let's consider a reaction in which the chemical species A and B (reactants) are transformed into species C and D (products).

$$aA + bB \rightarrow cC + dD$$
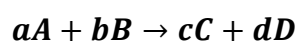
The coefficients a and b of the reaction are integers, represent the proportions in which the molecules of A and B combine.

$$2H_2 + O_2 \longrightarrow 2H_2O$$
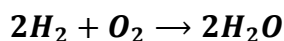
Most chemical reactions are accompanied by a thermal phenomenon, whether it's the release or absorption of heat. The heat involved in this process is referred to as **the heat of reaction**. When a reaction releases heat, it is called an exothermic reaction, whereas when heat is absorbed, it is referred to as an endothermic reaction.

Considering that the reacting substances are initially at room temperature, the heat of reaction corresponds to the total amount of heat (positive or negative) released during the entire process, until the system returns to its initial thermal state.

Note

- In the case of a combustion reaction, the heat of reaction is referred to as **the heat of combustion**. If it pertains to the formation of a compound from its constituent elements, it is called **the heat of formation** of the compound in question.

- The heats of reaction can be considered either at constant pressure or at constant volume. For example, in a reaction occurring in open air, that is, at atmospheric pressure, the heat of reaction is considered at constant pressure. In contrasta, for a reaction taking place in a closed system, such as in a calorimetric bomb, the heat of reaction at constant volume is takins into accointa.

IV.2.1 Heat of reaction at constant pressure

In a reaction occurring at constant pressure, there is an exchange of heat with the surroundings, and this heat is equivalent to the change in enthalpy ΔH_r.

« To the isobaric and isothermal reaction is associated a heat Q_p equal to the change in enthalpy of the system »

$$\Delta H_r = Q_p \qquad\qquad IV.1$$

IV.2.2 Heat of reaction at constant volume

In a reaction occurring at constant volume, the work involved is zero, and the heat exchanged is equal to the change in internal energy.

« The reaction at constant volume and temperature is accompanied by a thermal effect Q_v equal to the change in internal energy of the system »

$$\Delta U_r = Q_v \qquad\qquad IV.2$$

IV.2.3 Relationship between heat of reaction at constant volume and at constant pressure

The change in internal energy of a system at constant pressure is:

$$\Delta U_p = -P.\Delta V + Q_p$$

However ΔU_p, equated to the heat of reaction at constant volume, we have thus:

$$Q_v = -P.\Delta V + Q_p$$

Let us assume all the gases present are ideal gases and apply the ideal gas relation to them: $P.\Delta V = \Delta n.RT$

Δn: is the difference between the number of moles of gas in the final state and that in the initial state.

Let the reaction occur at constant pressure and temperature, we obtain:

$$Q_p = Q_v + \Delta n.RT \qquad\qquad IV.3$$

Application IV.1 Calculate the heat of combustion for ethanol at constant pressure, using its heat of combustion at constant volume (measured in a calorimetric bomb) Q_v =326.3 kcal/mol at 25 °C

Solution :

$$C_2H_5 - OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$$
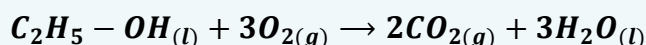
$\Delta n = 2 - 3 = -1\ mol$

$Q_p = Q_v + \Delta n.RT$

$Q_p = 326.3 - 2\ \times 10^{-3} \times 298 = 325.7\ kcal/mol$

IV.3 The standard state

The standard state reference of an element at a given temperature, typically at 25 °C, corresponds to the most stable physical state of the simple substance at that temperature. Regardless of the physical state of a constituent, its standard state is defined at a reference pressure P_0, which is conventionally set at 1 bar. This is known as standard pressure.

For a gas, the standard state corresponds to the state of a pure ideal gas at 1 bar.

Example:

Standard state references of some elements at T = 25 °C.

Gas: O_2, Cl_2, H_2 .

Liquid: *Br$_2$, Hg .*

Solid: *C(graphite), S , Fe, Cu.*

IV.4 <u>The standard enthalpy of formation $\Delta H_f°$</u>

The formation enthalpy of a compound corresponds to the change in enthalpy that occurs during the reaction forming one mole of this compound from its elements (simple substances) at constant pressure.

Example: for the **SO$_3$** :

It is defined by the reaction: $S + \frac{3}{2} O_2 \longrightarrow SO_3$ and not by $SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3$

The formation enthalpy becomes the standard enthalpy of formation when the constituent elements and the formed compound are considered under standard conditions, denoted as **$\Delta H_f°$.** This definition implies that the formation enthalpy of all pure elements in their standard state is zero.

<u>Example</u> at *T=298 K and P=1bar* $\Delta H_f°(N_2)=0, \quad \Delta H_f°(S)=0$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_f^°(H_2O)_{(g)}$$

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_f^°(H_2O)_{(l)}$$

$$C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_f^°(CO_2)_{(g)}$$

$$Fe_{(s)} + 2S_{(s)} \longrightarrow FeS_{2(s)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H_f^°(FeS_2)_{(s)}$$
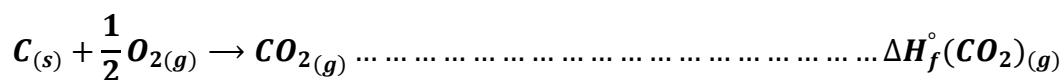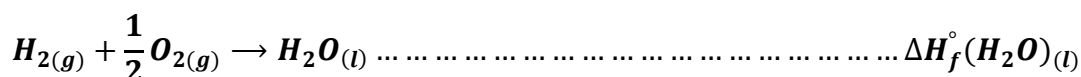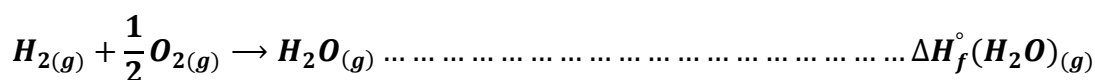
IV.5 <u>The enthalpy of dissociation</u>

The energy of a chemical bond (or bond dissociation enthalpy) refers to the change in enthalpy of a reaction that dissociates one mole of these bonds (symmetric cleavage). Bond energy represents the average amount of energy required to break a given bond in one mole of gaseous particles. It is also referred to as bond enthalpy.

Example:

At 25 °C and 1 bar, 436 kJ of heat must be supplied to completely dissociate one mole of dihydrogen gas into two moles of hydrogen atoms:

$$H_{2(g)} \longrightarrow 2H_{(g)}$$
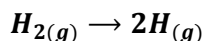
with **ΔH=+436kJ** . This represents the energy of the H-H bond, or the enthalpy of the dissociation reaction of H$_2$.

IV.6 <u>The phase change enthalpy</u>

A phase change of a pure substance involves a transfer of energy with the surroundings. The latent heat of phase change (whether it is fusion, vaporization, or sublimation) is defined

as the amount of heat or energy required to transform one unit of mass from phase 1 to phase 2, reversibly at constant temperature and pressure (T, P). This latent heat is denoted as L and is expressed in joules per kilogram (J/kg).

$$\Delta H = mL \qquad\qquad IV.4$$

With:

ΔH : Phase change enthalpy in joules.

m : Mass of the body in kilograms

L : Latent heat (mass energy) of phase change in joules per kilogram.

Figure VI.1 summarizes endothermic and exothermic phase changes.

• Exothermic phase changes (the substance releases energy, **L<0**).

• Endothermic phase changes (the substance absorbs energy, **L>0**).

The reverse transformation of melting, known as freezing, is characterized by an enthalpy **ΔH$_{freezing}$ = − ΔH$_{melting}$.** This relationship arises from the fact that enthalpy is a state function. Melting followed by solidification returns the system to its initial state, implying that the overall change in enthalpy **ΔH = ΔH$_{freezing}$ + ΔH$_{melting}$ = 0**.
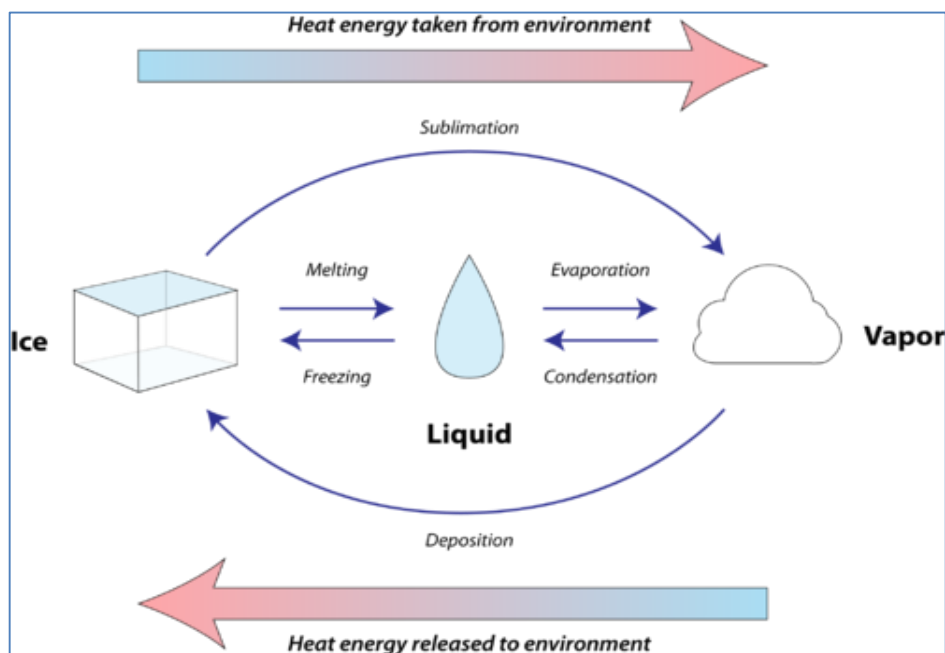
***Figure IV.1** Endothermic and exothermic phase changes*

IV.6.1 Enthalpy of fusion ΔH_{fus}

The enthalpy of fusion refers to the change in enthalpy that a substance experiences when it transitions from a solid state to a liquid state under standard conditions. Conversely, the enthalpy of solidification corresponds to this transformation in the reverse direction.

IV.6.2 Enthalpy of vaporization ΔH_{vap}

The enthalpy of vaporization represents the change in enthalpy that occurs when a substance transitions from a liquid state to a gaseous state. Conversely, the enthalpy of liquefaction corresponds to this process in the opposite direction.

IV.6.3 Enthalpy of sublimation ΔH_{sub}

The enthalpy of sublimation represents the change in enthalpy that occurs when a substance transitions directly from a solid state to a gaseous state. In contrast, the enthalpy of condensation corresponds to this process in the reverse direction.

IV.7 The enthalpy of a chemical reaction ΔH_r

IV.7.1 Hess's law

Hess's law, formulated by Germain Henri Hess (1802-1850), states that the amount of heat released or absorbed during a reaction at constant pressure or volume is independent of the different steps of the reaction and how they occur. It depends only on the initial and final states. It can be stated as follows:

« The change in enthalpy of a reaction corresponds to the difference between the sum of the formation enthalpies of the products (final state) and that of the reactants (initial state), taking into account the stoichiometry of the reaction ».

$$\Delta H_r = \sum \Delta H_f(products) - \sum \Delta H_f(reactants) \qquad\qquad IV.5$$

Application IV.2 Determine the change in enthalpy for the oxidation reaction of ethyl alcohol to acetic acid at 298 K under atmospheric conditions.

$$C_2H_5OH + O_2 \rightarrow CH_3COOH + H_2O$$
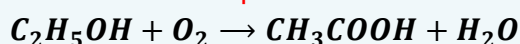
The enthalpies of formation are provided at 298 K and 1 atm

$\Delta H_f(C_2H_5OH) = -277.8\ kJ.mol^{-1}$ $\qquad$ $\Delta H_f(CH_3COOH) = -487.3\ kJ.mol^{-1}$

$\Delta H_f(O_2) = 0$ $\qquad\qquad\qquad$ $\Delta H_f(H_2O) = -285.8\ kJ.mol^{-1}$

Solution

$$\Delta H_r = \Delta H_f(CH_3COOH) + \Delta H_f(H_2O) - \Delta H_f(C_2H_5OH) - \Delta H_f(O_2)$$

$$\Delta H_r = -487.3 - 285.8 - (-277.8)$$

$$\Delta H_r = -495.3 kJ.mol^{-1}$$

In many cases, it is impossible to directly measure the heat of a reaction, either because the conditions (pressure, temperature, physical state of the substances) make calorimetric measurements incompatible, or because the reaction itself cannot be carried out. We can indirectly determine this heat of reaction through calculations or algebraic methods.

Application IV.3 Determine the change in enthalpy for the following reaction:

$$C_{graphite} + \frac{1}{2}O_2 \rightarrow CO_g$$
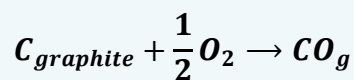
The isobaric combustion heats of graphite and carbon monoxide are given:

$$C_{graphite} + O_2 \rightarrow CO_{2(g)} \qquad\qquad \Delta H_1 = -94 \; kcal.mol^{-1}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_{2(g)} \qquad\qquad \Delta H_2 = -67.6 \; kcal.mol^{-1}$$

Determination using chemical reactions

$$\Delta H_1$$

$$C_{graphite} + O_2 \quad \rightarrow \quad CO_{2(g)}$$

$$\Delta H_3 \qquad\qquad\qquad \Delta H_2$$

$$CO + \frac{1}{2}O_2$$
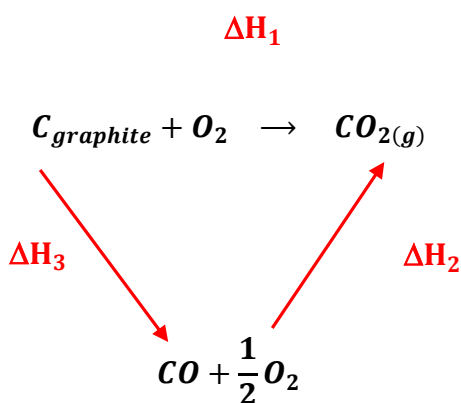
$$\Delta H_1 = \Delta H_3 + \Delta H_2 \Rightarrow \Delta H_3 = \Delta H_1 - \Delta H_2 = -94 + 67.6 = -26.4 \; kcal$$

Determination using algebraic calculations

The determination of reaction heats can be performed algebraically by arranging the various reactions (whether the heats are known or unknown) in the correct order.

$$C_{graphite} + O_2 \rightarrow CO_{2(g)} \qquad\qquad \Delta H_1 = -94 \; kcal.mol^{-1} \quad \textbf{(1)}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_{2(g)} \qquad\qquad \Delta H_2 = -67.6 \; kcal.mol^{-1} \; \textbf{(2)}$$

We are looking for :

$$C_{graphite} + \frac{1}{2}O_2 \rightarrow CO_g \qquad\qquad \Delta H_3$$

Let's write relation (2) in reverse; the heat of reaction changes sign:

$$CO_{2(g)} \rightarrow CO + \frac{1}{2}O_2 \qquad\qquad \Delta H_{2'} = +67.6 \; kcal.mol^{-1}$$

Let's sum the reactions (1) and (2'):

$$C_{graphite} + O_2 \rightarrow CO_{2(g)} \qquad\qquad \Delta H_1 = -94 \; kcal.mol^{-1}$$

$$CO_{2(g)} \rightarrow CO + \frac{1}{2}O_2 \qquad\qquad \Delta H_{2'} = +67.6 \; kcal.mol^{-1}$$

$$C_{graphite} + O_2 + CO_{2(g)} \rightarrow CO_{2(g)} + CO + \frac{1}{2}O_2 \qquad\qquad \Delta H_1 + \Delta H_{2'}$$
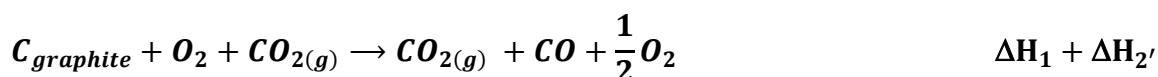
By eliminating the common substances on both sides:

$$C_{graphite} + \frac{1}{2}O_2 \rightarrow CO_g \qquad\qquad \Delta H_1 + \Delta H_{2'}$$

$$\Delta H_3 = \Delta H_1 + \Delta H_{2'} = -94 + 67.6 = -26.4\ kcal$$

Application IV.4 Determine the heat of reaction for the following reaction :

$$C_2H_{4(g)} + H_2 \rightarrow C_2H_{6(g)}$$
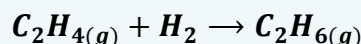
The heat of reactions for the reactions below are provided :

$$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)} \qquad\qquad \Delta H_1 = -337.3\ kcal$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \qquad\qquad \Delta H_2 = -68.3\ kcal$$

$$C_2H_{6(g)} + \frac{7}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad\qquad \Delta H_3 = -372.8\ kcal$$

Solution

$$\Delta H_r = \Delta H_f\left(C_2H_{6(g)}\right) - \Delta H_f\left(H_{2(g)}\right) - \Delta H_f\left(C_2H_{4(g)}\right)$$

$$\Delta H_1 = 2\Delta H_f\left(CO_{2(g)}\right) + 2\Delta H_f\left(H_2O_{(l)}\right) - \Delta H_f\left(C_2H_{4(g)}\right)$$

$$\Delta H_f\left(C_2H_{4(g)}\right) = 2\Delta H_f\left(CO_{2(g)}\right) + 2\Delta H_f\left(H_2O_{(l)}\right) - \Delta H_1$$

$$\Delta H_3 = 2\Delta H_f\left(CO_{2(g)}\right) + 3\Delta H_f\left(H_2O_{(l)}\right) - \Delta H_f\left(C_2H_{6(g)}\right)$$

$$\Delta H_f\left(C_2H_{6(g)}\right) = 2\Delta H_f\left(CO_{2(g)}\right) + 3\Delta H_f\left(H_2O_{(l)}\right) - \Delta H_3$$

$$\Delta H_2 = \Delta H_f\left(H_2O_{(l)}\right)$$

$$\Delta H_r = 2\Delta H_f\left(CO_{2(g)}\right) + 3\Delta H_f\left(H_2O_{(l)}\right) - \Delta H_3 - 2\Delta H_f\left(CO_{2(g)}\right) - 2\Delta H_f\left(H_2O_{(l)}\right) + \Delta H_1$$

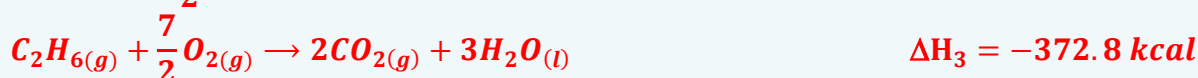$$\Delta H_r = \Delta H_1 + \Delta H_2 - \Delta H_3$$

$$\Delta H_r = -32.8\ kcal$$

IV.7.2 Bond energy or bond enthalpy

It is the energy released during the formation of a covalent bond between two atoms A and B that are free in the gaseous state. By definition, this energy corresponds to the change in enthalpy required to carry out the reaction for the formation of this chemical bond.

$$A_{(g)} + B_{(g)} \rightarrow A - B_{(g)}$$
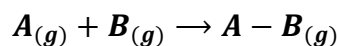
The bond formation enthalpies (ΔH formation) are always negative and are expressed in $J \cdot mol^{-1}$. This means that atoms in their free state combine, systematically releasing significant amounts of energy.

Example

Bond	H-H	C-H	C-C	C=C	C≡C	O=C
Energy (Kcal/mol)	−104	-99	-83	-147	-194	-118

The bond enthalpy indicates the strength of the bond. It therefore depends on the bond length, its nature, and its polarity.

The dissociation of a gaseous molecule AB corresponds to the breaking of the chemical bond between atoms A and B, resulting in two free atoms A and B in the gaseous state. To achieve this dissociation, energy must be supplied to the system. The dissociation enthalpy, referred to as bond energy, is denoted as $\Delta H_{diss}(A-B)$ or **D(A– B)** and is expressed in J·mol^{-1}. The enthalpy of any reaction is equal to the difference between the bond energies of the product molecules and those of the reactants.

$$\Delta H_r = \sum n_i \Delta H_{bond}(products) - \sum n_i \Delta H_{bond}(reactants) \qquad IV.6$$

Application IV.5 Determine the enthalpy change for the following reaction using bond energies:

$$C_2H_{2(g)} + 2H_2 \longrightarrow C_2H_{6(g)}$$

Solution :

$$H - C \equiv C - H + 2\,H - H \quad \longrightarrow \quad H_3C - CH_3$$

$$E_{C\equiv C} + 2E_{C-H} \qquad 2E_{H-H} \qquad\qquad E_{C-C} + 6E_{C-H}$$
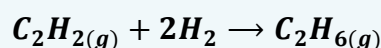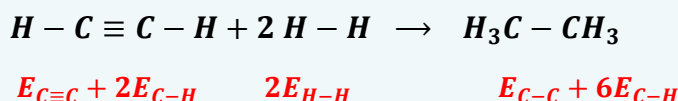
$\Delta H_r = \Delta H_f(C_2H_{6(g)}) - \Delta H_f(C_2H_{2(g)}) - 2\Delta H_f(H_{2(g)})$

$\Delta H_r = E_{C-C} + 6E_{C-H} - (E_{C\equiv C} + 2E_{C-H} + 2E_{H-H})$

$\Delta H_r = E_{C-C} - E_{C\equiv C} + 4E_{C-H} - 2E_{H-H}$

$\Delta H_r = -83 + 194 + 4(-99) + 2(+104)$

$$\Delta H_r = -77\ kcal$$

IV.7.3 Lattice energy (Born-Haber cycle)

The lattice energy or reticular energy **« Er»** 'Er' of an ionic compound measures the electrostatic force of attraction between positive and negative ions. It is defined as the energy required to dissociate one mole of solid into its constituent gaseous ions :

$$AB_{(s)} \longrightarrow A^+_{(g)} + B^-_{(g)}$$
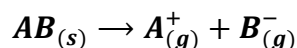
Lattice energy can be calculated theoretically, and it allows for the determination of the stability of an ionic solid in relation to its constituents through a thermodynamic cycle: **the Born-Haber cycle**, named after its two developers, German scientists **Max Born** and **Fritz Haber**, the Born-Haber cycle is a method for analyzing lattice energies (enthalpy of crystallization). This cycle presents a model that illustrates two ideal paths leading to the formation of an ionic compound from its elements: a direct pathway and another that goes through a series of intermediate reactions.

Example Calculation of the NaCl crystal lattice energy.

- Solid metallic sodium is converted into gaseous sodium; the energy required for this transformation corresponds to **the sublimation energy** :$\Delta H_{subl} = +107\text{kJ/mol}$

- Gaseous atomic sodium is ionized into Na⁺ ions ; the energy required is **the ionization energy: ΔH_I= +502kJ/mol**

- Gaseous dichlorine is homolytically dissociated into two gaseous chlorine atoms; the energy required is **the dissociation energy : ΔH_D= +121kJ/mol**

- Gaseous atomic chlorine gains one electron and becomes Cl⁻; the energy required is **the electron affinity energy** : A_E= **-355kJ/mol**

- **The formation energy**, which represents the energy released or absorbed during the formation of sodium chloride from the elements in their native state (solid sodium and gaseous dichlorine) : **ΔH_f= -411kJ/mol**

- By applying Hess's law, we can finally express the balance as follows :

$$E_r = \Delta H_f - \Delta H_{subl} - \Delta H_I - \frac{1}{2}\Delta H_D - A_E$$

$$E_r = -786 \; kJ.mol^{-1}$$
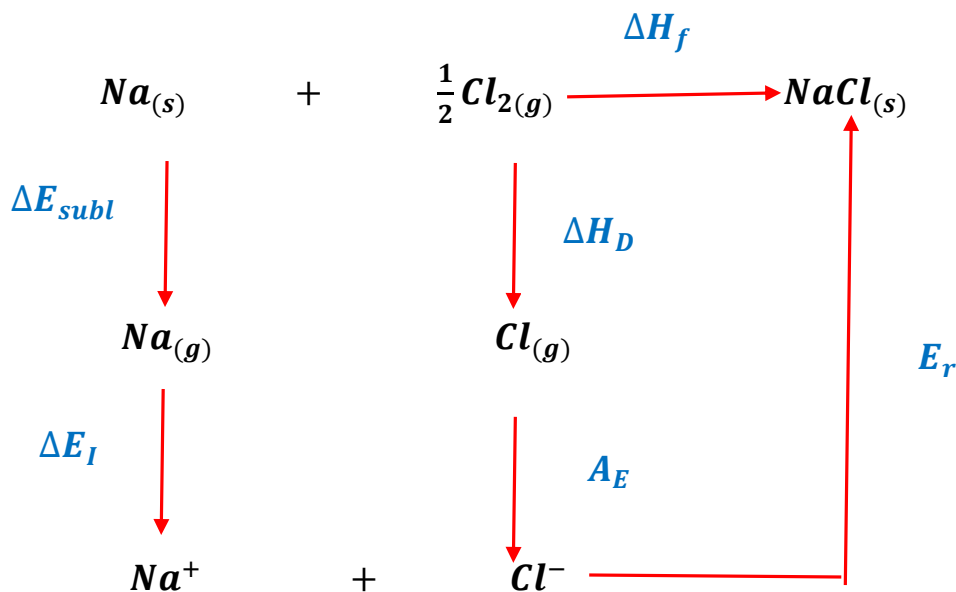
Figure IV.2 Schematic representation of the Born-Haber cycle for the NaCl molecule

IV.7.4 The formation enthalpy of gaseous atoms

The standard formation enthalpy of a compound, denoted ΔH_f° , corresponds to the enthalpy of the reaction that synthesizes the compound from its elements in their simple state, under standard atmospheric pressure. By convention, the enthalpy of formation of pure substances in their simple state is zero, regardless of temperature.

IV.7.5 Kirchhoff's Law

Kirchhoff's law allows us to determine the standard enthalpy change of a reaction at a given temperature, using the standard enthalpy change of that reaction at a temperature often set at 298 K, along with the heat capacities for which we have accurate measurements. Consider a transformation occurring at constant pressure at a temperature T_2, which transitions a thermodynamic system from an initial state (1) to a final state (2). We assume that this transformation absorbs an enthalpy ΔH_2^r **(see fig. VI.2)**
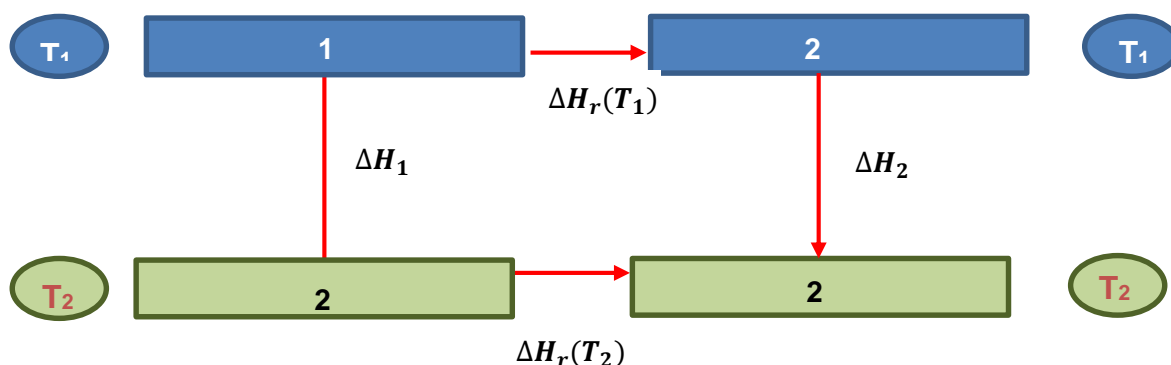
Figure IV.2 *Cycle of reactions carried out at temperatures T_1 and T_2*

Knowing the heat capacities of the products and reactants, as well as the enthalpy of the reaction at 298 K (or at another temperature), we can calculate the enthalpy $\Delta Hr(T_2)$ of the reaction at T_2.

According to the cycle: $\sum \Delta H_i = 0$ $\qquad\qquad \Delta H_r(T_1) + \Delta H_2 - \Delta H_r(T_2) - \Delta H_1 = 0$

$\Delta H_r(T_2) - \Delta H_r(T_1) = \Delta H_2 - \Delta H_1 \qquad \Delta H_1 = \int_{T1}^{T2} n_1 c_{P1}\, dT$ et $\Delta H_2 = \int_{T1}^{T2} n_2 c_{P2}\, dT$

If we consider that this thermodynamic system is a chemical reaction, the amount of heat (Q) is simply the change in enthalpy; thus:

$$\frac{d\Delta H_r}{dT} = \frac{d(\Delta H_2 - \Delta H_1)}{dT} = n_2 c_{P2} - n_1 c_{P1} = C_{P2} - C_{P1} = \Delta C_p$$

With: $\Delta C_P = \sum C_P(products) - \sum C_P(reactants)$ $\qquad\qquad\qquad$ *IV*. 7

In general:

If we know $\Delta H_r(T_1)$ and want to calculate $\Delta H_r(T_2)$, it is sufficient to integrate the previous equation, which leads to Kirchhoff's equation, stated as follows:

$$\Delta H_r(T_2) = \Delta H_r(T_1) + \int_{T1}^{T2} \Delta C_P\, dT \qquad\qquad\qquad\qquad IV. 8$$

Note

- Cp is generally a function of temperature.
- In cases where there is a phase change within the interval [**T_1-T_2**], the enthalpies of phase change must be taken into account when calculating the enthalpy.

- If Cp is not a function of temperature (Cp = constant), we will have:

$$\Delta H_r(T_2) = \Delta H_r(T_1) + \Delta C_P \int_{T1}^{T2} dT \qquad\qquad IV.9$$

- In the case of an isochoric transformation, we actually have: $dU = \delta Q = C_V dT$

Kirchhoff's law will then apply to internal energy:

$$\Delta U_r(T_2) = \Delta U_r(T_1) + \int_{T1}^{T2} \Delta C_V\, dT \qquad\qquad IV.10$$

Application IV.6 The reforming reaction of gaseous heptane produces toluene $C_6H_5{-}CH_{3(g)}$ and hydrogen gas.

1. Write the balanced equation for this reaction.
2. At 298 K, the standard enthalpy of this reaction is +237.8 kJ·mol⁻¹. In industry, this reaction is carried out at higher temperatures. Provide the expression for the standard enthalpy ΔH_r as a function of temperature using:

a- The standard heat capacities at 298 K

b- The standard heat capacities valid between 298 K and 1000 K.

3. Calculate its value at 750 K in both cases.

Data: Standard molar heat capacities at constant pressure Cp in **J.mol⁻¹.K⁻¹**.

	298 K	298 K to 1000 K
$C_7H_{16(g)}$	166,0	98,75 + 0,290 T
$H_{2(g)}$	28,8	28,30 + 0,002 T
$C_6H_5{-}CH_{3(g)}$	103,7	46,40 + 0,229 T

Solution

1- $C_7H_{16(g)} \rightarrow C_6 H_5CH_{3\ (g)} + 4H_{2\ (g)}$

2- We apply Kirchhoff's law $\Delta H_r(T_2) = \Delta H_r(T_1) + \int_{T_1}^{T_2} \Delta C_p\, dT$

$\Delta C_p = C_p\left(C_6H_5CH_{3(g)}\right) + 4C_p(H_2) - C_p\left(C_7H_{16(g)}\right)$

Case (a) $\Delta C_p = 52.9\, j.mol^{-1}.K^{-1}$

Case (b) $\Delta C_p = -98.75 - 0.209T + 46.4 + .229T + 4 \times (28.3 + 0.002T)$

$\Delta C_p = 60.9 - 0.053T \ \ j.mol^{-1}.K^{-1}$

In both cases, applying Kirchhoff's law gives: $\Delta H_r(T) = \Delta H_r(298) + \int_{298}^{T} \Delta C_p\, dT$

Case (a) $\Delta H_r(T) = 237.8 + \int_{298}^{T} 52.9 \times 10^{-3}\ (T - 298) = 222 + 52.9 \times 10^{-3}T$

$$\Delta H_r(750) = 261.7 \ \ Kj.mol^{-1}$$

Case (b) $\Delta H_r(T) = 237.8 + \int_{298}^{T}(60.9 - 0.053T) \times 10^{-3}\, dT$

$$= 237.8 + 60.85 \times 10^{-3}(T - 298) - \frac{0.053}{2} \times 10^{-3}(T^2 - 298^2)$$

$$= 222 + 60.9 \times 10^{-3}T - 26.5 \times 10^{-6}T^2$$

$\Delta H_r(750) = 252.8 \ \ Kj.mol^{-1}$

Application IV.7 The combustion of one mole of methanol under standard pressure and temperature conditions releases 725.20 kJ, as shown in the following reaction :

$$CH_3OH_{(l)} + 3/2O_{2\ (g)} \rightarrow CO_{2\ (g)} + 2H_2O_{(l)}$$

1. Calculate the change in internal energy for this reaction.
2. Calculate the change in enthalpy for this reaction at a temperature of 127 °C and under a pressure of one atmosphere, considering that water boils at 100 °C and methanol boils at 64.5 °C, with respective vaporization heats of 44 kJ/mol and 35.4 kJ/mol.
3. Calculate the energy of the O-H bond in gaseous methanol, knowing that:

Standard enthalpy of carbon sublimation	$\Delta H_{sub}°\ (C_{(s)})$=718 KJ/mol
Standard enthalpy of formation of liquid methanol	$\Delta H_f°\ (CH_3OH_{(l)})$=-238,7KJ/mol
Enthalpy of H-H bond formation	$\Delta H_f°(H\text{-}H)$ = -436 kJ/mol
Enthalpy of O=O bond formation	$\Delta H_f°(O\text{=}O)$= -493 kJ/mol
Formation enthalpy of the C-H bond in $CH_3OH(g)$.	$\Delta H_f°(C\text{-}H)$= -413 kJ/mol
Formation enthalpy of the C-O bond in $CH_3OH(g)$.	$\Delta H_f°(C\text{-}O)$= -315 kJ/mol

Standard molar heat capacities at constant pressure, C_p, are given in $J \cdot mol^{-1} \cdot K^{-1}$

$CH_3OH_{(l)}$	$CH_3OH_{(g)}$	$O_{2\ (g)}$	$H_2O_{(l)}$	$CO_{2(g)}$	$H_2O_{(g)}$
81,6	53,5	34,7	75,2	36,4	38,2

Solution
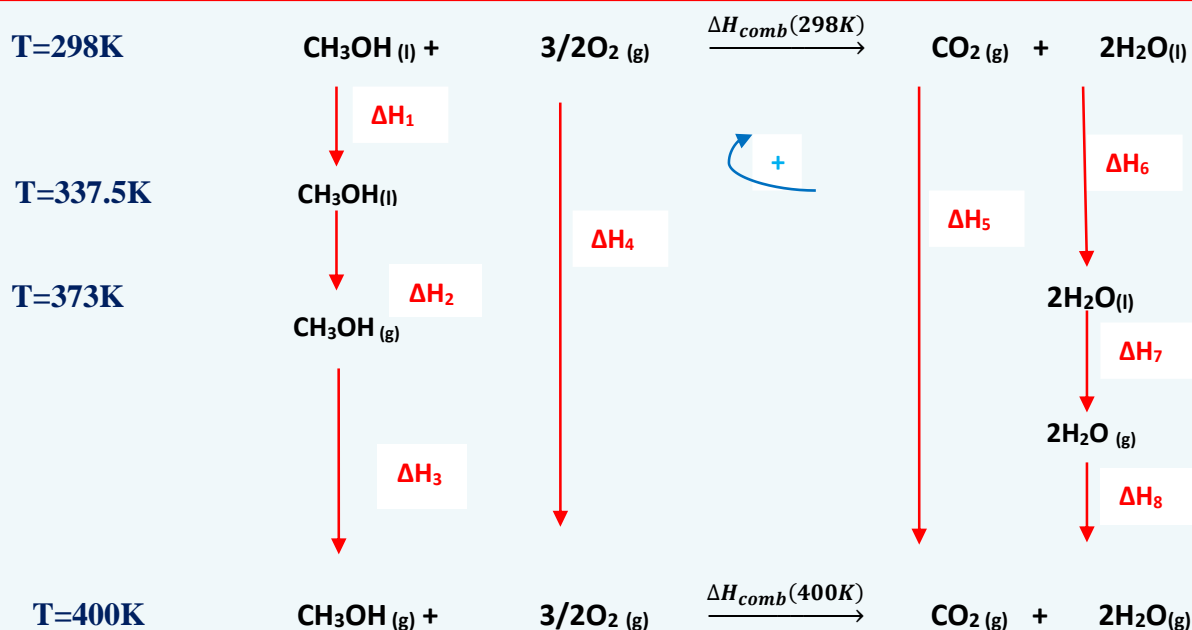
1- $\Delta H = \Delta U + \Delta nRT \Rightarrow \Delta U = \Delta H - \Delta nRT$

With : $\Delta n = \sum n_{i(products)g} - \sum n_{i(ractants)g}$

$$\Delta n = 1 - \frac{3}{2} = -\frac{1}{2}\ mole$$

$\Rightarrow \Delta U$= -725.20 -0.5×8.32 10^{-3} ×298 $\Delta U = $ **-726.44 Kj**

2- We form the following cycle:

$$\Delta H_1 = \int_{298}^{337.5} C_p\left(CH_3OH_{(l)}\right) dT = \mathbf{3,82 Kj}$$

$$\Delta H_2 = \Delta H_{vap}(CH_3OH) = \mathbf{35,4\ Kj}$$

$$\Delta H_3 = \int_{337.5}^{400} C_p\left(CH_3OH_{(g)}\right) dT = \mathbf{3,34 Kj}$$

$$\Delta H_4 = \frac{3}{2}\int_{298}^{400} C_p\left(O_{2(g)}\right) dT = \mathbf{5,31 Kj}$$

$$\Delta H_5 = \int_{298}^{400} C_p\left(CO_{2(g)}\right) dT = \mathbf{3,71 Kj}$$

$$\Delta H_6 = 2\int_{298}^{373} C_p\left(H_2O_{(l)}\right) dT = \mathbf{11,28\ Kj}$$

$$\Delta H_7 = 2\Delta H_{vap}(H_2O) = \mathbf{88\ Kj}$$

$$\Delta H_8 = 2\int_{373}^{400} C_p\left(H_2O_{(g)}\right) dT = \mathbf{2,06\ Kj}$$

By applying Hess's law:
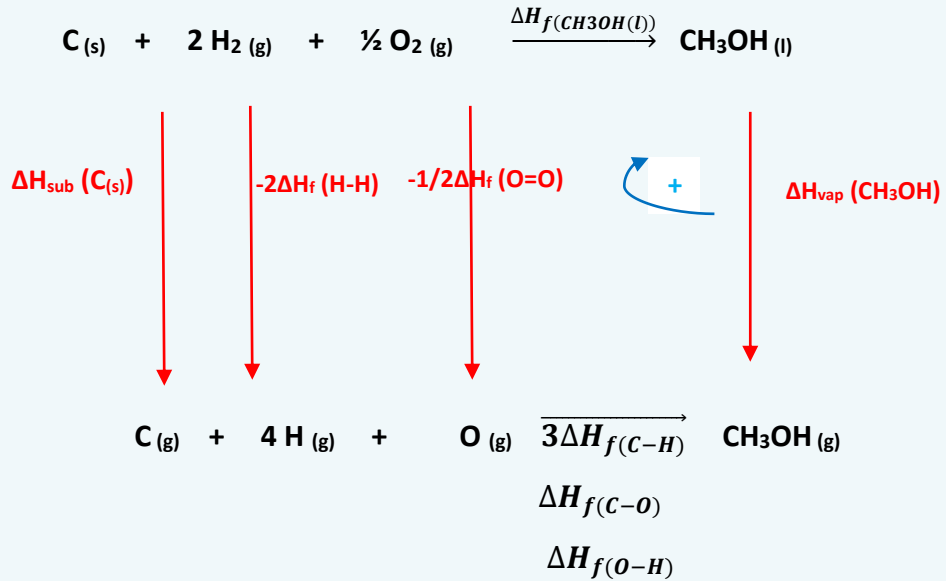
$$\sum \Delta H_i = 0$$

$$-\Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8 + \Delta H_{comb}^{(298K)} - \Delta H_{comb}^{(400K)} = 0$$

$$\Delta H_{comb}(400K) = \Delta H_{comb}(298K) - \Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 + \Delta H_8$$

$$\mathbf{\Delta H_{comb}(400K) = -668\ Kj}$$

3- The energy of the O-H bond

$$C_{(s)} + 2 H_{2 (g)} + \frac{1}{2} O_{2 (g)} \xrightarrow{\Delta H_{f(CH3OH(l))}} CH_3OH_{(l)}$$

ΔH_{sub} (C$_{(s)}$)   -2ΔH_f (H-H)   -1/2ΔH_f (O=O)   + ΔH_{vap} (CH$_3$OH)

$$C_{(g)} + 4 H_{(g)} + O_{(g)} \xrightarrow{3\Delta H_{f(C-H)}} CH_3OH_{(g)}$$

$$\Delta H_{f(C-O)}$$

$$\Delta H_{f(O-H)}$$

$$\sum \Delta H_i = 0$$

$$\Delta H_f(CH_3OH_{(l)}) + \Delta H_{vap}(CH_3OH) - 3\Delta H_f(C - H) - \Delta H_f(C - O) - \Delta H_f(O - H)$$

$$+ \frac{1}{2}\Delta H_f(O = O) + 2\Delta H_f(H - H) - \Delta H_{sub}(C_{f(s)}) = 0$$

$$\Delta H_f(O - H) = \Delta H_f(CH_3OH_{(l)}) + \Delta H_{vap}(CH_3OH) - 3\Delta H_f(C - H) - \Delta H_f(C - O)$$

$$+ \frac{1}{2}\Delta H_f(O = O) + 2\Delta H_f(H - H) - \Delta H_{sub}(C_{(s)})$$

$$\mathbf{\Delta H_f(O - H) = -4815.8 \, KJ.mol^{-1}}$$

IV.7.6 Flame temperature and explosion pressure

There are often temperature variations during a chemical reaction. If this variation is too abrupt, the reaction occurs in an adiabatic manner, allowing us to define two specific temperatures:

- The flame temperature, which is the temperature reached by an adiabatic reaction at constant pressure.
- The explosion temperature, which is the temperature reached by an adiabatic reaction at constant volume.

To calculate the flame temperature, the following thermochemical cycle is used:
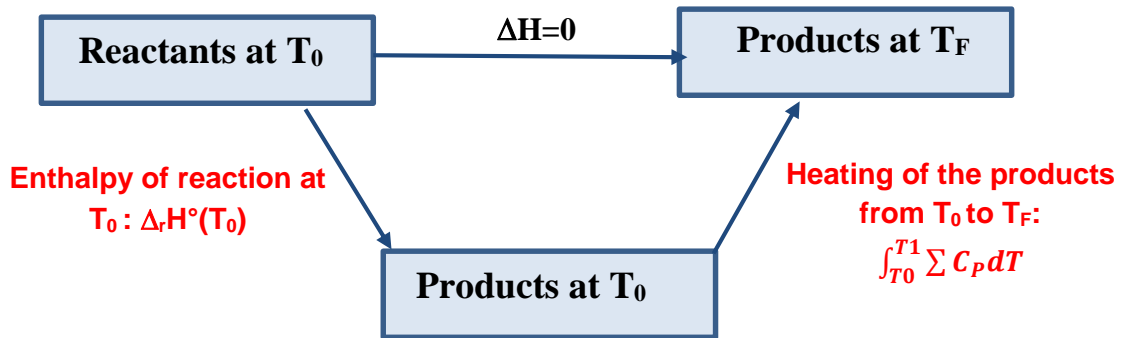
The first step is the complete reaction of n moles of reactants at constant temperature, so the associated change in enthalpy is: ΔH_1

The second step is the heating of the final product mixture, so the change in enthalpy is:

$$\Delta H_2 = \int_{T0}^{T1} \sum C_P dT$$

The process being adiabatic and at constant pressure, the change in enthalpy is zero, so:

$$\Delta H = \Delta H_1 + \Delta H_2 = 0$$

$$\Rightarrow \Delta T = \frac{-\Delta H_1}{\Delta H_2} = \frac{-\Delta H_r^{\circ}}{\sum C_P}$$

The standard enthalpy of reaction can be calculated at room temperature (around 298 K) using the enthalpies of formation.

Note

For an explosion temperature, the reasoning is similar, but it involves the change in internal energy and the heat capacities at constant volume.

Application IV.8 Calculate the flame temperature of CO burning in air, assuming the initial gases are at 298 K.

$$CO_{(g)} + \frac{1}{2} O_{2(g)} + 2N_{2(g)} \rightarrow CO_{2(g)} + 2N_{2(g)}$$
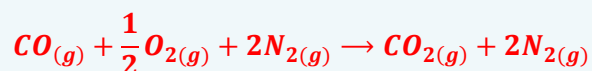
The standard molar enthalpies of formation and the standard molar heat capacities at constant pressure, Cp are given in cal·mol^{-1}·K^{-1}.

$$\Delta H_f(CO_{2(g)}) = -94.05 \ kcal.mol^{-1} \qquad \Delta H_f(CO_{(g)}) = -26.4 \ kcal.mol^{-1}$$

$$C_P(CO_{2(g)}) = 7.3 + 47.8 \ 10^{-4} \ T \qquad C_P(N_{2(g)}) = 6.5 + 10^{-3} \ T$$

It is assumed that such a reaction takes place at 298 K in an adiabatic enclosure. The heat released by the combustion is used to raise the temperature of the reaction products.

Solution

$$CO_{(g)} + \frac{1}{2}O_{2(g)} + 2N_{2(g)} \rightarrow CO_{2(g)} + 2N_{2(g)}$$
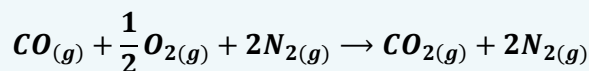
To calculate the standard enthalpy of the combustion reaction, Hess's law can be used:

$$\Delta H_r^{298} = \sum \Delta H_f(products) - \sum \Delta H_f(reactants)$$

$$\Delta H_r^{298} = \Delta H_f\left(CO_{2(g)}\right) - \Delta H_f\left(CO_{(g)}\right)$$

$$\Delta H_r^{298} = -67,65 \text{ Kcal}$$

All the heat released during complete combustion is used to raise the temperature of the products. This heat is therefore absorbed by the products, making the enthalpy positive in this case.

$$-\Delta H_r^{298} = \int_{298}^{T} \left(C_P\left(CO_{2(g)}\right) + 2C_P\left(N_{2(g)}\right)\right) dT$$

$$-\Delta H_r^{298} = \int_{298}^{T} (7.3 + 47.8 \ 10^{-4} \ T + 2(6.5 + 10^{-3} \ T)) dT$$

$$-\Delta H_r^{298} = 20.3[T - 298] + 6.78 \ 10^{-3} \left[\frac{T^2}{2} - \frac{298^2}{2}\right]$$

$$67650 = 3.39 \ 10^{-3} \ T^2 + 20.3 \ T - 6350.445$$

$$\Rightarrow \quad T = 2555 \ K$$

CHAPTER V

SECOND LAW OF THERMODYNAMICS

V.1 Introduction

The first principle (conservation of energy) imposes limits on possible thermodynamic transformations: for an isolated system, a transformation from state (a) to state (b) is only achievable if U(a)=U(b), meaning ΔU=0. Accordons to this first principle, if the transformation from (a) to (b) is possible, then the transformation from (b) to (a) is also possible. However, observations show that there is only one well-defined equilibrium state for each system (and each choice of U,V,N...), and that any isolated system spontaneously evolves irreversibly towards this equilibrium state. The first principle of thermodynamics isn't sufficient to explain this observation, necessitating a second principle, also known as the principle of evolution, to determine the equilibrium state. This principle, based on experimental facts, allows for predicting the evolution of systems and thus clarifies the nature of a transformation (reversible or irreversible) through a new state function called **entropy (S).**

V.1.1 Irreversibility and the evolution of natural phenomena

The observation of natural phenomena reveals a large number of spontaneous transformations that always occur in a specific direction. These transformations are irreversible, such as:

1. In an adiabatic enclosure, when a hot body is placed next to a cold body, it is observed that their temperatures eventually equalize.

2. A moving wheel is brought to a stop by the friction of the brake, which causes the brake to heat up. The change in internal energy of the brake corresponds to the loss of kinetic energy of the wheel. In contrast, the reverse process, where coping would convert into kinetic energy, although consistent with the first principle, never occurs.

V.1.2 Statements of the second law of thermodynamics

The second law, known in France as S. Carnot's principle, emerged in the early industrial era, between 1810 and 1860, from reflections on the operation of thermal machines. It was first articulated by the French physicist Sadi Carnot (1796 -1832) in 1824. Since then, it has undergone numerous generalizations and reformulations by Clapeyron (1834), Clausius (1850), Lord Kelvin, Ludwig Boltzmann in 1873, and Max Planck. The statements of this principle are:

General statement

  « An isolated system that has undergone an evolution cannot return to its initial state ».

Clausius statement

   « It is impossible to build a machine that, operating in a cycle of transformations, produces no effect other than transferring a certain positive amount of heat from a cold body to a hot body during the cycle ».

Kelvin statement

« It is impossible to build a machine that, operating in a cycle of transformations, produces at the end of the cycle no effect other than extracting a positive amount of heat from a single source and generating positive work (ven. when operating reversibly) ».

It can be easily demonstrated that these three statements are rigorously equivalent: the assertion of one of them allows for the demonstration of the others.

V.2 Concept of entropy

V.2.1 Introduction of the entropy function S of a system

We can define, for any system, a state function called entropy (noted S), which quantifies the disorder of a system. While internal energy measures the amount of energy, entropy evaluates how that energy is distributed. Low entropy indicates low disorder, whereas high entropy reflects significant disorder. The concept of entropy, as a state function SSS, was introduced by Clausius in 1854 on strictly mathematical grounds. The change dS of this function during an infinitesimal reversible transformation is expressed by the formula:

$$dS = \frac{dQ_{rev}}{T} \qquad\qquad V.1$$

The change in entropy during any elementary transformation of the system is the sum of two contributions

$$\Delta S_{tot} = \Delta S_{system} + \Delta S_{\text{External environment}} \qquad\qquad V.2$$

Entropy has the following properties:

1- It is an extensive additive quantity: if the system is divided into different parts, the entropy of the system is the sum of the partial entropies.

2- The entropy of a system strictly increases in an irreversible adiabatic transformation; it remains constant in a reversible or ideal adiabatic transformation.

3- In a non-adiabatic transformation, the change in entropy is the sum of two terms: one related to heat exchanges with the external environment, which can have any sign, and the other related to internal transformations, which varies as in case 2.

4- A transfer of work doesn't affect entropy by itself.

V.2.2 General Expression of the second law of thermodynamics

Considering the two postulates of Clausius and Kelvin, we envisions a transformation cycle during which:

- A machine extracts heat **Q** from a cold source at temperature $T_2 < T_1$ and transfers it entirely to a hot source at temperature T_1

- Since $T_2 < T_1$, this transfer of heat is impossible according to Clausius's statement, making this cycle practically irreversible
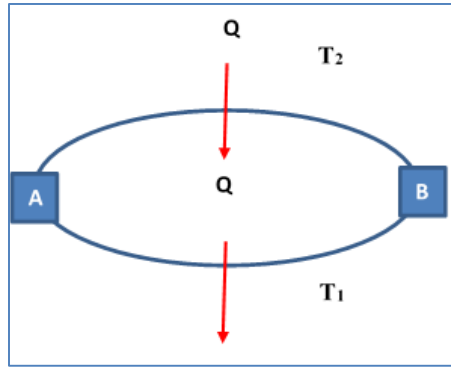
Figure V.1 *Imaginary cycle of a heat engine.*

The energy balance performed on this machine is written as follows:

$$\oint \frac{dQ}{T} = \frac{dQ}{T_2} + \frac{dQ}{T_1} \qquad\qquad V.3$$

$$\Rightarrow \int_A^B \frac{dQ}{T_2} + \int_A^B \frac{dQ}{T_1} = \int_A^B \frac{dQ}{T_2} - \int_A^B \frac{dQ}{T_1} = \frac{Q}{T_2} - \frac{Q}{T_1} > 0$$

$$\Rightarrow \sum \frac{dQ}{T} > 0$$

Given that it is impossible, according to Clausius, to transfer a quantity of heat from a cold source to fully give it to another hot source, we can conclude that in a real cycle of a machine, Clausius's theorem is upheld:

$$\sum \frac{dQ}{T} < 0 \qquad\qquad V.4$$

Therefore, we can deduce that for a reversible cycle:

$$\sum \frac{dQ}{T} = 0$$

And for an irreversible cycle:

$$\sum \frac{dQ}{T} < 0$$

Consider a thermodynamic cycle consisting of two reversible transformations: from A to B (transformation 1) and from B to A (transformation 2).
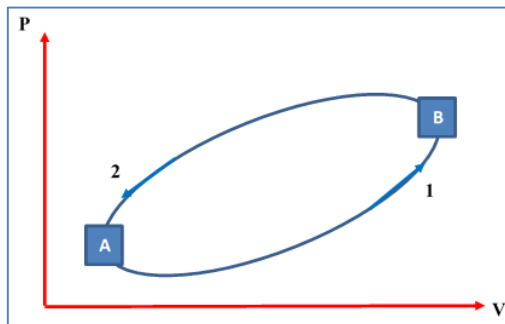
Figure V. 2 *Cycle of a reversible transformation*

Performing an energy balance on the cycle :

$$\sum \frac{dQ}{T} = \int_A^B \frac{dQ_1}{T} + \int_B^A \frac{dQ_2}{T} = 0$$

$$\Rightarrow \int_A^B \frac{dQ_1}{T} - \int_A^B \frac{dQ_2}{T} = 0$$

$$\Rightarrow \int_A^B \frac{dQ_1}{T} = \int_A^B \frac{dQ_2}{T} = \int_A^B \frac{dQ_{rev}}{T}$$

We deduce that the integral $\int_A^B \frac{dQ_{rev}}{T}$ for a reversible transformation:

- It depends only on the initial state (A) and the final state (B).
- It doesn't depend on the path taken.
- $\int_A^B \frac{dQ_{rev}}{T}$ is a state function known as entropy (S).

If we assume that :

$$S = \frac{dQ_{rev}}{T}$$

Then the change in entropy :

$$\Delta S = S_B - S_A = \int_A^B \frac{dQ_{rev}}{T} \qquad\qquad V.5$$

Now considering an irreversible cycle composed of an irreversible transformation from the initial state (A) to the final state (B) and a reversible transformation from (B) to (A).
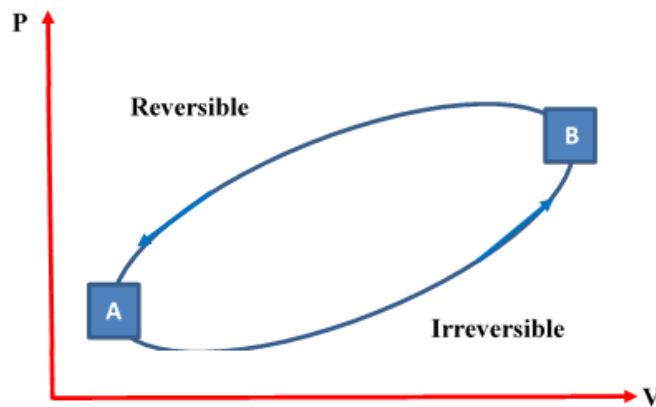
***Figure V.3** Cycle of an irreversible transformation*

Performing an energy balance on the cycle:

$$\sum \frac{dQ}{T} = \int_A^B \frac{dQ_{irrev}}{T} + \int_B^A \frac{dQ_{rev}}{T} < 0$$

$$\Rightarrow \int_A^B \frac{dQ_{irrev}}{T} - \int_A^B \frac{dQ_{rev}}{T} < 0$$

$$\Rightarrow \int_A^B \frac{dQ_{irrev}}{T} < \int_A^B \frac{dQ_{rev}}{T} \quad ; \frac{dQ_{irrev}}{T} < dS$$

$$\Delta S > \int_A^B \frac{dQ_{irrev}}{T} \qquad\qquad V.6$$

V.2.3 The entropy function SSS depends on P and T

Since S is an extensive state function that depends on T and P,we can break down this transformation into two steps so that only one parameter varies at a time
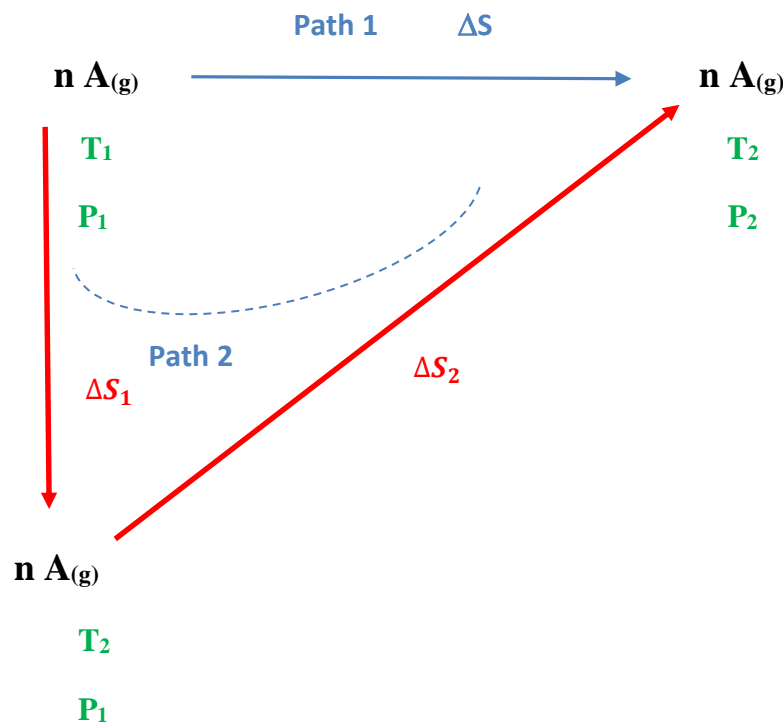
ΔS being a state function, we have: $\Delta S = \Delta S_1 + \Delta S_2$

The entropy is equal to:

$$\Delta S = nC_P \, ln\frac{T_2}{T_1} + nRln\frac{P_1}{P_2}$$

Calculation of the change in entropy

Depending on the type and nature of the transformation, the entropy of a thermodynamic system is given as follows :

Isothermal reversible transformation

$$\Delta S = \int_1^2 \frac{dQ_{rev}}{T} = \frac{1}{T}\int_1^2 dQ_{rev} = \frac{Q_{rev}}{T}$$

$$T = Cte \quad \Rightarrow \quad \Delta U = 0 \quad \Rightarrow Q = -W$$

$$W = \int_1^2 -PdV = -nRT \int_1^2 \frac{dV}{V} = -nRTln\frac{V_2}{V_1} = nRTln\frac{V_1}{V_2}$$

$$Q_{rev} = nRTln\frac{V_2}{V_1} = nRTln = \frac{P_1}{P_2}$$

$$\Delta S = \frac{Q_{rev}}{T} = nRln\frac{V_2}{V_1} = nRln = \frac{P_1}{P_2} \qquad\qquad V.7$$

Isobaric reversible transformation

$$P = Cte \quad \Longrightarrow \quad dQ_{rev} = dQ_P = nC_P dT$$

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = \int_1^2 \frac{dQ_P}{T} = \int_1^2 nC_P \frac{dT}{T}$$

$$\Delta S = nC_P ln\frac{T_2}{T_1} \qquad\qquad V.8$$

Isochoric reversible transformation

$$V = Cte \quad \Longrightarrow \quad dQ_{rev} = dQ_V = nC_V dT$$

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = \int_1^2 \frac{dQ_V}{T} = \int_1^2 nC_V \frac{dT}{T}$$

$$\Delta S = nC_V ln\frac{T_2}{T_1} \qquad\qquad V.9$$

Reversible adiabatic transformation

$$dQ_{rev} = 0$$

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dQ_{rev}}{T} = 0 \qquad\qquad V.10$$

Application IV.1 A mass of 25 g of dry air occupies a volume of 20 liters at +7 °C and under a pressure of 1 bar. It undergoes the following transformations:

- Isothermal compression to a pressure of 4 bars ;
- Isobaric process to return to the initial volume ;
- Isochoric process to return to the initial temperature.

Calculate the changes in entropy for each transformation, as well as for the total transformation.

Data**:**   **C_P=0.24 cal.g^{-1}.K^{-1}**   **C_V=0.17 cal.g^{-1}.K^{-1}**   **γ=1.4**

Solution :

1st state: A $\begin{cases} P_A = 1bar \\ V_A = 20\ l \\ T_A = 280\ K \end{cases}$ **2nd state: B** $\begin{cases} P_B = 4bar \\ V_B = \frac{P_A V_A}{P_B} = 5\ l \\ T_B = T_A = 280\ K \end{cases}$

3rd state: C $\begin{cases} P_C = P_B = 4bar \\ V_C = V_A = 5\ l \\ T_C = \frac{P_C V_C}{P_B V_B} T_B = 1120\ K \end{cases}$

Transformation AB (T=Cte)

$$\Delta S = \frac{Q_{rev}}{T} = nRln\frac{V_B}{V_A} = -2.36\ cal.\,K^{-1}$$

Transformation BC (P=Cte)

$$\Delta S = mC_P ln\frac{T_C}{T_B} = 8.29\ cal.\,K^{-1}$$

Transformation CA (V=Cte)

$$\Delta S = mC_V ln\frac{T_A}{T_C} = -5.92\ cal.\,K^{-1}$$

For the complete cycle, which is closed, the total change in entropy must be zero.

$$\Delta S_{tot} = \sum \Delta S_i = -2.36 + 8.29 - 5.92 = 0$$
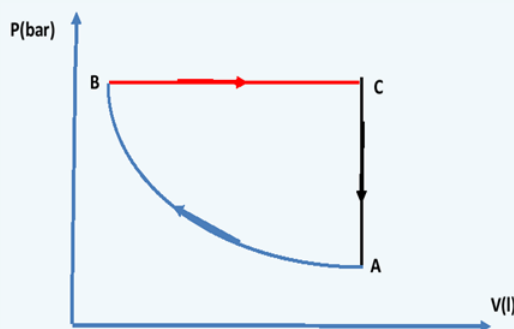
V.2.4 The entropy of a solid and a liquid

According to the first law of thermodynamics, we have seen that for liquids and solids:

$$dH \approx dU \approx CdT$$

Where **C** is the specific heat:

$$\text{As elsewhere } dU = dQ - PdV = TdS - PdV \qquad\qquad V.11$$

$$\text{And } dH = TdS + VdP \qquad\qquad V.12$$

We have :

$$dS = \frac{dU}{T} = C\frac{dT}{T} \qquad\qquad V.13$$

The specific heat of solids and liquids being approximately constant, we can integrate this expression and obtain:

$$\Delta S = S_2 - S_1 = C\frac{dT}{T} \qquad\qquad V.14$$

V.2.5 The entropy of an ideal gas

The entropy of an ideal gas is obtained directly from equations V.11 and V.12, the expressions for internal energy and enthalpy and the ideal gas law :

$$TdS = dU + PdV = C_V dT + PdV$$

By dividing by T:

$$dS = C_V\frac{dT}{T} + \frac{P}{T}dV = C_V\frac{dT}{T} + R\frac{dV}{V} \qquad\qquad V.15$$

We obtain by integrating

$$\Delta S = S_2 - S_1 = \int_1^2 C_V\frac{dT}{T} + nRln\frac{V_2}{V_1} \qquad\qquad V.16$$

Similarly,

$$TdS = dH - VdP = C_P dT - VdP$$

By dividing by T :

$$dS = C_P\frac{dT}{T} - \frac{V}{T}dP = C_P\frac{dT}{T} - nR\frac{dP}{P} \qquad\qquad V.17$$

We obtain by integrating

$$\Delta S = S_2 - S_1 = \int_1^2 C_P\frac{dT}{T} - nRln\frac{P_2}{P_1} \qquad\qquad V.18$$

With the approximation of constant specific heats, these two expressions can be integrated analytically :

$$\Delta S = S_2 - S_1 = C_V ln\frac{T_2}{T_1} + nRln\frac{V_2}{V_1} \qquad\qquad V.19$$

$$\Delta S = S_2 - S_1 = C_P ln\frac{T_2}{T_1} - nRln\frac{P_2}{P_1} \qquad\qquad V.20$$

V.2.6 The entropy of ideal gases mixture

For a mixture of two distinct ideal gases, denoted as (1) and (2), which are initially under the same pressure and temperature conditions, confined in an adiabatic chamber and separated by a wall **(fig V-4).**
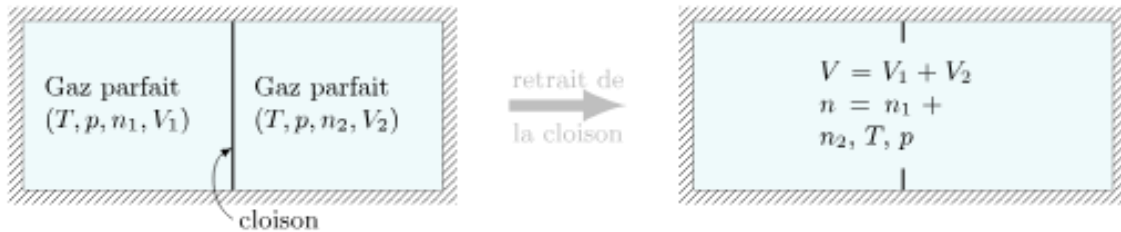
Figure V.4 Mixture of two ideal gases

Let's remove the wall and wait for thermodynamic equilibrium to be reached. During this transformation, the temperature and pressure remain constant. Indeed, considering the system made up of the two gases, there is neither heat transfer nor work done, which means that the internal energy remains unchanged.

$$\Delta U = \int_{T}^{T_f} C_{V1} \, dT + \int_{T}^{T_f} C_{V2} \, dT = 0 \qquad\qquad V.21$$

It follows that the temperature doesn't change : $T_f = T.$ The same applies to the pressure, due to the conservation of matter: $n = n_1 + n_2.$ Let :

$$\frac{P_f(V_1 + V_2)}{RT} = \frac{PV_1}{RT} + \frac{PV_2}{RT} \qquad\qquad V.22$$

The removal of the partition releases an internal constraint and allows for chemical equilibrium. This relaxation produces entropy, referred to as **mixing entropy**. Let's use formula V.19 to express the change in entropy of the system:

$$\Delta S = \Delta S_1 + \Delta S_2 = n_1 R ln\left(\frac{V_1 + V_2}{V_1}\right) + n_2 R ln\left(\frac{V_1 + V_2}{V_2}\right) \qquad\qquad V.23$$

For an ideal gas, we have:

$$\frac{V_1 + V_2}{V_1} = \frac{1}{x_1} \; et \; \frac{V_1 + V_2}{V_2} = \frac{1}{x_2}$$

We arrive at the result

$$\Delta S = -(n_1 R ln \, x_1 + n_2 R ln \, x_2) \qquad\qquad V.24$$

Since the mole fractions x_1 and x_2 are between 0 and 1, the change in entropy is necessarily positive. Mixing is an irreversible phenomenon.

V.2.7 The entropy of phase change

Phase changes between phase α and phase β occur at constant pressure or temperature, as during the entire transformation, phases α and β coexist, and the pressure must equal the coexistence pressure: $\mathbf{P = P_{\alpha\beta}(T).}$

Let's consider the reversible transformation, at constant P and T, from state A with all the matter in phase **α** to state B with all the matter in phase **β**. We want to calculate the heat Q received by the system. The transformation is isobaric, so **Q = ΔH**, but the transformation is also reversible and isothermal, so the entropy is equal to:

$$\Delta S = \frac{\Delta H}{T} \qquad\qquad V.25$$

ΔH : The molar enthalpy of phase change or molar latent heat of phase change at P = C^{ste}.

T : The transformation temperature at which the two states are in equilibrium.

Example**:**

During the melting of one mole of ice at 273.15 K under a pressure of one atmosphere:

$$H_2O_{(solid)} \rightarrow H_2O_{(liquid)} \qquad\qquad \Delta H_{fusion} = 1436\ cal.mol^{-1}$$

The change in entropy is positive and corresponds to an initial state that is more ordered than the final state:

$$\Delta S = \frac{\Delta H_{fusion}}{T} = \frac{1436}{273.15} = 5.257\ cal.K^{-1}$$

V.2.8 The entropy of reversible and irreversible adiabatic transformations

Consider an infinitesimal adiabatic transformation of an arbitrary system. The amount of heat **dQ** received by the system is zero. This immediately leads us to conclude that **dS ≥ 0**. The entropy of a system cannot décriasse in an adiabatic transformation.

If the **adiabatic** transformation is **real (irreversible),** we will have:

$$\frac{dQ}{T} \leq dS$$

$$dQ = 0 \Longrightarrow dS > 0$$

In any irreversible adiabatic transformation, the entropy of the system continuously increases, and the calculation is made using intermediate paths rather than the direct path.

If the **adiabatic** transformation **is reversible**, we will have:

$$\frac{dQ}{T} = dS$$

$$dQ = 0 \Longrightarrow dS = 0$$

In any reversible adiabatic transformation, the entropy of the system remains constant.

V.2.9 Creation of entropy due to irreversible transformations

The change in entropy of a system during any transformation can be described as the sum of two terms:

$$dS_{sys} = dS_{int} + dS_{ext}$$

dS_{int} This refers to the variation of internal entropy, which reflects the creation of entropy within the system. It does not depend on exchanges with the external environment and varies only with the degree of irreversibility of the transformation and the resulting disorder within the system.

- During a **reversible** transformation, the system is in equilibrium at all times → **dS_int = 0**
- During an **irreversible** transformation, entropy is created: **S_int↗→ dS_int > 0**

dS_{ext} is the change in external entropy due to heat exchanges **dQ** with the external environment.

$$dS_{ext} = \frac{dQ}{T}$$

$$dS_{sys} = dS_{int} + \frac{dQ}{T}$$

$$\Delta S_{sys} = \Delta S_{crée} + \frac{dQ}{T} \qquad\qquad V.26$$

When dealing with an irreversible transformation, the change in entropy of an isolated system can be assessed by considering reversible processes that would lead the system to the same final state. From a microscopic perspective, the molecular disorder of a system and its environment remains constant during a reversible transformation, while it increases in the case of an irreversible transformation.

Application V.2 Calculate the entropy created when one liter of water at 98°C is brought into contact with the atmosphere at 20°C, in the following two cases:

- Sudden **contact (irreversible path).**
- Gradual and slow contact **(reversible path)**.

Solution

S is a state function⇒ ΔS_rev = ΔS_irrev

$$\Delta S_{rév} = \int_{371}^{293} \frac{mcdT}{T} + \Delta S_{crée} = -236,029 \; cal.K^{-1}$$

With $\Delta S_{crée} = 0$

Moreover $\quad \Delta S_{irrév} = \frac{mc(T_f - T_i)}{T_{ext}} + \Delta S_{crée} = -266.21 \; cal.K^{-1} + \Delta S_{crée}$

$$\Delta S_{crée} = 266.21 - 236.029 = 30.18 \; cal.K^{-1}$$

V.2.10 Entropy balance

To make an entropy balance, the following steps must be followed:

a) Model the system, generally a perfect gas or an incompressible and non-dilatable phase.

b) Calculate the total change in entropy

- For perfect gas $\Delta S = C_v \ln\frac{T_f}{T_i} + nR\ln\frac{V_f}{V_i}$
- For an incompressible and non-dilatable phase $\Delta S = mc \ln\frac{T_f}{T_i}$

It is sometimes useful to express ΔS in terms of other quantities using the equation of state of an ideal gas.

c) Calculate the entropy received by the system with T_0 as the temperature of the thermostat.

d) Calculate the entropy created within the system. $S_{created} = \Delta S - S_r$

e) Conclude regarding the reversible nature **(S_c =0)** or irreversible nature **(S_c>0)** of the transformation.

V.2.11 Criteria for the evolution of an isolated system (dS created≥ 0)

According to the second law of thermodynamics, which states that during a spontaneous transformation, the entropy S of the universe (system + surroundings) can only increase. Its change is zero for a reversible transformation and positive for an irreversible transformation. $\Delta S_{universe} = \Delta S_{system} + \Delta S_{environment}$

For isolated systems, ΔS_environment = 0, and ΔS_universe = ΔS_system. The change in entropy of the system can then be:

- It is **positive** if it leads to an **increase in disorder**, ΔS > 0 ;
- It is **negative** if it leads to an **increase in order**., ΔS < 0.

V.3 Thermal machines

Thermal machines typically operate using a fluid subjected to cyclical transformations, during which there is an exchange of energy with the environment: the system receives both work and heat. According to the second law of thermodynamics, a thermal machine cannot operate with a single heat source. In other words, it is impossible for a machine, during a cycle of transformations, to produce work by extracting heat from just one source. Thermal machines must satisfy the two laws of thermodynamics:

- First law: $W_{cycle} + Q_1 + Q_2 = 0$

- Second law: $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$ **Reversible cycle**

V.3.1 Application of the Carnot cycle

A system is said to undergo a diathermal cycle when it exchanges heat with two heat sources at temperatures **T₁** and **T₂**, with which it is successively in contact. The Carnot cycle

is an ideal cycle, achieving maximum efficiency compared to other cycles. It is a reversible cycle described by a diathermal machine, consisting of two **isothermal** transformations at the temperatures of the sources, and two **adiabatic (isentropic)** transformations separating the two isotherms.

- ✓ **1-2:** Isothermal expansion (with heat input): **$T_1 = T_2$ (Hot source).**
- ✓ **2-3 :** Adiabatic expansion : from **T_2 to T_3**
- ✓ **3-4:** Isothermal compression (with cooling): **$T_3 = T_4$ (Cold source).**
- ✓ **4-1 :** Adiabatic compression : from **T_4 to T_1.**

The shape of this cycle is shown in Figure V.5 below:
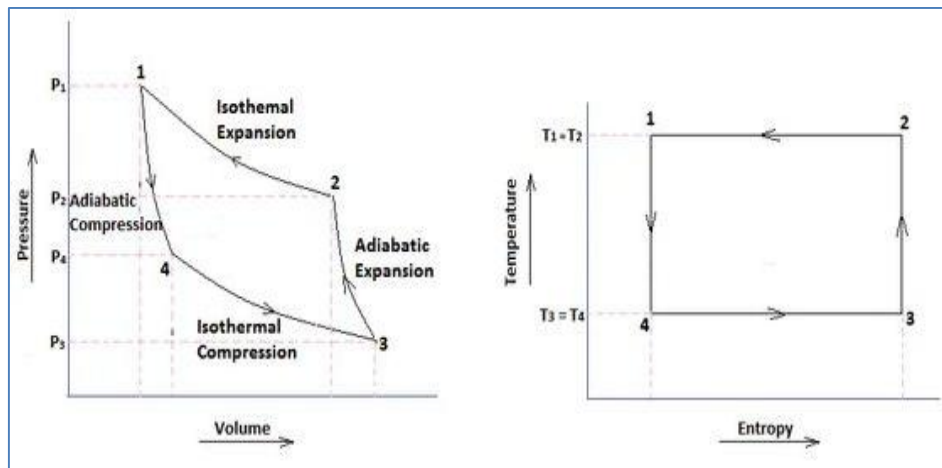
Figure V.5 *Clapeyron diagram (P, V) and (T, S) diagram for the Carnot cycle.*

Heat exchange balance of the Carnot cycle

1- The transformations AB and CD are isothermal, therefore PV = Cte

$$\mathbf{P_A V_A = P_B V_B} \rightarrow \frac{V_B}{V_A} = \frac{P_A}{P_B} \qquad \dots\dots (A)$$

$$\mathbf{P_C V_C = P_D V_D} \rightarrow \frac{V_C}{V_D} = \frac{P_D}{P_C} \qquad \dots\dots (B)$$

The transformations BC and DA are adiabatic $P V^\gamma = C^{te}$ and $T V^{\gamma-1} = C^{te}$

Between BC $\qquad \mathbf{T_B V_B^{\gamma-1} = T_C V_C^{\gamma-1}} \qquad \dots\dots (1)$

Between DA $\qquad \mathbf{T_D V_D^{\gamma-1} = T_A V_A^{\gamma-1}} \qquad \dots\dots (2)$

We have $\quad T_B = T_A = T_2 \qquad$ and $\quad T_C = T_D = T_1$

$$(1) \rightarrow V_C = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} V_B \qquad \dots\dots (a)$$

$$(2) \rightarrow V_D = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} V_A \qquad \dots\dots (b)$$

$(a)\big/(b)$ we obtain; $\quad \dfrac{V_C}{V_D} = \dfrac{V_B}{V_A} \qquad \dots\dots (C)$

En combinant les équations (A), (B) et (C) on obtient : By combining equations (A), (B), and (C) we obtain:

$$\frac{V_C}{V_D} = \frac{V_B}{V_A} = \frac{P_D}{P_C} = \frac{P_A}{P_B}$$

2- The literary calculation of the different energies.

Transformation AB is isothermal

$$\Delta U_{AB} = 0$$

$$W_{AB} + Q_{AB} = 0 \rightarrow Q_{AB} = -W_{AB}$$

$$W_{AB} = -\int_A^B P \, dV = -\int_A^B \frac{nRT}{P} \, dV = -nRT_2 \ln \frac{V_B}{V_A}$$

$$Q_{AB} = -W_{AB} = nRT_2 \ln \frac{V_B}{V_A}$$

Transformation BC is adiabatic

$$Q_{BC} = 0$$

$$\Delta U_{BC} = W_{BC} = nC_V (T_C - T_B) = nC_V (T_1 - T_2)$$

Transformation CD is isothermal

$$\Delta U_{CD} = 0$$

$$W_{CD} + Q_{CD} = 0 \rightarrow Q_{CD} = -W_{CD}$$

$$W_{CD} = -\int_C^D P \, dV = -\int_C^D \frac{nRT}{P} \, dV = -nRT_1 \ln \frac{V_D}{V_C}$$

$$Q_{CD} = -W_{CD} = nRT_1 \ln \frac{V_D}{V_C}$$

Transformation DA is adiabatic

$$Q_{DA} = 0$$

$$\Delta U_{DA} = W_{DA} = nC_V (T_A - T_D) = nC_V (T_2 - T_1)$$

3- The calculation of the change in internal energy of the cycle

$$\Delta U_{cycle} = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CD} + \Delta U_{DA}$$

$$\Delta U_{cycle} = 0 + nC_V (T_1 - T_2) + 0 + nC_V (T_2 - T_1) = 0 \, J$$

$$\Delta U_{cycle} = W_{cycle} + Q_{cycle} = 0 \Rightarrow W_{cycle} + Q_{AB} + Q_{BC} = 0 \Rightarrow W_{cycle} = -(Q_{AB} + Q_{BC})$$

Two cases can arise depending on whether the system operates as an **engine** providing work (W < 0) or as a **refrigeration machine** (receiver) absorbing work.

V.3.1.1 Thermal engines

The system operates as an engine, we have **W<0** and **Q_1+Q_2>0.**

There are three hypotheses that can be considered:

Hypothesis (a) $Q_1 > 0$ and $Q_2 > 0$

The two sources have each supplied heat to the system. Considering a third source, at a higher temperature than the other two, capable of returning the respective quantities of heat **Q_1** and **Q_2** to bring them back to their initial state through a single source, this would lead to a system with only one source. Since such a system could not produce positive work, this hypothesis is therefore dismissed.

Hypothesis (b) $Q_1 < 0$ et $Q_2 > 0$ with $|Q_1| < Q_2$

The hot source received heat and the cold source supplied it. Considering a third source at an intermediate temperature between the two sources to bring them back to their initial state, resulting in a system with only one source, is impossible.

Hypothesis (c) $Q_1 > 0$ et $Q_2 < 0$ with $Q_1 > |Q_2|$

The hot source supplies heat and the cold source receives it.

The condition $Q_1 + Q_2 > 0$ implies that $|Q_2| < Q_1$. This case, that of the steam engine, is the only possible one.

Conclusion:

A machine with two heat sources receives heat from the hot source and return a fraction to the cold source; the work produced corresponds to the difference between the amount of heat taken from the hot source and the amount of heat given to the cold source.

V.3.1.2 Refrigeration machines

The system operates as a receiving machine, we have **W>0** and **Q_1+Q_2<0.**

There are three hypotheses that can be considered :

Hypothesis (a) $Q_1 < 0$ and $Q_2 < 0$

The work absorbed is converted into heat, which is distributed between the two sources. This case has little practical interest.

Hypothesis (b) $Q_1 > 0$ et $Q_2 < 0$ with $Q_1 < |Q_2|$

The hot source supplies heat, the cold source receives this heat and additionally receives the equivalent of the work absorbed by the machine, which is even less interesting than the previous case.

Hypothesis (c) $Q_1 < 0$ et $Q_2 > 0$ with $|Q_1| > Q_2$

The cold source supplies heat, the hot source receives this heat and also receives the equivalent of the work absorbed by the machine. This very interesting case is that of refrigeration machines : it allows for removing heat from the cold source (cooling it), but it also enables the use of the heat given to the hot source as a means of heating.

V.3.1.3 Clausius equality

It must be verified that:

$$\sum \frac{Q_i}{T_i} = 0$$

$$\frac{Q_{AB}}{T_2} + \frac{Q_{CD}}{T_1} ?? = ?? 0$$

$$Q_{AB} = -W_{AB} = nRT_2 \ln \frac{V_B}{V_A} \quad \text{and} \quad Q_{CD} = -W_{CD} = nRT_1 \ln \frac{V_D}{V_C}$$

$$\frac{Q_{AB}}{T_2} + \frac{Q_{CD}}{T_1} = nR\ln \frac{V_B}{V_A} + nR\ln \frac{V_D}{V_C} = nR\ln \frac{V_B}{V_A} - nR\ln \frac{V_C}{V_D}$$

$$= nR\ln \frac{V_B}{V_A} - nR\ln \frac{V_B}{V_A} = 0$$

(Since; $\frac{V_C}{V_D} = \frac{V_B}{V_A}$) therefore the **Clausius equality is verified.**

V.3.1.4 The thermal efficiency of a machine

The efficiency of an engine is the percentage of absorbed energy that the engine can convert into useful work. The equation for this is :

$$\eta = \frac{|W|}{Q_{Hot\ source}}$$

W **:** Work done

$Q_{Hot\ source}$ **:** Energy absorbed

$$\begin{cases} \Delta U = Q_f + Q_c + W = 0 \\ \Delta S = \frac{Q_c}{T_c} + \frac{Q_f}{T_f} = 0 \end{cases} \Rightarrow \begin{cases} W = -(Q_f + Q_c) \\ \frac{Q_c}{T_c} + \frac{Q_f}{T_f} \leq 0 \end{cases} \Rightarrow W \geq -Q_c + \frac{Q_c T_f}{T_c} = -Q_c \left(1 - \frac{T_f}{T_c}\right)$$

Thus, the efficiency can be rewritten:

$$\eta = \frac{|W|}{Q_{Hot\ source}} = 1 - \frac{T_f}{T_c}$$

- The efficiency is always less than 1.
- The maximum efficiency (or Carnot efficiency) corresponds to an engine operating reversibly.

### V.3.2 Application to some engine cycles

V.3.2.1 Joule cycle (or Brayton cycle)

The theoretical Brayton cycle, also known as the Joule cycle, is the fundamental cycle for systems equipped with gas turbines, in which combustion occurs at constant pressure. It was first proposed by George Bailey Brayton, an American mechanic (1830-1892), in the alternative piston engine he developed around 1870.

The cycle undergoes a series of four processes: two isentropic processes (reversible adiabatic) alternated with two isobaric processes **(fig V.6)**.

- Isentropic compression.
- Isobaric heating (combustion).
- Isentropic expansion.
- Isobaric cooling (exhaust)
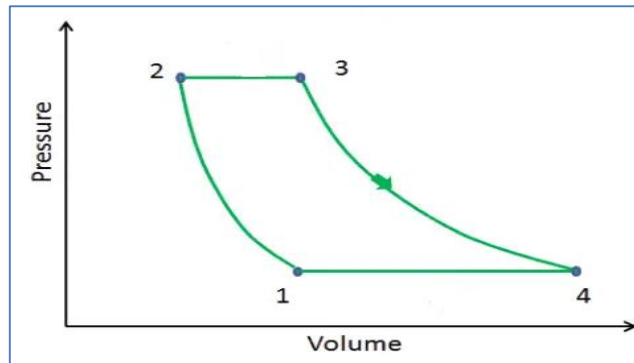
Figure V. 6 *Clapeyron diagram (P, V) for the Joule cycle*

V.3.2.2 Otto cycle (or Beau de Rochas cycle)

In 1876, Nikolaus August Otto (German engineer, 1832-1891) advanced the study of thermal engines by building the first operational four-stroke engine. It was a stationary engine using a coal-air-gas mixture as fuel. The Otto cycle describes the operation of internal combustion engines (which use gasoline), such as automobiles and lawnmowers. Unlike the Carnot cycle, the Otto cycle doesn't perform isothermal processes, as these must be carried out very slowly. In an ideal Otto cycle, the system undergoing the cycle undergoes a series of four internally reversible processes: two isentropic processes (reversible adiabatic) alternated with two isochoric processes **(fig V.7).**

- Adiabatic compression (ignition phase)
- Isochoric compression.
- Adiabatic expansion.
- Isochoric decompression (exhaust stroke)
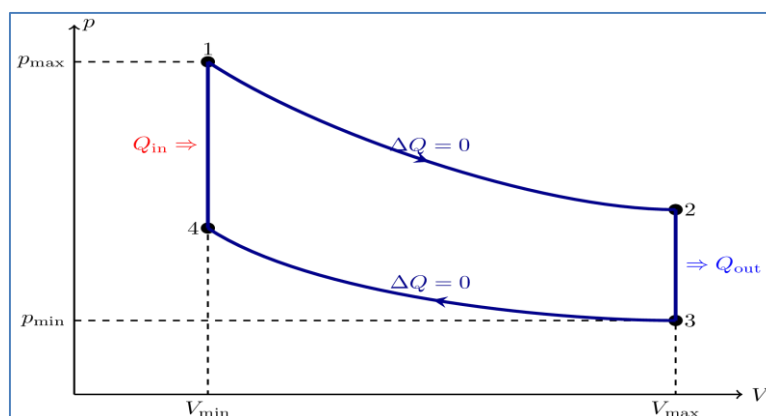
Figure V.7 *Clapeyron diagram (P, V) for the Otto cycle*

V.3.2.3 Diesel cycle

In the 1890s, a German inventor, **Rudolf Diesel (**1858-1913), patented his invention of an efficient internal combustion engine with slow combustion, which bears his name. The theoretical diesel cycle is a thermodynamic process that describes the operation of diesel engines, commonly found in transport vehicles, generator sets, and industrial machinery.

The theoretical diesel engine cycle consists of four reversible transformations represented in the Clapeyron diagram below **(fig V.8)**

- Adiabatic compression
- Reversible isobaric transformation
- Adiabatic expansion.
- Reversible isochoric transformation.
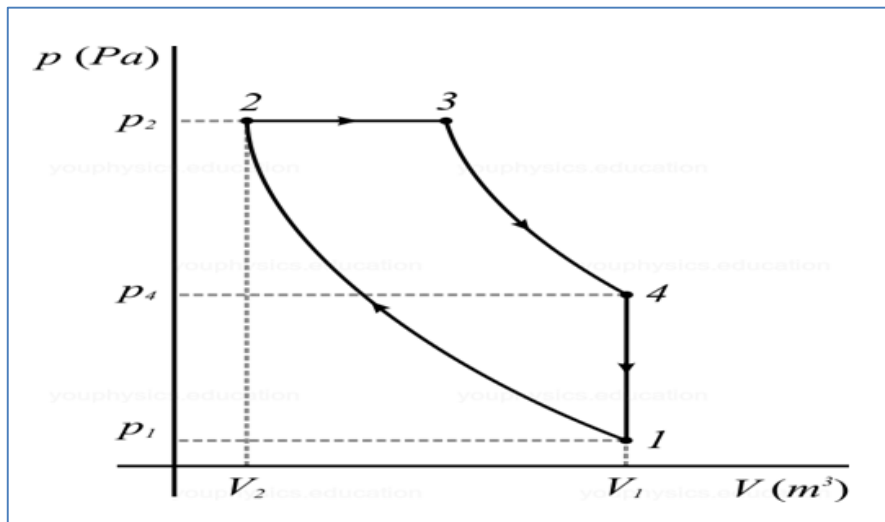
Figure V.8 *Clapeyron diagram (P, V) for the Diesel cycle*

V.3.2.4 Stirling cycle

The Stirling engine is an external combustion engine, invented by Robert Stirling in 1816. It is a motor that operates on a closed cycle. This characteristic differentiates it from other types of engines, such as the Otto engine or the diesel engine, which are internal combustion engines.

The cycle undergoes a series of four processes: two isothermal processes alternated with two isochoric processes **(fig V.9):**

- Isothermal compression.
- Isochoric heating.
- Isothermal expansion.
- Isochoric cooling.
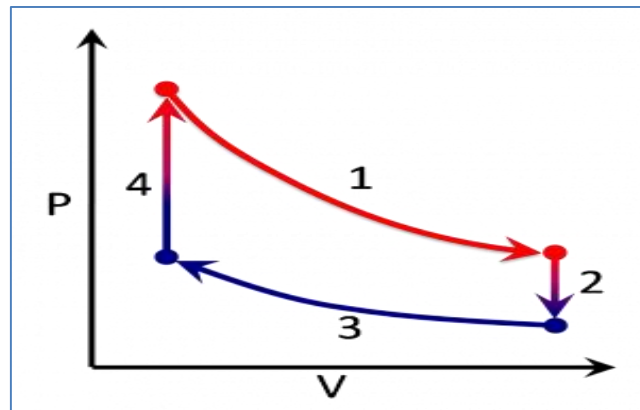
Figure V.9 *Clapeyron diagram (P,V) for the Stirling cycle*

CHAPTER VI

THIRD PRINCIPLE AND ABSOLUTE ENTROPY

VI.1 <u>Statement of the 3rd principle, absolute entropy at zero kelvin (0 K)</u>

The third principle of thermodynamics, also known as Nernst's theorem or Nernst's postulate, deals with the entropy and temperature of a physical system. Based on the results of experiments conducted at low temperatures on pure substances (notably in electrochemistry and calorimetry), Nernst (German physicist and chemist, 1864-1941) formulated the principle that bears his name. « At a temperature of zero kelvin, the entropy of any pure substance, perfectly crystallized in its stable form (solid with ordered structure), is zero : S = 0».

This means that the crystalline structure has the maximum level of order (perfect crystal). Moreover, at this temperature, thermal energy is at its minimum due to the absence of thermal agitation.

<u>Note:</u> Gases have higher entropies than liquids and solids.
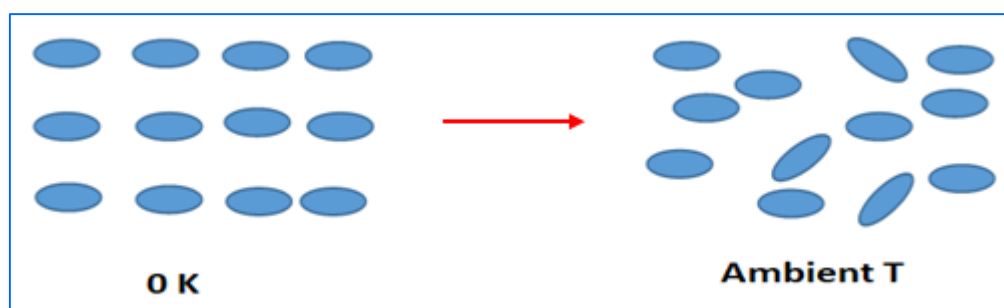
Figure VI.1 *Crystalline structure of the solid at 0 K and at ambient temperature*.

VI.2 <u>Standard molar absolute entropy of a pure substance S_{298K}^0</u>

In the standard state, the molar absolute entropy of a pure substance A at a temperature of 298 K is denoted $S_{A,298}^0$: It is the change in entropy ΔS of a transformation carried out under reversible conditions and at a pressure of 1 bar. If we assume that species A is in the gaseous state at 298 K, we cané write: $A_s(0K) \rightarrow A_g(298\ K)$

$$\Delta S = S_{A(g)298K}^0 - S_{A(s)0k}^0 \qquad\qquad VI.1$$

Since $S_{A(s)0k}^0$

So $\Delta S = S_{A(g)298K}^0$

The change in entropy is equal to the entropy of the final state minus the entropy of the initial state, which is zero (third principle).

Table VI.1 Standard molar entropies of some elements at T=298K and P=1bar			
Substance	**S° (J.mol^{-1}.K^{-1})**	**Substance**	**S° (J.mol^{-1}.K^{-1})**
$H_{2(g)}$	130.7	$Fe_{(s)}$	27.3
$O_{2(g)}$	205.2	$FeO_{(s)}$	58.6
$H_2O_{(l)}$	70.0	$Fe_2O_{3\,(s)}$	87.4
$H_2O_{(g)}$	188.8	$Fe_3O_{4\,(s)}$	146.4
$H_2O_{2(l)}$	109.6	$FeCl_{2\,(s)}$	118.0
$H_2O_{2(g)}$	232.7	$C_{(graphite)}$	5.7
$N_{2(g)}$	191.6	$CO_{2(g)}$	213.8
$NH_{3(g)}$	192.8	$CH_{4(g)}$	186.3

VI.3 Standard molar absolute entropy at T Kelvin (TK)

The molar absolute entropy of a pure compound A at temperature T is the change in its entropy between zero Kelvin and temperature T.

$$\Delta S^{\circ} = S^{\circ}_{final} - S^{\circ}_{initial} = S^{\circ}_T(A) - S^{\circ}_0(A) = \quad S^{\circ}_T(A) - 0 = \quad S^{\circ}_T(A) \qquad VI.2$$

$S^{\circ}_T(A)$: The molar absolute entropy at temperature T.

$S^{\circ}_0(A)$: The molar absolute entropy at zero Kelvin (T=0 K).

VI.4 Standard molar absolute entropy S$_T$ of a pure (solid, liquid, gas)

The molar absolute $S_T(A)$ of a pure substance at any temperature T can be calculated by considering all entropy terms, from the initial state (T = 0 K, S$_0$ = 0) to the temperature in question.

$$\Delta S^{\circ} = S^{\circ}_T(A) = \int_0^T \frac{\delta Q_{rev}}{T} = \int_0^T \frac{C_P dT}{T} \qquad VI.3$$

Example: For the calculation of the pure substance entropy in the gaseous state, the following transformations are taken into account:
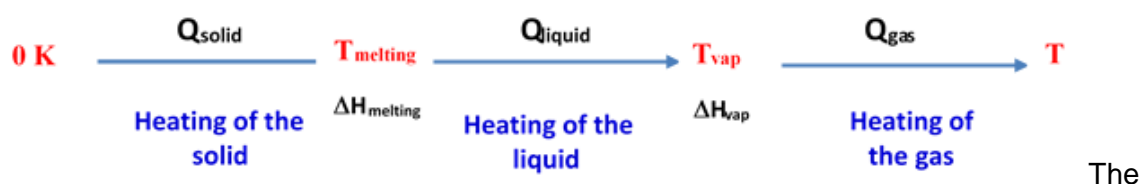
The absolute entropy at temperature T is the sum of the entropies of the various changes illustrated in Figure V.2:

$$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$$

With:

ΔS_1 Change in entropy during the heating of the solid.

ΔS_2 Change in entropy during melting.

ΔS_3 Change in entropy during the heating of the liquid.

ΔS_4 Change in entropy during vaporization.

ΔS_5 Change in entropy during the heating of the gas.

$$S_T = \int_0^{Tmelt} \frac{C_P(s)dT}{T} + \frac{\Delta H_{melting}}{T_{fmelting}} + \int_{Tmelt}^{Tvap} \frac{C_P(l)dT}{T} + \frac{\Delta H_{vap}}{T_{vap}} + \int_{Tvap}^{T} \frac{C_P(g)dT}{T} \quad VI.4$$

The calculation of molar absolute entropy requires knowledge of the enthalpy changes associated with phase transitions and the heat capacities in the solid, liquid, and gas states
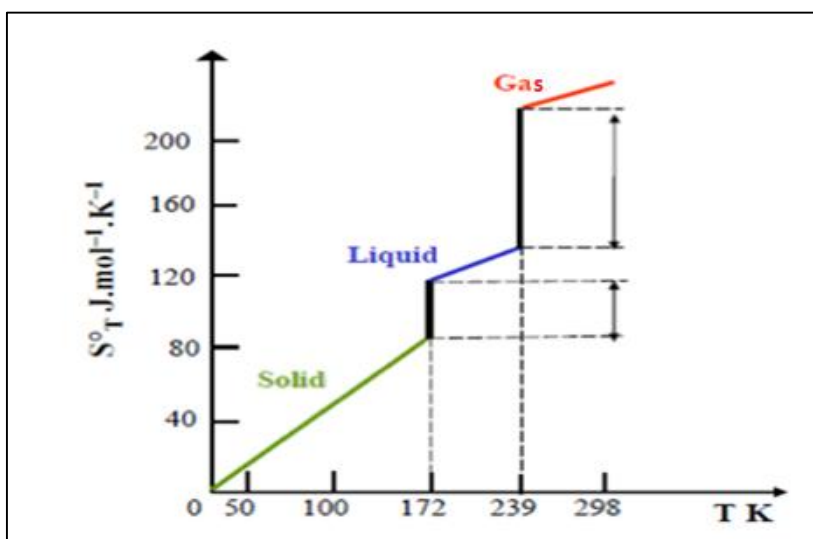
Figure VI.2 *Variation of the chlorine entropy (Cl₂) with temperature*

It is noted that $\Delta S^{\circ}_{vap} > \Delta S^{\circ}_{melting}$ implies an increase in disorder $\Rightarrow$ the number of microscopic states is greater during vaporization than during melting.

VI.5 <u>The change in entropy of a chemical reaction ΔS_R</u>

The reaction entropy ΔS_r, or the change in entropy associated with a chemical reaction, corresponds to the difference between the sum of the absolute entropies of the products and that of the reactants, under the temperature and pressure conditions of the reaction. For an ideal system, the molar entropies of the pure substances are considered:

$$\Delta S_r = \sum n_i S_{i(products)} - \sum n_i S_{i(reactants)} \qquad VI.5$$

If the reaction occurs under standard conditions, the standard reaction entropy is expressed as:

$$\Delta S^{\circ}_r = \sum n_i S^{\circ}_{i(products)} - \sum n_i S^{\circ}_{i(reactants)} \qquad VI.6$$

<u>Note:</u>

The entropy of a chemical reaction can be **positive** if the reaction **is spontaneous** and **zero** if it is **reversible** (in equilibrium).

Application VI.1

1. What is the standard molar absolute entropy of water at 25°C, given that:

$$S_{273}^{\circ}(H_2O, s) = 10.28 \; cal.\,mol^{-1}.K^{-1}$$

$$L_{melting} = \Delta H_{melting,273}^{\circ} = 1440 \; cal.\,mol^{-1}$$

$$C_P(H_2O, l) = 11.2 + 7.17 \; 10^{-3}T \; cal.\,mol^{-1}.K^{-1}$$

2. What is the standard molar entropy of water formation at 25°C, given that:

$$S_{298}^{\circ}(H_2, g) = 31.21 \; cal.\,mol^{-1}.K^{-1} \quad and \quad S_{298}^{\circ}(O_2, g) = 49.00 \; cal.\,mol^{-1}.K^{-1}$$

3. Calculate the standard entropy change accompanying the following reaction at 25°C, using :

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(l)}$$

    a) The standard molar formation entropies $\Delta S_{f,298}^{\circ}$

    b) The standard absolute molar entropies S_{298}° .

Solution

1. The standard molar absolute entropy of water at 298K is $S_{298}^{\circ}(H_2O, l)$

$$H_2O \; (s) \rightarrow H_2O \; (l) \rightarrow H_2O \; (l)$$

273K   273K   298K

$$\Delta S_{syst}^{\circ} = S_{298}^{\circ}(H_2O, l) - S_{273}^{\circ}(H_2O, s)$$

$$\Delta S_{syst}^{\circ} = \Delta S_{273}^{\circ}(melting) + \Delta S^{\circ}(\text{Heating})$$

$$S_{298}^{\circ}(H_2O, l) - S_{273}^{\circ}(H_2O, s) = \Delta S_{273}^{\circ}(melting) + \Delta S^{\circ}(Heating)$$

$$S_{298}^{\circ}(H_2O, l) = S_{273}^{\circ}(H_2O, s) + \Delta S_{273}^{\circ}(melting) + \Delta S^{\circ}(Heating)$$

$$S_{298}^{\circ}(H_2O, l) = S_{273}^{\circ}(H_2O, s) + \frac{\Delta S_{273}^{\circ}(melting)}{T_{melting}} + \int_{273}^{298} nC_P(H_2O, l)\frac{dT}{T}$$

$$S_{298}^{\circ}(H_2O, l) = 10.28 + \frac{1440}{273} + \int_{273}^{298} \frac{11.2dT}{T} + 7.17 \; 10^{-3} \; dT$$

$$S_{298}^{\circ}(H_2O, l) = 16.71 cal.\,mol^{-1}.K^{-1}$$

2. The standard molar entropy of water formation at 298 K is $\Delta S_{f,298}^{\circ}(H_2O, l)$

$$\mathbf{H_2\ (g) + 1/2\ O_2(g) \rightarrow H_2O\ (l)} \qquad \text{à } \mathbf{298K}$$

$$\Delta S_{r,298}^{\circ} = \sum n_i \Delta S_{f.298\ (products)}^{\circ} - \sum n_i \Delta S_{f,298(reactants)}^{\circ}$$

$$\Delta S_{r,298}^{\circ} = \Delta S_{f,298}^{\circ}(H_2O(l)) - \frac{1}{2}\Delta S_{f,298}^{\circ}(O_2(g)) - \Delta S_{f,298}^{\circ}(H_2(g))$$

$\Delta S_{f,298}^{\circ}(O_2(g)) = \Delta S_{f,298}^{\circ}(H_2(g)) = \mathbf{0}$, because the standard molar entropy change of formation of a pure element is zero.

$$\Delta S_{r,298}^{\circ} = \Delta S_{f,298}^{\circ}(H_2O(l))$$

$$\Delta S_{f,298}^{\circ}(H_2O(l)) = S_{298}^{\circ}(H_2O(l)) - \frac{1}{2}S_{298}^{\circ}(O_2(g)) - S_{298}^{\circ}(H_2(g))$$

$$\Delta S_{f,298}^{\circ}(H_2O(l)) = \mathbf{16.17 - 31.21} - \frac{1}{2}(\mathbf{49.00}) = \mathbf{\color{red}{-39\ cal.\,K^{-1}}}$$

3. a) Calculation of the standard entropy change of the reaction using the standard molar entropies of formation:

$$\mathbf{2\ H_2\ (g) + O_2(g) \rightarrow 2\ H_2O\ (l)} \qquad \text{à } \mathbf{298K}$$
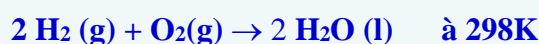
$$\Delta S_{r,298}^{\circ} = \sum n_i \Delta S_{f.298\ (products)}^{\circ} - \sum n_i \Delta S_{f,298(reactants)}^{\circ}$$

$$\Delta S_{r,298}^{\circ} = 2\Delta S_{f,298}^{\circ}(H_2O(l)) - \Delta S_{f,298}^{\circ}(O_2(g)) - 2\Delta S_{f,298}^{\circ}(H_2(g))$$

$$\Delta S_{r,298}^{\circ} = 2\Delta S_{f,298}^{\circ}(H_2O(l))$$

$\Delta S_{f,298}^{\circ}(O_2(g)) = 2\Delta S_{f,298}^{\circ}(H_2(g)) = \mathbf{0}$, because the standard molar entropy change of formation of a simple substance is zero.

$$\Delta S_{r,298}^{\circ} = \mathbf{2(-39)} = \mathbf{\color{red}{-78\ cal.\,K^{-1}}}$$

b) Calculation of the standard entropy change of the reaction using the standard molar absolute entropies:

$$\Delta S_{r,298}^{\circ} = 2S_{298}^{\circ}(H_2O(l)) - S_{298}^{\circ}(O_2(g)) - 2S_{298}^{\circ}(H_2(g))$$

$$\Delta S_{r,298}^{\circ} = \mathbf{2(19.71) - 2(31.21) - 49} = \mathbf{\color{red}{-78\ cal.\,K^{-1}}}$$

VI.6 The change in entropy of a chemical reaction at a temperature T

The standard entropy of reaction at T = 298 K is generally known, but to determine it at a temperature T, we apply Hess's law and take into account any changes in physical states for the reactants and products.

- No change of state between T and T'

    We assume that the reactants and products are in the same physical state at 298 K and at temperature T; we use the following Hess's cycle:

$$\Delta S^{\circ}_{R(T')}$$

| Reactants at T' | $\longrightarrow$ | Products at T' |

$$\sum_R -n_R C_P ln\frac{T'}{T} \qquad\qquad \sum_P n_P C_P ln\frac{T'}{T}$$

$$\Delta S^{\circ}_{R(T)}$$

| Reactants at T | $\longrightarrow$ | Products at T |
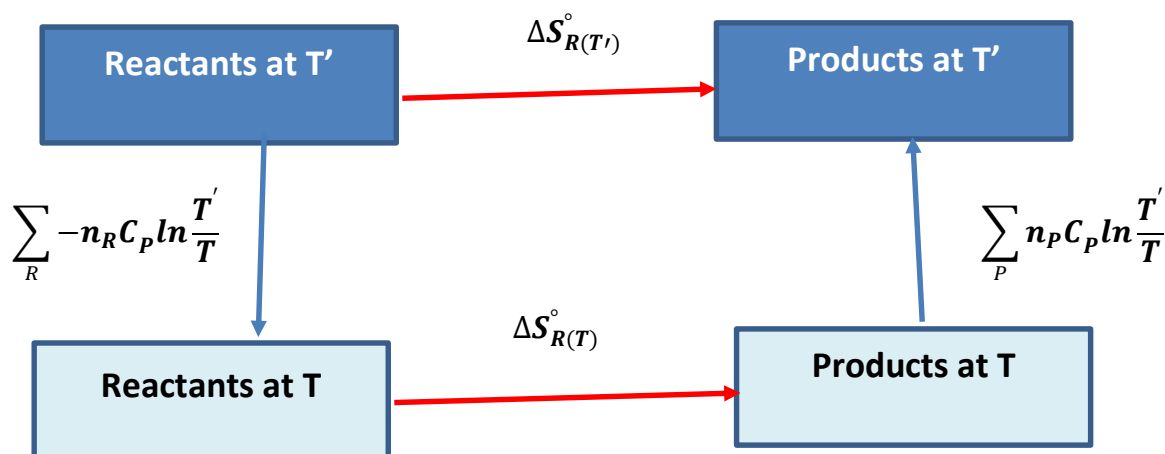
Since S is a state function, we can write:

$$\Delta S^{\circ}_{R(T')} - \sum_P n_P C_P ln\frac{T'}{T} - \Delta S^{\circ}_{R(T)} + \sum_R n_R C_P ln\frac{T'}{T} = 0$$

$$\Delta S^{\circ}_{R(T')} = \Delta S^{\circ}_{R(T)} + \sum_P n_P C_P ln\frac{T'}{T} - \sum_R n_R C_P ln\frac{T'}{T}$$

$$\Delta S^{\circ}_{R(T')} = \Delta S^{\circ}_{R(T)} + \Delta C_P ln\frac{T'}{T} \qquad\qquad VI.7$$

With: $\Delta C_P = \sum_P n_P C_{P(products)} - \sum_R n_R C_{P(reactants)}$

Application VI.2 Consider the reaction: $3C_2H_{2(g)} \rightarrow C_6H_{6(g)}$

Calculate ΔS_{298}° and ΔS_{773}° for this reaction.

Data: $S_{298}^{\circ}(C_2H_{2(g)}) = 48 \; cal.mol^{-1}.K^{-1}$ $S_{298}^{\circ}(C_6H_{6(g)}) = 64.4 \; cal.mol^{-1}.K^{-1}$

$C_P(C_2H_{2(g)}) = 10.5 \; cal.mol^{-1}.K^{-1}$ $C_P(C_6H_{6(g)}) = 19.54 \; cal.mol^{-1}.K^{-1}$

Solution

$$\Delta S_{298}^{\circ} = \sum n_i \Delta S_{f.298 \; (products)}^{\circ} - \sum n_i \Delta S_{f,298(reactants)}^{\circ}$$

$$\Delta S_{298}^{\circ} = S_{298}^{\circ}(C_6H_{6(g)}) - 3S_{298}^{\circ}(C_2H_{2(g)})$$

$$\Delta S_{298}^{\circ} = -79.6 \; cal.K^{-1}$$

$$\Delta S_{773}^{\circ} = \Delta S_{298}^{\circ} + \int_{298}^{773} \Delta C_P \frac{dT}{T} == \Delta S_{298}^{\circ} + \Delta C_P ln\left(\frac{773}{298}\right)$$

$$\Delta C_P = C_P(C_6H_{6(g)}) - 3C_P(C_2H_{2(g)})$$

$$\Delta C_P = -11.99 \; cal.K^{-1}$$

$$\Delta S_{773}^{\circ} = -79.6 - 11.99 ln\left(\frac{773}{298}\right)$$

$$\Delta S_{773}^{\circ} = -91.03 \; cal.K^{-1}$$

- <u>Change of physical state of the products and reactants between T and T'</u>

Example: Determination of the molar combustion entropy of $H_{2(g)}$ at T = 390 K.
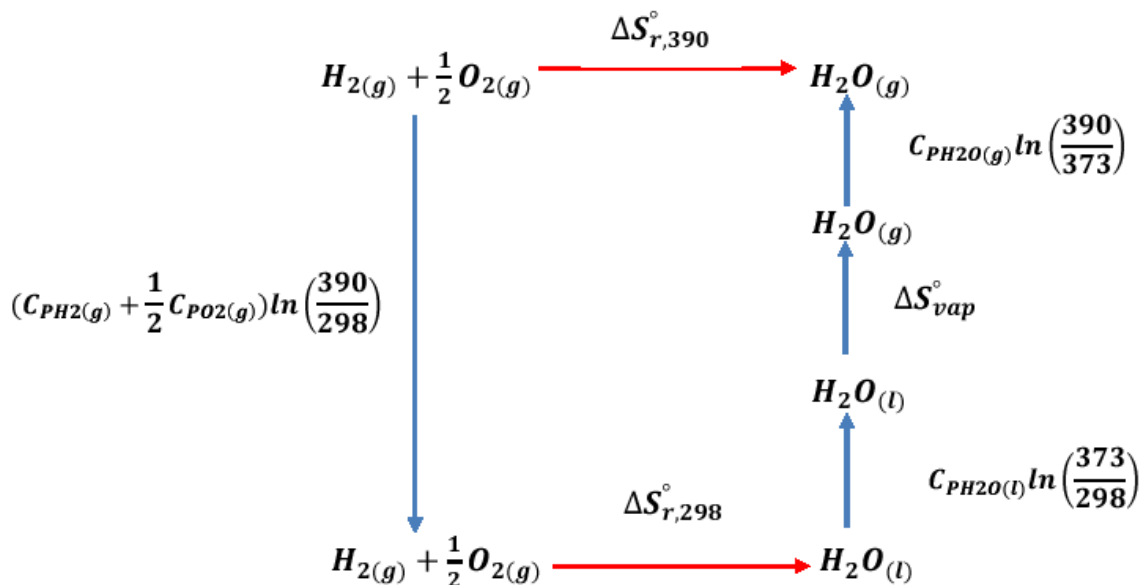
$$\Delta S^{\circ}_{r,390} = \Delta S^{\circ}_{r,298} + \Delta S^{\circ}_{vap} + C_{PH2O(g)} ln\left(\frac{390}{373}\right) + C_{PH2O(l)} ln\left(\frac{373}{298}\right) + (C_{PH2(g)}$$

$$+ \frac{1}{2} C_{PO2(g)}) ln\left(\frac{390}{298}\right) = 0$$

Standard reaction enthalpies are greater than transition entropies, which in turn are greater than the temperature change entropies of pure substances.

CHAPTER VII

FREE ENERGY AND ENTHALPY - CRITERIA FOR THE EVOLUTION OF A SYSTEM

VII.1 Introduction

The second law of thermodynamics allows us to assess the spontaneity of a process. To predict whether a chemical reaction will occur spontaneously in the forward or reverse direction (or if the system remains at equilibrium), it is relevant to use two new functions that characterize the system based on two criteria:

- **Maximum entropy criterion:** the system evolves toward the state with the highest statistical probability (number of microstates).
- **Minimum energy criterion:** the system evolves toward the state of lowest energy (the most stable).

The two functions to use are free energy and enthalpy.

VII.2 Free energy and enthalpy

VII.2.1 Free energy

Called **Helmholtz function**, and denoted **F**, it is a state function because it is defined from two state functions (U and **S**) and a state variable (**T**). It is an extensive quantity whose variation allows us to determine the work that can be performed by a system.

The elementary variation of **dF** of the function **F** is expressed as:

$$dF = d(U - TS) \qquad\qquad VII.1$$

$$dF = dU - TdS - SdT = \delta W + \delta Q - TdS - SdT = -PdV + TdS - TdS - SdT$$

$$dF = -PdV - SdT \qquad\qquad VII.2$$

The differential of the state function **F** as a function of **V** and **T** is written as :

$$dF = \left(\frac{dF}{dV}\right)_T dV + \left(\frac{dF}{dT}\right)_V dT \qquad\qquad VII.3$$

With :

$$\left(\frac{dF}{dV}\right)_T = -P \qquad\qquad\qquad \left(\frac{dF}{dT}\right)_V = -S$$

Note: The role of the function **F** (free energy) is much less significant in thermochemistry than that of the free enthalpy function, which is essential for the study of chemical equilibria.

VII.2.2 Free enthalpy

Called **Gibbs function**, and denoted **G**, it is a state function because it is defined from two state functions **(H** and **S)** and a state variable **(T).**

The elementary variation of **dG** of the function **G** is expressed as:

$$dG = d(H - TS) \qquad\qquad VII.4$$

$$dG = dH - TdS - SdT = d(U + PV) - TdS - SdT$$

$$dG = dU + PdV + VdP - TdS - SdT = \delta W + \delta Q + PdV + VdP - TdS - SdT$$

With: $\delta W = \delta W_P + \delta W'$

$\delta W_P = -P_{ext}dV$ Work done by the external pressure force.

$\delta W' = 0$ Work done by other external forces.

In addition $dQ = TdS$ (Second law of thermodynamics)

$$dG = -PdV + TdS + PdV + VdP - TdS - SdT$$

$$dG = +VdP - SdT \qquad\qquad VII.5$$

The differential of the state function **G** as a function of **P** and **T** is written as :

$$dG = \left(\frac{dG}{dP}\right)_T dP + \left(\frac{dG}{dT}\right)_P dT \qquad\qquad VII.6$$

With :

$$\left(\frac{dG}{dP}\right)_T = V \qquad\qquad\qquad \left(\frac{dG}{dT}\right)_P = -S$$

VII.2.3 Standard free enthalpy of formation

The standard free enthalpy of formation of a compound is defined as the change in free enthalpy that occurs during the formation reaction of that compound from its elements, with the products and reactants considered in their standard state (1 atm and 298 K) and physically separated.

The standard free enthalpy of formation of all simple substances is zero$\Delta G^{\circ}_{f,298} = 0$

We can write, according to the definition of free enthalpy :$\Delta G^{\circ}_f = \Delta H^{\circ}_f - T\Delta S^{\circ}_f$

ΔG°_f of a compound is a measure of its stability relative to simple substances at a given temperature.

- $\Delta G^{\circ}_f < 0$, the simple substances spontaneously form the compound at this temperature.

Example: $N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta G^{\circ}_f = -16.5 kJ.mol^{-1}$

- $\Delta G^{\circ}_f > 0$, it is the reverse reaction, meaning the decomposition of the compound, that is instantaneous.

Example: $H_2 + I_2 \rightarrow 2HI$ $\Delta G^{\circ}_f = +1.69\ kJ.mol^{-1}$

It is useless to try to prepare HI from H_2 and I_2 at this temperature, but for the reverse reaction $2HI \rightarrow H_2 + I_2$ $\Delta G^{\circ}_f = -1.69\ kJ.mol^{-1}$, the reaction is spontaneous.

VII.2.4 Free enthalpy of a chemical reaction (Hess's law)

The change in free enthalpy ΔG during a reaction carried out at constant temperature and pressure is the difference between the formation free enthalpies of the products and the formation free enthalpies of the reactants.

$$\Delta G^{\circ}_{r,298} = \sum n_i \Delta G^{\circ}_{f,298(products)} - \sum n_i \Delta G^{\circ}_{f,298\,(reactiants)} \qquad VII.7$$

We can also write, according to the definition of free enthalpy: $\Delta G^{\circ}_r = \Delta H^{\circ}_r - T\Delta S^{\circ}_r$

If the reaction occurs at a temperature **T** different from the reference temperature (298 K), ΔG_T can be calculated using the following relationship:

$$\Delta G_T = \Delta H_T - T\Delta S_T \qquad VII.8$$

ΔH_T and ΔS_T are calculated using Kirchhoff's law.

To determine the direction in which a reaction proceeds, it is enough to know the sign of the change in free enthalpy ΔG.

➢ $\Delta G_r < 0$, the process is **exergonic** and will proceed spontaneously in the forward direction, to form more products.

➢ $\Delta G_r > 0$, the process is **endergonic** and therefore non-spontaneous in the forward direction. In contrast, it will be spontaneous in the reverse direction, to produce more reactants.

➢ $\Delta G_r = 0$, the system is at **equilibrium**, and the concentrations of the reactants and products will remain constant

Application VII.1

Calcium carbonate $CaCO_3$ (s) decomposes according to the following reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2 (g)$$

1- Under standard conditions (P = 1 atm and T = 25°C), is this reaction thermodynamically feasible?

2- At what temperature does it become feasible?

Data: The molar enthalpies of formation and the absolute molar entropies at standard state.

	$CaCO_{3(s)}$	$CaO_{(s)}$	$CO_{2(g)}$
$\Delta H_f°$ (kJ. mol^{-1})	-1210,11	-393,14	-634,11
s° (J. K^{-1}. mol^{-1})	92,80	213,60	39,71

Solution

1- To determine if the reaction is thermodynamically feasible under standard conditions, it is necessary to calculate the standard free enthalpy of the reaction

$$\Delta G_{298}^0 = \Delta H_{298}^0 - T\Delta S_{298}^0$$

$$\Delta H_{reaction}^0 = \Delta H_f^0(CO_{2(g)}) + \Delta H_f^0(CaO_{(s)}) - \Delta H_f^0(CaCO_{3(s)})$$

$$\Delta H_{reaction}^0 = 182.86 \; KJ$$

$$\Delta S_{reaction}^0 = S_f^0(CO_{2(g)}) + S_f^0(CaO_{(s)}) - S_f^0(CaCO_{3(s)})$$

$$\Delta S_{reaction}^0 = 160.51 \; KJ$$

$\Delta G_{298}^0 = 135 \; KJ \; \Delta G_{298}^0 > 0$, The reaction is **impossible.**

2- For the decomposition of $CaCO_3$ to be feasible, it is essential that $\Delta G_{298}^0 \leq 0$

$$\Delta H_{298}^0 - T\Delta S_{298}^0 \; = 0 \quad \Rightarrow \quad T = \frac{\Delta H_{298}^0}{\Delta S_{298}^0} \quad T = 1139.24 \; K$$

VII.3 Chemical equilibria

When two or more bodies capable of interacting are placed together, and the system is observed after a certain period of time, once the changes have stopped, two situations may arise:

- The entire reactive substance participated in the reaction, which is then classified as **total**.

- Only a portion of the reactive substance reacted, with the remainder present in the mixture along with the products of the reaction. In this case, the reaction is classified as limited; the resulting state corresponds to an equilibrium, which can be understood by stating that the system is the site of two simultaneous inverse

reactions occurring in opposite directions. A reaction known as reversible is represented by an equation of the following form: $aA + bB \rightleftharpoons cC + dD$

On peut distinguer deux types d'équilibres :

- **Homogeneous Equilibrium**, where the reaction medium consists of only one phase (liquid or gas).

- **Heterogeneous Equilibrium**, where multiple phases interact with each other (for example, a gas phase and one or more solid phases, a liquid phase and one or more solid phases, multiple solid phases, ...).

VII.3.1 Law of mass action and equilibrium constants

The law of mass action was formulated in 1879 by Norwegian chemists **Cato Guldberg (1836-1902)** and **Peter Waage (1833-1900),** based on their joint discovery published in 1864. This law defines the equilibrium of a reaction system undergoing a chemical reaction that has reached a state of equilibrium. In this system, the concentrations of the initial reactants and the products formed are related by an expression whose value remains constant at a given temperature."

VII.3.2 Guldberg and Waage relation for homogeneous equilibria

When a certain mass of an ideal gas undergoes an infinitely small reversible change at constant temperature, its free enthalpy varies by:

$$dG = dH - TdS = dU + d(PV) - TdS = dQ + VdP - TdS$$

As the evolution is reversible, we have: $= TdS$, whence:

$$dG = VdP = nRT\frac{dP}{P}$$

and consequently:

$$G_i = nRT\ln P_i + G_i^{\circ} \qquad\qquad VII.9$$

Considering a mixture of gases reacting according to the reaction: $aA + bB \rightleftharpoons cC + dD$

$$\Delta G = \sum n_i G_{(products)} - \sum n_i G_{(reactants)}$$

$$\Delta G = \left[\left(cRT\ln P_C + G_C^{\circ}\right) + \left(dRT\ln P_D + G_D^{\circ}\right)\right] - \left[\left(aRT\ln P_A + G_A^{\circ}\right) + \left(bRT\ln P_B + G_B^{\circ}\right)\right]$$

$$\Delta G = \left[\left(G_C^{\circ} + G_D^{\circ}\right) - \left(G_A^{\circ} + G_B^{\circ}\right)\right] + \left[\left(cRT\ln P_C + dRT\ln P_D\right) - \left(aRT\ln P_A + bRT\ln P_B\right)\right]$$

$$\Delta G = \Delta G^{\circ} + RT[(c\,\ln P_C + d\ln P_D) - (a\ln P_A + b\ln P_B)]$$

$$\Delta G = \Delta G^{\circ} + RT\ln\frac{P_C^C \times P_D^d}{P_A^a \times P_B^b} \qquad\qquad VII.10$$

Where K_P is called the Guldberg and Waage equilibrium constant. It is a value that indicates the relative amounts of reactants and products in a system at equilibrium.

$$K_P = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

At equilibrium, $\Delta G = 0$ and consequently $\Delta G^\circ = -RTlnK$ $VII.11$

The ideal gas law, applied to A, is written as: $P_A V = n_A RT \Rightarrow P_A = \left(\frac{n_A}{V}\right) RT$

With: $\frac{n_A}{V} = [A]$ so $P_A = [A]RT$

Similarly for the other pressures $P_B = [B]RT, P_C = [C]RT, P_D = [D]RT$

The law of mass action concerning concentrations is expressed as:

$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} = \frac{(P_C^C \times P_D^d)}{(P_A^a \times P_B^b)} RT^{a+b-c-d}$$

Let: $K_P = K_c RT^{c+d-a-b}$ $VII.12$

We can also express K_p in terms of x_i , the molar fraction of compound **i**.

$$x_i = \frac{n_i}{n_{tot}} = \frac{P_i}{P_{tot}}$$

n_i : Number of moles of constituent i.

n_{tot} : Total number of moles.

P_i : Partial pressure.

P_{tot} : Total pressure.

$$K_P = \frac{P_C^C \times P_D^d}{P_A^a \times P_B^b} = \frac{x_C^C \times x_D^d}{x_A^a \times x_B^b} P_{tot}^{(c+d)-(a+b)}$$

Let

$$K_P = K_x P_{tot}^{\Delta n}$$ $VII.13$

Application VII.2

The pure nitrogen oxychloride (NOCl) gas is heated to 240 °C in a one-liter container, resulting in the following chemical equilibrium:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2\,(g)}$$

At equilibrium, the total pressure is 1 atm and the pressure of NOCl is 0.64 atm.
1. Calculate the partial pressures of the gases.
2. Calculate the equilibrium constant K

Solution

$1-\ P_{tot} = P_{NOCl} + P_{NO} + P_{Cl_2} \Rightarrow P_{NO} + P_{Cl_2} = P_{tot} - P_{NOCl}$

$$P_{NO} + P_{Cl_2} = 1 - 0.64 = 0.36\ atm$$

$$\frac{n_{NO}}{n_{Cl_2}} = 2\ \Rightarrow P_{NO} = 2\ P_{Cl_2}$$

$$P_{NO} = \frac{2}{3} \times 0.36 = 0.24\ atm$$

$$P_{Cl_2} = \frac{1}{3} \times 0.36 = 0.12\ atm$$

$2-\ K_P = \dfrac{P_{Cl_2} \times P_{NO}^2}{P_{NOCl}^2} = \dfrac{0.12 \times 0.24^2}{0.64^2} = 0.017$

VII.3.3 <u>Influence of temperature on equilibrium constants</u>

Equilibrium constants vary with changes in the temperature of the system. In contrast, changes in concentration, pressure, and the presence of catalysts don 't affect the equilibrium constant. This change is explained by the heat involved in a chemical reaction; a temperature change can result in either a gain or a release of heat, which affects the direction of the reaction (toward the products or the reactants). This will lead to a change in the concentrations of the reactants and products, thereby establishing a new equilibrium constant **K**.

VII.3.3.1 <u>Van't Hoff relation</u>

The value of K at temperature T is derived from the relation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -RTlnK$$

We can determine the values of ΔH° and ΔS° from the equilibrium constants (K_1 and K_2) at two different temperatures, respectively:

$$\Delta H^{\circ} - T_1\Delta S^{\circ} = -RT_1lnK_1\ \Rightarrow\ lnK_1 = \frac{-\Delta H^{\circ}}{RT_1} + \frac{\Delta S^{\circ}}{R}$$

$$\Delta H^\circ - T_2 \Delta S^\circ = -RT_2 lnK_2 \Rightarrow lnK_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

$$lnK_2 - lnK_1 = \frac{-\Delta H^\circ}{RT_2} - \frac{-\Delta H^\circ}{RT_1}$$

$$ln\frac{K_2}{K_1} = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad\qquad VII.14$$

The above equation is the Van't Hoff equation.

The variation of the standard enthalpy or the standard entropy of a chemical reaction are determined from graphs obtained from experimental studies.

VII.3.4 Laws of equilibrium shift (Le Chatelier's principle)

When a change (in concentration, temperature, or pressure) is applied to a chemical system at equilibrium, it tends to evolve toward a new equilibrium state to mitigate the impact of this change. In other words, the system adjusts to compensate for the disturbance experienced.

VII.3.4.1 Effect of temperature (Van't Hoff law)

At constant pressure or constant volume, an increase in temperature shifts the equilibrium toward the endothermic reaction **(direction of heat absorption).**
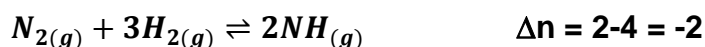
Example: $2NH_{(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$ $\qquad\qquad\qquad\qquad \Delta H = 91.8\ kJ$

ΔH > 0 $\Rightarrow$ Direction (1) endothermic $\Rightarrow$ an increase in temperature shifts the equilibrium toward direction (1).

VII.3.4.2 Effect of pressure (Le Chatelier's law)

An increase in pressure causes the equilibrium to shift in the direction that decreases the total number of gaseous molecules.
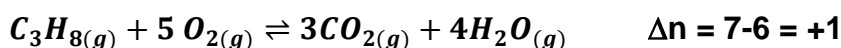
Example :

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{(g)}$ $\qquad\qquad$ **Δn = 2-4 = -2**

4 moles $\qquad\qquad$ **2 moles**

Direction of the reaction's progression when pressure increases

$C_3H_{8(g)} + 5\ O_{2(g)} \rightleftharpoons 3CO_{2(g)} + 4H_2O_{(g)}$ $\qquad$ **Δn = 7-6 = +1**

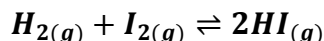$\qquad$ **6 moles** $\qquad\qquad$ **7 moles**

Direction of the reaction's progression when pressure increases

VII.3.4.3 Effect of the concentration of constituents

An increase in the concentration of a constituent leads to a shift in the equilibrium toward the reaction that consumes the added substance.

Example :

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

- An increase in the concentration of **[H₂]** shifts the equilibrium in the direction **(1)** ⇒ the consumption of H_2

- A decrease in the concentration of **[I₂]** shifts the equilibrium in the direction **(2)** ⇒ the formation of I_2

VII.3.5 Complementary aspect of the study of equilibria

VII.3.5.1 Dissociation coefficient

The equilibrium state is characterized by a constant called the dissociation coefficient or degree of dissociation, denoted as "α", which represents the fraction of moles dissociated relative to the initial number of moles.

$$\propto = \frac{Number\ of\ moles\ dissociated}{Initial\ number\ of\ moles} \qquad 0 < \alpha < 1 \qquad VII.15$$

Application VII.3

We introduce PCl₅ into a container where it dissociates according to the following reaction:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2\ (g)}$$

At equilibrium, the total pressure stabilizes at P = 1.2 P₀. Calculate the dissociation coefficient of PCl₅

Solution

t	$PCl_{5(g)}$	$PCl_{3(g)}$	$Cl_{2\ (g)}$
t₀	P_0	0	0
t	$P_0(1-\alpha)$	$P_0\alpha$	$P_0\alpha$

The total pressure is: $P_0(1-\alpha) + P_0\alpha + P_0\alpha = (1+\alpha)\,P_0$

The pressure at equilibrium is 1.2 P₀, hence $\alpha = 0.2$

VII.3.5.2 Progress degree of a chemical reaction

The progress degree of **(ξ)** introduced in 1922 by **Théophile de Donder (1872-1957)**, is used to describe the evolution of a chemical reaction from its initial state to its final state. The dissociation coefficient can also be expressed in the following manner in terms of the degree of progress:

$$\propto = \frac{n_0 - n}{n_0} = \frac{2\xi}{n_0} \Longrightarrow \xi = \frac{\propto n_0}{2} \qquad\qquad VII.16$$

Example: Consider the following equilibrium:
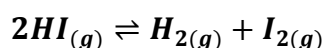
$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

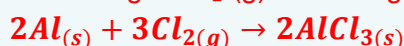| t	$HI_{(g)}$	$H_{2(g)}$	$I_{2(g)}$
Initial	n_0	**0**	**0**
Equilibrium	$n = n_0 - 2\xi$ $n_0(1-\alpha)$	ξ $\frac{1}{2}n_0\alpha$	ξ $\frac{1}{2}n_0\alpha$

VII.3.5.3 The yield of a chemical reaction

The yield, denoted as **ρ**, is the ratio of the mass of the product recovered (experimental mass) at the end of the experiment to the mass of the product theoretically obtained (theoretical mass). It is a dimensionless number, ranging from **0** to **1**, and it can also be expressed as a percentage.

$$\rho = \frac{m_{experimental}}{m_{theoretical}} \times 100\% \qquad\qquad VII.17$$

The theoretical mass is the mass that would be obtained if all the reactants were completely consumed.

Application VII.4

2.8 g of aluminum (s) reacts with 4.15 g of Cl_2 (g) according to the following equation:
$$2Al_{(s)} + 3Cl_{2(g)} \rightarrow 2AlCl_{3(s)}$$
What is the yield of this reaction?

Solution

1- **Determination of the limiting reactant :**

$$n_{Al} = \frac{m}{M} = \frac{2.8}{27} = 0.104 \; moles$$

$$n_{Cl_2} = \frac{m}{M} = \frac{4.15}{71} = 0.0585 \; moles$$

The ratio between the moles number of Al and Cl_2 required by the balanced equation is:

$$\frac{n_{Al}}{n_{Cl_2}}(theoretical) = \frac{2}{3} = 0.66$$

And the ratio that we actually have is :

$$\frac{n_{Al}}{n_{Cl_2}} \text{(actual)} = \frac{0.104}{0.0585} = 1.77$$

The actual ratio is greater than the theoretical ratio, indicating that there is more Al than necessary to completely react with Cl_2. Therefore, **Cl_2 is the limiting reactant**.

2- Calculation of the yield

Since Cl_2 is the limiting reactant, the maximum amount of $AlCl_3$ that can be obtained is:

$$5.85 \times 10^{-2} \ moles \ of \ Cl_2 \times \frac{2 \ moles \ of \ AlCl_3}{3 \ moles \ of \ Cl_2} = 3.90 \times 10^{-2} \ moles \ of \ AlCl_3$$

$$Actual \ mass \ AlCl_3 = 3.90 \times 10^{-2} \times 133.5 = 5.2065 \ g$$

$$Theoretical \ mass \ AlCl_3 = 2 \times 133.5 = 267 \ g$$

$$\rho = \frac{5.2065}{267} \times 100\% = \textbf{1.95} \ \%$$

VII.3.5.4 The variance of a system at equilibrium and the phase rules

The variance represents the maximum number of intensive parameters (temperature T, total pressure, and partial pressure) needed to quantitatively describe a system at equilibrium. These parameters aren't independent; they are interconnected by relationships. Therefore, by imposing just one of these parameters, the state of the system is fully defined. The variance is calculated using the formula known as the **« phase rule »,** also referred to as Gibbs' law.
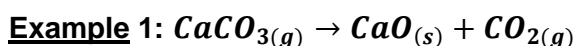
$$\boldsymbol{v = c + 2 - \varphi} \qquad\qquad \boldsymbol{VII.18}$$

$\boldsymbol{v}$ **:** The variance.

$\boldsymbol{c}$ **:** The number of independent constituents (the number of chemical compounds involved minus the number of relationships among them)

$\boldsymbol{\varphi}$ **:** The number of phases.

The number **2** represents the total pressure and temperature.

<u>Example</u> 1: $\boldsymbol{CaCO_{3(g)} \rightarrow CaO_{(s)} + CO_{2(g)}}$

For the dissociation of $CaCO_3$, we have 3 pure substances: $CaCO_3$, CaO, and CO_2, and an equilibrium among these substances, leading to c=3−1=2; three phases are present (2 solid phases and 1 gaseous phase); hence the variance: $\boldsymbol{v = 2 + 2 - 3 = 1}$
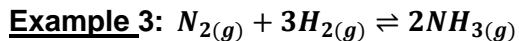
When the temperature is kept constant, the equilibrium pressure is clearly defined.

<u>Example</u> 2: $\boldsymbol{Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(l)}}$
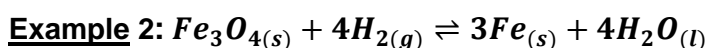
For the reduction of Fe_3O_4 by hydrogen, we have 4 substances, 1 equilibrium, and 3 phases, hence:

$$v = 3 + 2 - 3 = 2$$

We can adjust the temperature and one of the partial pressures separately, for example.

**Example 3:** $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

We have a single phase (gaseous) and 3 substances, 1 equilibrium, hence :

$$v = 2 + 2 - 1 = 3$$

We can arbitrarily choose the temperature, pressure, and for example, the molar concentration **[N₂]** of nitrogen.

Example 4: Let's introduce solid carbon and the gases O_2, CO, and CO_2; we have 4 substances that can react according to 2 independent equilibria:

$$C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$$

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$$
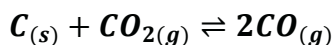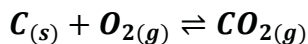
Hence: $c = 4 - 2 = 2$

And the variance is : $v = 2 + 2 - 2 = 2$

we can fix, for example, the temperature and the pressure.

BIBLIOGRAPHIC REFERENCES

[1] Olivier Cleynen, Thermodynamique de l'ingénieur, 3ème édition, Thermodynamique.fr (2021)

[2] Jeans Louis Burgot, Le concept d'activité en chimie, EDP Sciences (2020)

[3] J.P.Pérez,Thermodynamique Fondements et applications, 3ème Edition, Dunod (2020)

[4] C.Comninelis, C.K.W.Friedeli, A.S.Migirdicyan, Exercices de chimie générale, 3ème Edition, Presses Polytechniques et Universitaires Romandes (2018)

[5] Nivaldo J.Tro, Chimie des solutions une approche moléculaire, 2ème Edition, Pearson ERPI (2017)

[6] Donald Voet, Judith.G. Voet, Biochimie,3ème Edition, Deboeck (2016)

[7] A.Sevin, F.Brochardj-Wyart, C.D.Dandinee , S.Griveau, F.Volatran, Chimie générale - Tout le cours en fiches Licence, PACES, CAPES, 2ème édition, Dunod (2016)

[8] F. De La Baume et J.Calafell, Physique Chimie exos résolus PRÉPAS, Hachette (2015)

[9] Nadia Boulekras, Thermodynamique recueil d'exercices corrigés, OPU (2015)

[10] John C. Kotz, Paul Treichel, Chimie générale, Deboeck (2006)

[11] G. J.VanWylen, R. E.Sonntag et P. Desrochers, Thermodynamique apliquée, Editions du renouveau Pédagogique Inc (1992)

[12] Jerome L.Rosenberg, Chimie générale, Série Schaum (1991)

[13] Bernard Gendreau, Thermodynamique physique, Ellipses (1990)

[14] Kurt C. Rolle, Themodynamics and Heat Power, 6th Edition, Pearson (1989)

[15] R.Ouahes et S.Devallez, Chimie générale, OPU (1988)

[16] M.Bertin, J.P.Faroux et J. Renault, Thermodynamique, Dunod (1984)

[17] René Suardet, Thermodynamique, Technique et documentation (Lavoisier) (1982)

[18] Jean Charles Sisi, Principes de thermodynamique, Mcgraw-Hillf (1981)

[19] R.Kling,Thermodynamique générale et applications, Editions TECHNIP(1980)

[20] M.Suard, B. Praud et L.Praud, Elements de chimie générale, Flammarion médecine science (1977)

[21] R. Annequin et J.Boutigny, Cours de sciences physiques thermodynamique, Vuibert (1972)

[22] M.Bailly, Thermodynamique technique, Bordas (1971)

Summary:

This handout aims to help first-year university students (L1 in Sciences and Technology) absorb knowledge and master the key concepts of thermodynamics, a discipline often difficult to grasp. To make this subject more accessible and facilitate learning, the fundamental principles are presented through seven detailed chapters, based on precise definitions, clear explanations, practical applications, and solved exercises closely related to the official curriculum.

Keywords: Transformation - ideal gas - first law - second law - thermochemistry - equilibrium and free energy.

Résumé :

Ce polycopié a pour objectif d'aider l'étudiant du premier cycle universitaire (L1 Sciences et techniques) à assimiler les connaissances et à maîtriser les concepts clés de la thermodynamique, une discipline souvent difficile à appréhender. Afin de rendre cette matière plus accessible et de favoriser son apprentissage, les principes fondamentaux sont présentés à travers sept chapitres détaillés, reposant sur des définitions précises, des explications claires, des applications concrètes et des exercices corrigés étroitement liés au contenu du programme officiel.

Mots Clés : transformation- gaz parait- premier principe- deuxième principe- thermochimie – équilibre et énergie libre

الملخص:

يهدف هذا الدليل إلى مساعدة طالب السنة الأولى في الجامعة (العلوم والتقنيات) على استيعاب المعارف وإتقان المفاهيم الأساسية في الديناميكا الحرارية، وهي مادة غالبًا ما يصعب فهمها. من أجل جعل هذه المادة أكثر سهولة وتعزيز تعلمها، تم تقديم المبادئ الأساسية من خلال سبعة فصول مفصلة، تعتمد على تعريفات دقيقة، وشروحات واضحة، وتطبيقات عملية، وتمارين محلولة مرتبطة ارتباطًا وثيقًا بمحتوى البرنامج الرسمي.

الكلمات المفتاحية: التحولات ـالغاز المثالي ـالمبدأ الأول ـالمبدأ الثاني ـالكيمياء الحرارية ـالتوازن والطاقة الحرة.