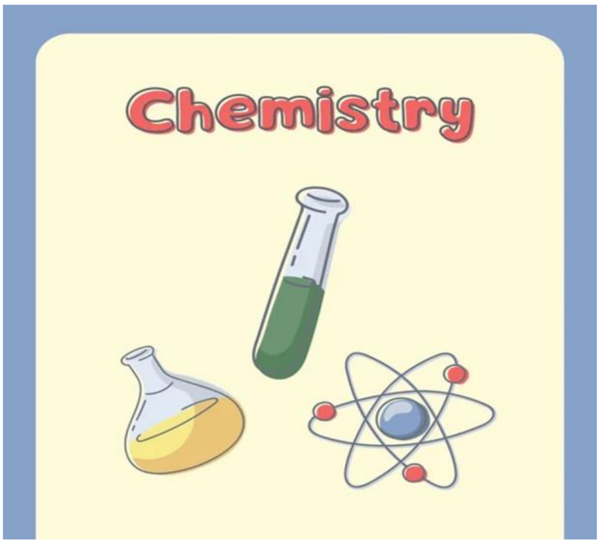
People’s Democratic Republic of Algeria

Ministry of Higher Education and Scientific Research

University of Djelfa

Faculty of Exact and Computer Sciences

Department of Matter Sciences



BASIC CONCEPT IN THERMODYNAMICS CHEMISTRY II

2023-2024

ABSTRACT

Like all sciences, thermodynamics is based on principles and laws formulated using a precise vocabulary. This allows concepts and definitions to be definitions without ambiguity. The Chapter therefore presents the basic elements study thermodynamics and solve practical problems. We begin the chapter with a general discussion of thermodynamics. The system of units used in this book is also clarified. Next, we define basic concepts system, control volume, thermodynamic variables, thermodynamic equilibrium, evolutions and cycles. The notions of temperature and temperature scales are introduced, then we determine the composition of gas mixtures

Dr. Regadia Aissaoui

Basic concept in thermodynamics

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I. Course information

Faculty: Exact and Computer Sciences

Department: Matter Sciences

Course title: **Chemistry II**

Credit :06

Coefficient :03

Duration: 15 Week (67.5 h)

Schedule: Tuesdays and Sundays: 08h30-10h00

Room: Amphi B

Teacher: Dr. Regadia AISSAOUI

Contact: by e-mail at r.aissaoui@univ-djelfa.dz.

Availability:

In the office: Sunday, Tuesday, Thursday from 11:00 to 12:00

Answer on the forum: any question related to the course must be posted on the dedicated forum so that you can all benefit from my answer. I undertake to answer posted questions within 48 hours.

By e-mail: I undertake to reply by e-mail within 48 hours of receipt of the message, except in the case of unforeseen circumstances. I would like to inform you that the preferred channel of communication is the forum. E-mail is reserved for "emergencies" (in the event of problems accessing the platform) and should be used with discretion.

II. Course presentation

This course is the fruits of years of teaching experience in L1 whether in **ST** since 2004-2016 or in **SM** since 2016 to date. It is aimed primarily at first-year **SM** learners, not forgetting ST and SNV Science and Technology learners.

Chapter I covers the basics of thermodynamics, with definitions that are - for the most part - essential to understanding the chapters that follow.

The chapters that follow develop the first two principles of thermodynamics and their application to perfect gases. This is one of the fundamental postulates assimilated to principles, and serves as the foundation for the imposing edifice of macroscopic thermodynamics and the various cycles of thermal machines.

The last two chapters provide an indispensable basis for any kinetic study of a chemical process, covering both the elementary notions of formal kinetics and the mathematical bases concerning the notion of the speed of a chemical reaction and its evolution over time, the parameters influencing the speed of a reaction and the determination of the order of a reaction by physical-chemical methods. The form in which this handout is presented is the result of reading numerous basic works and documents, most of which are cited in the bibliography.

III. Contents

This module consists of three main strands, each of which is based on the theoretical foundations of the previous strand. The strands are closely interrelated, and each is supported by a series of tutorials, applied assignments and other activities to understand and acquire the necessary knowledge. The detailed module plan can be accessed via the online module by clicking on Detailed plan.

1) **Chapter I:**

Covers the basics of thermodynamics, with definitions that are - for the most part - essential to understanding the chapters that follow.

2) **The chapters that follow** develop the first two principles of thermodynamics and their application to perfect gases. This is one of the fundamental postulates assimilated to principles, and serves as the foundation for the imposing edifice of macroscopic thermodynamics and the various cycles of thermal machines.

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IV.Prerequisites:

Prerequisites: In order to follow all courses, learners must:

- Know the basics of thermodynamics, such as the energy and notion of system in thermodynamics, introduced by means of two principles which are statements deduced from experience.

- Know at least some of the basic laws of 2nd thermodynamic principle - Chemical equilibria, such as calculating Stoichiometric ratio of reactants (noted R), etc.

- We therefore propose an exercise or application to test the learner's understanding of these fundamental principles.

To do the application, please return to the teacher's area. You can use the username and code provided by your teacher.

The exercise will be available from the first week, with no specific time limit.

In case of problems, we have placed a link to a reminder of the most important general chemistry courses in the same space. Please refer to it.

V. Learning objectives:

This module is the fundamental basis for learning chemistry in the various modules that follow it in the first-year program. The skills targeted through this module are:

1. The ability to define and understand thermodynamics. Learners should be able to define and understand Basic concept in thermodynamics.
2. Understand the laws of thermodynamics and their applications.
3. Analyze thermodynamic systems using various thermodynamic properties and equations.
4. Apply thermodynamic principles to solve problems involving heat transfer, work, and energy.
5. Interpret and utilize thermodynamic diagrams, such as pressure-volume (PV) and temperature-entropy (TS) diagrams.
6. Comprehend the concept of entropy and its role in determining the direction of processes.
7. Explore applications of thermodynamics in engineering, physics, chemistry, and environmental science.
8. Develop critical thinking skills to analyze real-world systems and processes using thermodynamic principles.

9. Demonstrate proficiency in performing thermodynamic calculations and solving thermodynamic problems.
10. Gain hands-on experience with laboratory experiments related to thermodynamics.
11. Evaluate the efficiency and performance of thermodynamic cycles, such as the Carnot cycle and Rankine cycle.

VI. Learning Evaluation Methods:

The information acquired by the learner is evaluated using several methods, the most important of which are as follows:

A- Continuous and regular evaluation:

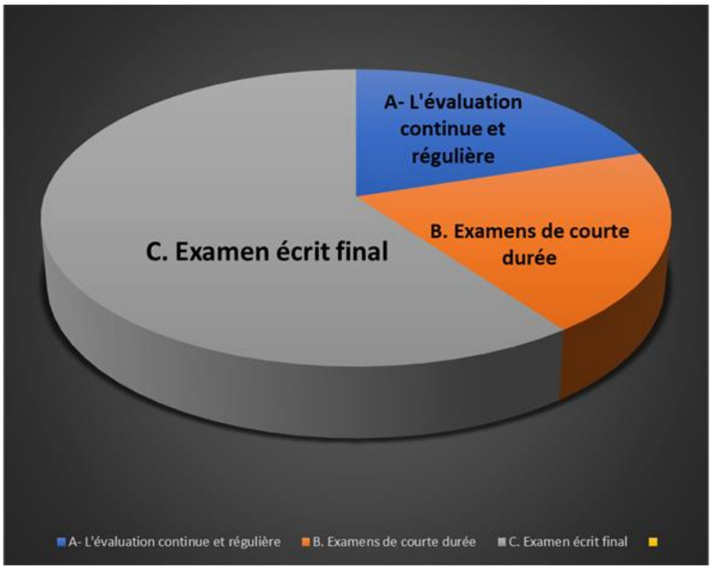
Accounting for 20% of the final marks, this continuous and regular assessment is carried out throughout the semester. It is based on the learner's attendance at courses and tutorials, his or her participation in solving exercises and problems, and his or her completion of assignments, tests and research.

B. Short examinations:

These represent 20% of the final marks for the course, where short exams lasting 60 to 30 minutes are organized every two months. The subject is related to what was already being taught at the time, using examples and exercises similar to those presented in the conference and tutorials. It is largely based on writing exercises and questions on the application of theoretical concepts.

C. Final written exam:

This accounts for 60% of the final module marks, as it comprises a comprehensive study of all the information and cognitive gains made by the learner during the training period and throughout the semester, and is characterized by questions derived from lectures and tutorials. It includes theoretical questions and practical exercises for each semester, for an hour and a half.



Picture: A diagram showing the different ways of evaluating knowledge for the matter structure module.

VII. Teaching-learning activities

Here are some specific teachings and learning activities for thermodynamics:

A. Physical presence:

1. Conceptual Discussions:

Engage students in discussions about fundamental concepts like heat, temperature, energy, entropy, and the laws of thermodynamics. Encourage them to relate these concepts to everyday experiences.

2. Problem-Solving Sessions:

Provide students with a variety of problems related to thermodynamics, ranging from basic calculations to more complex scenarios. Encourage them to work in groups to solve these problems, promoting collaboration and critical thinking. 3. Interactive Demonstrations:

Use interactive demonstrations to illustrate thermodynamic principles. For example, demonstrate the expansion and contraction of gases using balloons or show the transfer of heat through conduction, convection, and radiation using simple setups.

3. Simulation Software:

Utilize simulation software to allow students to explore thermodynamic processes in a virtual environment. This enables them to visualize abstract concepts and conduct experiments that may be difficult to perform in a traditional laboratory setting.

4. Case Studies:

Present real-world examples and case studies where thermodynamic principles are applied, such as in the design of engines, refrigeration systems, or renewable energy technologies. Encourage students to analyze these cases and discuss the thermodynamic principles at play.

5.Laboratory Experiments:

Conduct hands-on laboratory experiments to reinforce theoretical concepts. This could include experiments on heat transfer, phase transitions, or the behavior of ideal gases. Provide guidance on experimental procedures, data analysis, and interpretation of results.

6.Project-Based Learning:

Assign projects that require students to apply thermodynamic principles to solve practical problems or design innovative solutions. This could involve designing an energy-efficient device, optimizing a thermodynamic process, or investigating the environmental impact of different energy sources.

7.Peer Teaching:

Encourage students to take turns teaching each other about specific thermodynamic topics. This not only reinforces their own understanding but also promotes communication and teamwork skills.

B. Distance learning:

The importance of making courses available on the Moodle platform can be summed up in three main points:

1) Putting each semester's courses in PDF and SCORM format will enable learners to organize their main ideas and the points they have learned by attending the courses, this pedagogical support is followed by teaching aids are followed by examples and videos to help the learners deepen their understanding through practical examples of the ideas presented.

2) At the end of each course, several exercises and self-evaluation questions are offered to students to reinforce the concepts presented.

3) Online Resources:

Provide access to online resources such as videos, interactive tutorials, and educational websites that supplement classroom learning and allow students to explore thermodynamics at their own pace. By incorporating these activities into teaching approach, can enhance students' understanding and appreciation of thermodynamics while fostering their problem-solving skills and creativity.

VIII. Pedagogical alignment

In thermodynamics, pedagogical alignment ensures that the learning objectives, instructional activities, and assessment methods are all geared towards helping students develop a strong understanding of thermodynamic principles and their practical applications. Here's how pedagogical alignment can be implemented in the context of teaching thermodynamics:

1. Learning Objectives:

Clearly define the learning objectives for the thermodynamics course or unit. These objectives may include understanding the laws of thermodynamics, applying thermodynamic principles to solve problems, and analyzing thermodynamic processes in real-world scenarios.

2. Instructional Activities:

Develop instructional activities that align with the learning objectives and promote active engagement with the content. This could involve a combination of lectures, demonstrations, laboratory experiments, simulations, problem-solving sessions, and group discussions. For example, conducting experiments to demonstrate the transfer of heat or using simulations to explore thermodynamic processes.

3. Assessment Methods:

Choose assessment methods that accurately measure students' achievement of the learning objectives. This could include traditional exams, quizzes, homework assignments, projects, and practical assessments. Assessments should require students to apply thermodynamic principles to solve problems and analyze situations, rather than just regurgitating facts.

4. Feedback and Reflection:

Provide timely feedback to students on their performance in relation to the learning objectives. Encourage students to reflect on their understanding of thermodynamics and identify areas for improvement. Feedback can be provided through graded assignments, in-class discussions, and one-on-one interactions with students.

5. Alignment with Real-World Applications:

Ensure that instructional activities and assessments are aligned with real-world applications of thermodynamics. This could involve incorporating case studies, industry examples, and current research into the curriculum to help students see the relevance of thermodynamics in various fields such as engineering, physics, chemistry, and environmental science. By aligning learning objectives, instructional activities, assessment methods, and real-world applications, educators can create a cohesive and effective learning experience that supports students' development of a deep understanding of thermodynamics and their ability to apply it in practical contexts.

IX. Operating procedures

The courses are organized as follows:

- First: A theoretical course in the form of two conferences per week aimed at introducing the basic concepts of the thermodynamics. The basic concepts of the thermodynamics are based on the general concepts of chemistry, and each course is presented in detail, covering its various aspects.

The courses are delivered face-to-face in the form of conferences and remotely via a dedicated area which includes courses, practical examples etc. that learners can consult, download and interact with.

-Second: A weekly tutorial session designed to train learners to use the knowledge acquired in the course to solve a variety of problems and exercises.

- Third: A practical course every two weeks, in which the knowledge acquired in course teaching and tutorials is consolidated and its practical applications observed through a variety of experiments. In addition to all the above, there is a digital platform through which learners support their knowledge and find solutions to their problems.

The course is explained using examples and videos, plus various practical exercises, as well as external resources for further reading.

X. Support resources

We provide you with resources (located on a digital platform) that will help you understand the thermodynamics chemistry II module course. All programmed courses are available in PDF and SCORM format, with examples and applications.

1. "Thermodynamics: An Engineering Approach" by Yunus A. Çengel and Michael A. Boles

2. "Introduction to Chemical Engineering Thermodynamics" by J.M. Smith, Hendrick C. Van Ness, and Michael M. Abbott

3. "Thermodynamics: Concepts and Applications" by Stephen R. Turns

4. "Thermodynamics in Materials Science" by Robert DeHoff

Online Resources:

1. Khan Academy: Thermodynamics

2. MIT Open Courseware: Online courses on thermodynamics

3. Coursera: Online courses on thermodynamics offered by various universities
4. National Science Teaching Association (NSTA):

Educational resources on thermodynamics for science teachers Scientific Articles:

1. "Introduction to Thermodynamics" by Enrico Fermi, published in "Thermodynamics" (Dover Books on Physics)

2. "A review on teaching and learning thermodynamics" by Leandro A. Sphaier et al., published in "Entropy"

3. "Investigating students' understanding of concepts related to heat and temperature" by David F. Treagust et al., published in "Journal of Research in Science Teaching"

These references cover a range of topics and approaches for teaching and learning thermodynamics effectively.

Basic concept in thermodynamics

Like all sciences, thermodynamics is based on principles and laws formulated using a precise vocabulary. This allows concepts and definitions to be definitions without ambiguity. The Chapter I therefore presents the basic elements study thermodynamics and solve practical problems. We begin the chapter with a general discussion of thermodynamics. The system of units used in this book is also clarified. Next, we define basic concepts system, control volume, thermodynamic variables, thermodynamic equilibrium, evolutions and cycles. The notions of temperature and temperature scales are introduced, then we determine the composition of gas mixtures.

I.1 Definition

Thermodynamics comes from the Greek thermos and dynamis, meaning heat and energy. It provides general and effective methods for studying and understanding complex physical and chemical phenomena. Thermodynamics is concerned solely with the macroscopic properties of matter, such as pressure, temperature, volume and composition.

I.2 Description of thermodynamic systems

I.2.1 State of matter

There are three states of matter: solid, liquid and gas. and we can switch from one state to another (Figure I.1).

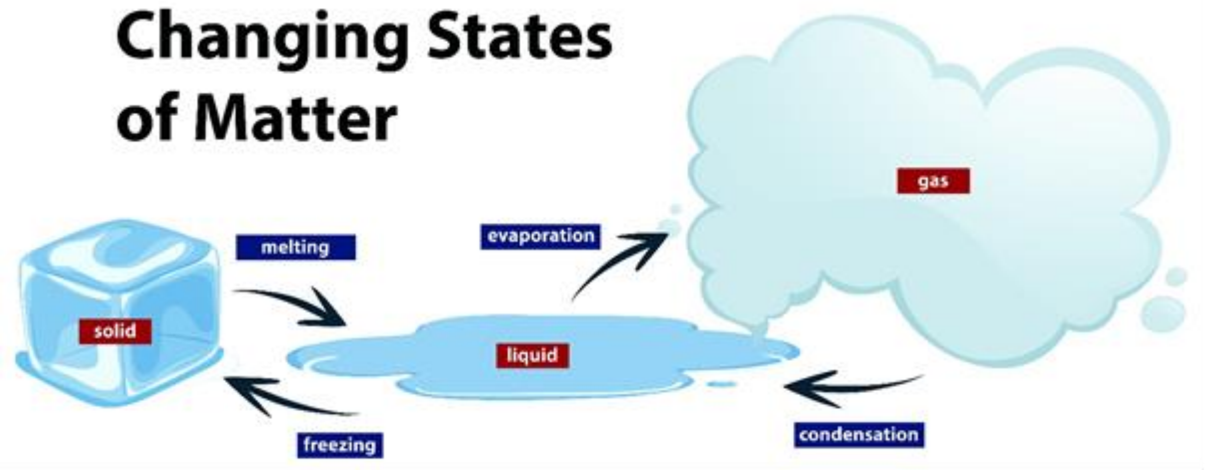


Figure I.1: Different changes in the physical state of matter

I.2.2 System classification

There are two types of system classification:

I.2.2.1 From the point of view of the matter contained in the system. There are two types of system:

1. Homogeneous system

A system is homogeneous if it consists of a single phase whose physical properties are the same throughout the matter.

Example

O_2, gas, H_2O liquid, ...etc.

2. Heterogeneous system

A system is heterogeneous if it comprises several phases, or if the single phase has different properties in different regions.

Example

water-ice, water-oil...etc.

I.2.2.2 Exchanges between system and external environment

The evolution of a system's state over time is determined by knowledge of the nature of exchanges with the outside world. These exchanges are of an energetic nature, such as work or heat. We distinguish three types of thermodynamic system:

1. Open system

The open system exchanges matter and energy with the external environment (Figure I.2).

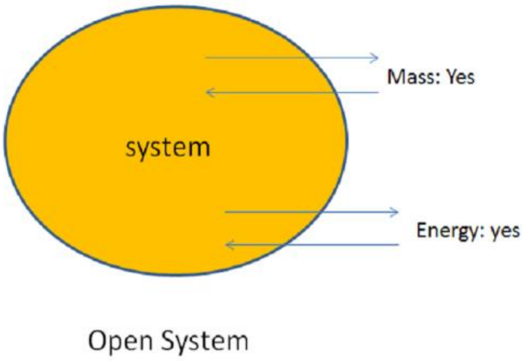
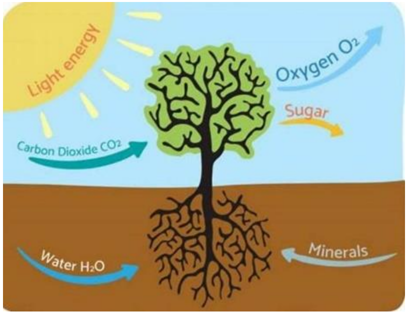


Figure I.2: Open system

Example

Tree: exchange of CO_2 and O_2 mineral salts Heating



2. Closed system

The closed system retains its quantity of matter, but exchanges energy with the external environment (Figure I.3).

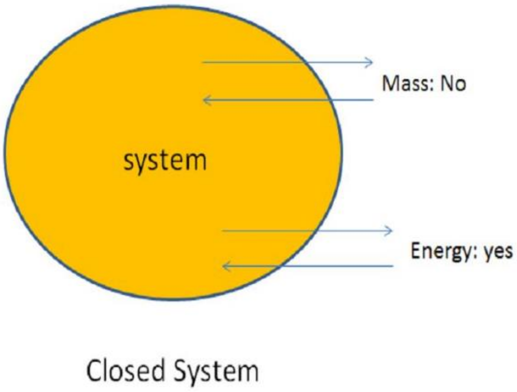


Figure I.3: Closed system

Example

Oil-bath heating

3. Isolated system

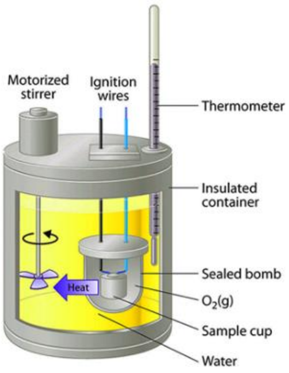
An isolated system cannot exchange either matter or heat with the external environment (Figure I.4)

Figure I.4: Isolated system

Example

Thermo coffee

calorimeter



Calorimeter

I.3 System phase

Any homogeneous part of a system constitutes a phase

A single-phase system has only one phase.

A mixture of gases constitutes a single-phase system.

A polyphase system has several phases and is a heterogeneous system.

A gas containing smoke is a polyphase system.

Note

Sign conventions

Everything received by the system is counted positively.

Everything given up by the system is counted negatively.

I.4 State of a system and state quantity

The thermodynamic state of a system is represented by macroscopic quantities relating to the microscopic state of the matter making up the system. All macroscopic quantities macroscopic quantities, whether directly measurable or not, that can describe the state of a system are called state quantities.

Example

Volume (V), pressure (P), temperature (T), mass (m)...etc.

I.5 Intensive and extensive quantities

I.5.1 Intensive quantities (intensive variables)

These are independent of the quantity of matter in the system. These variables are non-additive.

Example

Pressure, temperature, mole fraction, etc.

I.5.2 Extensive quantities (extensive variables)

These are proportional to the quantity of matter in the system. They are additive variables.

Examples

Mass, volume, etc.

gas (m, v, T) + gas (m, v, T) gives→ gas (2m, 2v, T)

Note

$$\text{intensive} = \frac{\text{extensive}}{\text{extensive}}, \rho = \frac{\text{m}}{\text{v}} \Longrightarrow \text{intensive}$$

I.6 Perfect gas

This is a theoretical gas model in which, apart from collisions, no account is taken of interactions between molecules.

$$PV = n\,RT$$

P: pressure (atm, Pa, 1 atm = 1.013 105 Pa, mmHg)

V : volume (L, m^3 1L = 10^{-3} m^3)

N: number of moles (mol)

R: perfect gas constant (R = 0.0082 L am/mol K = 8.31 J /mol K = 2 cal/mol K)

T : temperature (°C, K, T (K) = T (°C) + 273)

I.7 Transformation of a system

The transformation of a system is the passage of the system from a state of thermodynamic equilibrium, called the initial state, to another state of thermodynamic equilibrium, known as the final state.

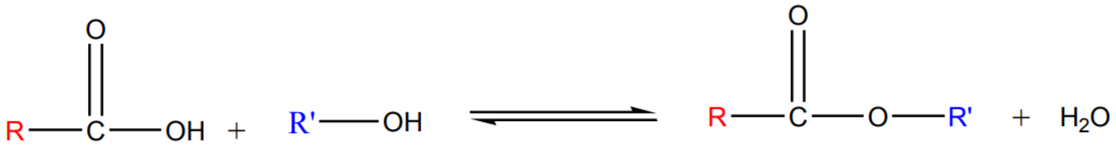
I.7.1 Reversible transformation

A reversible transformation is a transformation consisting of a continuous sequence of thermodynamic equilibrium states. During a reversible transformation, the system is in thermodynamic equilibrium at all times. A reversible transformation can be carried out in the opposite direction by through the same states of equilibrium. In practice, a transformation can be considered reversible if: It is carried out very slowly.

There are no dissipative forces (friction, diffusion=matter transfer), inhomogeneity of the system (e.g. heat transfer), etc.), both within the system and between the system and the external system.

Example

Esterification reaction.



$$R-C(=O)-OH + R'-OH \rightleftharpoons R-C(=O)-O-R' + H_2O$$

I.7.2 Irreversible transformation

An irreversible transformation is one during which the system is out of equilibrium out of equilibrium when moving from the initial to the final state. In practice, an irreversible transformation is one which :

1. either takes place rapidly.
2. takes place in the presence of frictional forces.
3. takes place rapidly and in the presence of friction.

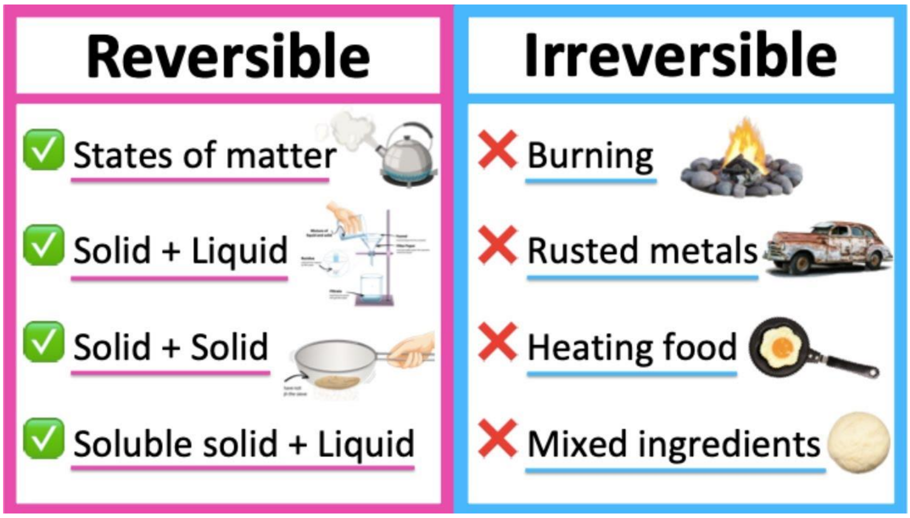
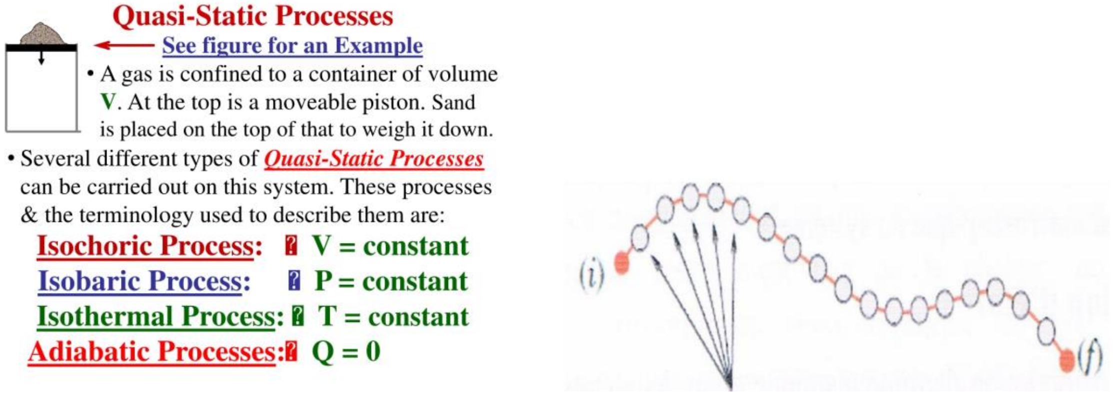


Figure I.6: Reversible and irreversible transformation of a mixture

1.7.3 Infinitely slow transformation (quasi-static)

This is a transformation slow enough for the system to pass through a continuous series of infinitely neighboring equilibrium states from i to f.



Quasi-Static Processes

See figure for an Example

- A gas is confined to a container of volume **V**. At the top is a moveable piston. Sand is placed on the top of that to weigh it down.
- Several different types of *Quasi-Static Processes* can be carried out on this system. These processes & the terminology used to describe them are:

Isochoric Process: ▯ **V = constant**

Isobaric Process: ▯ **P = constant**

Isothermal Process: ▯ **T = constant**

Adiabatic Processes:▯ **Q = 0**

Figure I.7: Quasi-static transformation

By adding infinitesimal masses dm to the piston we achieve an infinitely slow transformation. The response time of the system (relaxation time) must be very low so that after each elementary disturbance, the state parameters are immediately defined. For an infinitely slow transformation the system is a state of inert thermodynamic equilibrium at each moment.

I.7.4 Particular transformation.

There are several ways to transform a system: A system can undergo a transformation at fixed temperature (T = ste). The transformation is called **isothermal**. According to the ideal gas law:

$$P\,V = \underbrace{n\,R\,T}_{ste} \Longrightarrow PV = ste$$

$(1)\xrightarrow{T\ =\ ste}(2)$

P_1 P_2

v_1 v_2

$P_1v_1 = P_2v_2 \Longrightarrow \boxed{\frac{P_1}{P_2} = \frac{v_2}{v_1}}$ **Boyle-Mariotte Law**

Increase or decrease in the volume of a gas at constant temperature

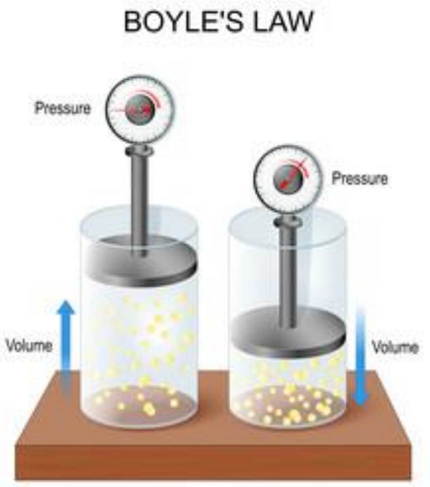


Figure I.8: Schematic illustration of the Boyle-Mariotte law

The graphic representation of the Boyle-Mariotte law is shown in the following figure

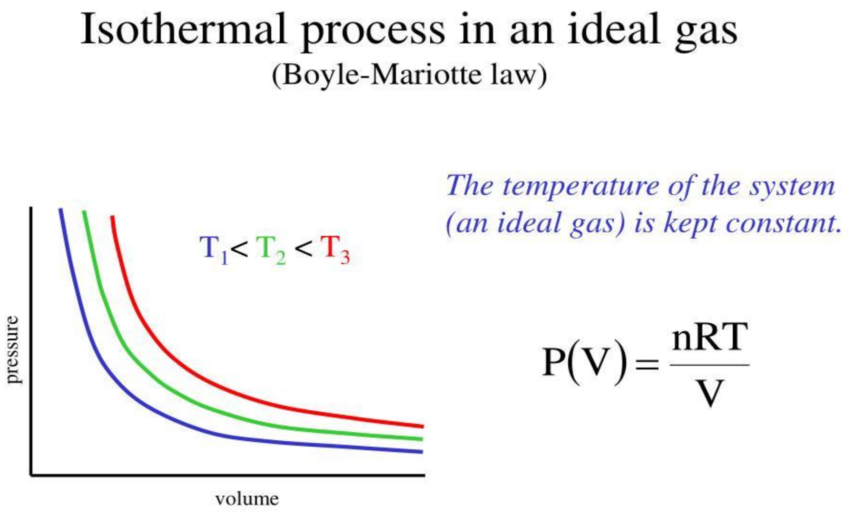


Figure I.9: Boyle –Mariotte law for an isothermal transformation

A system can undergo a transformation at fixed pressure (P =ste). The transformation is called **isobaric**. According to the ideal gas law:

$$P\,v = nRT \Rightarrow \frac{v}{T} = \frac{n\,R}{\underbrace{P}_{ste}} \Longrightarrow \frac{v}{T} = ste$$

$$(1)\underrightarrow{P\ =\ ste}(2)$$

$$\begin{array}{ll} v_1 & v_2 \\ T_1 & T_2 \end{array}$$

$$\frac{v_1}{T_1} = \frac{v_2}{T_2} \Longrightarrow \boxed{\frac{v_1}{v_2} = \frac{T_1}{T_2}}$$ **Charles' Law**

Charles' Law Heating or cooling a gas at constant pressure

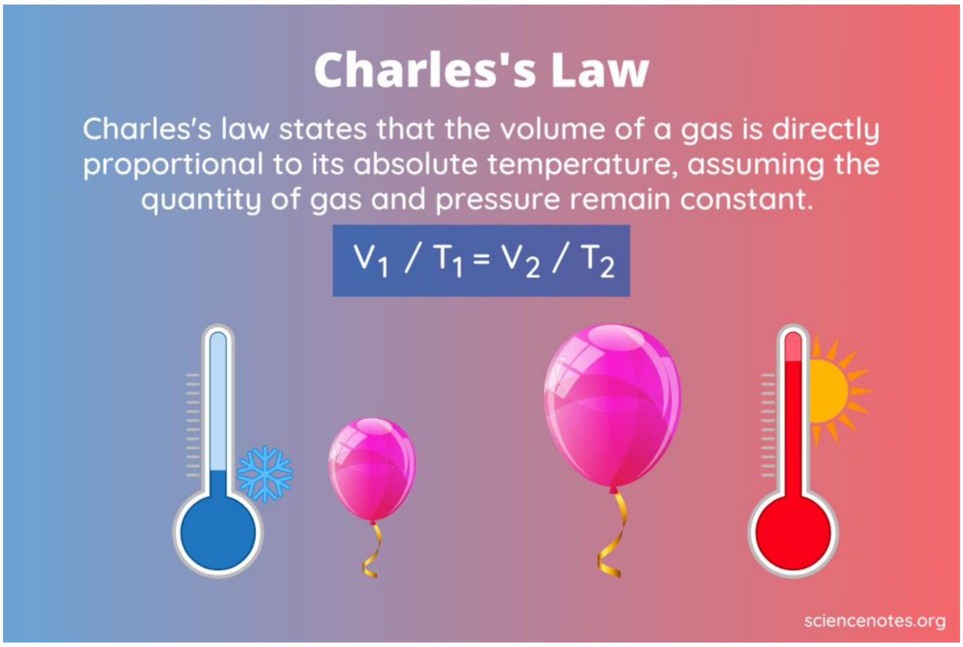
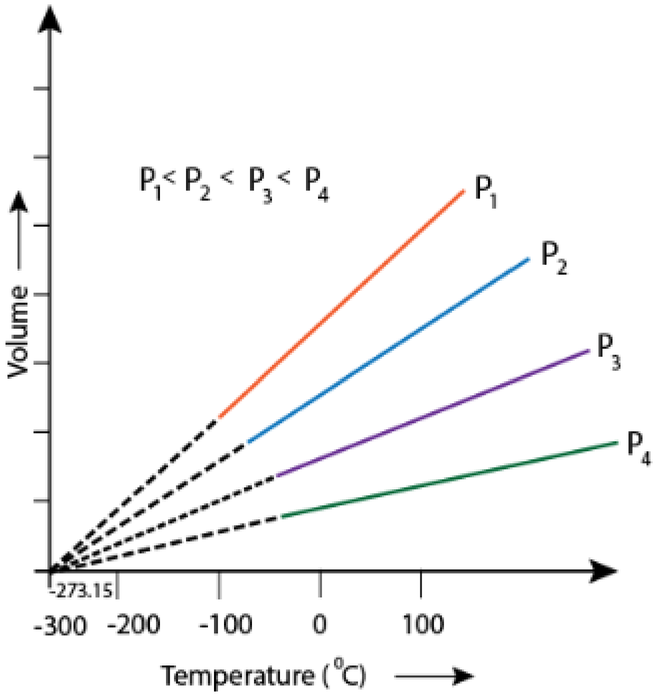


Figure I.10: Schematic illustration of Charles' law

The graphic representation of Charles' law is shown in the following figure



Volume Vs Temperature graph (°C)

Figure I.11: Charles' law for an isobaric transformation

A system can undergo a transformation at fixed volume (V = ste).

The transformation is called **isochoric**. According to the ideal gas law:

$$P\,v = nRT \Rightarrow \frac{P}{T} = \frac{n\,R}{\underbrace{v}_{ste}} \Longrightarrow \frac{P}{T} = ste$$

$$(1)\underrightarrow{v\ =\ ste}(2)$$

$$\begin{array}{ll} P_1 & P_2 \\ T_1 & T_2 \end{array}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Longrightarrow \boxed{\frac{P_1}{P_2} = \frac{T_1}{T_2}}$$ **Charles' Law**

Heating or cooling a gas at constant volume

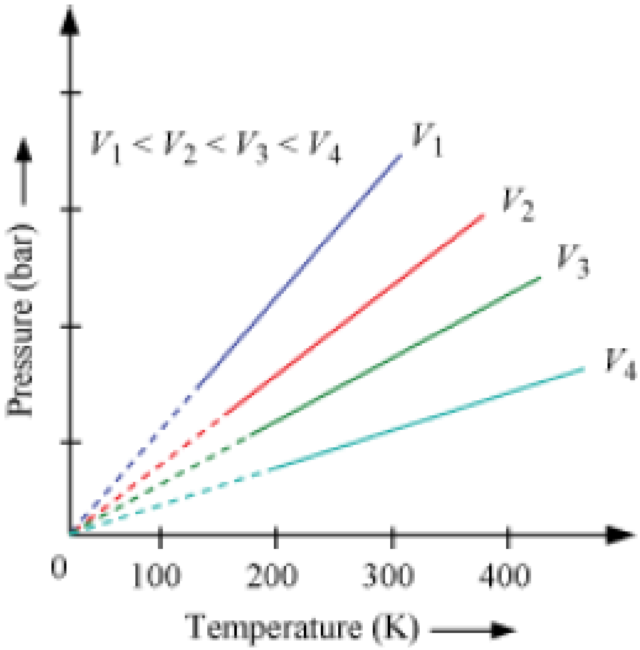


Figure I.13: Charles' law for an isobaric transformation

A system can undergo a transformation where the quantity of heat is conserved but the temperature can change over time. The transformation is called **adiabatic**. $\sum Q = 0$ / Q: quantity of heat This transformation is characterized by the Laplace equation: Pv^{γ} = ste γ is the atomicity constant, it depends on the nature of the gas studied: Monatomic gases such as rare gases (last column of the periodic table). Diatomic gases such as nitrogen (N_2), oxygen (O_2)...

Note

a- Open transformations

An open transformation is a transformation where the final state of the system is different from the initial state (**Figure I.14**).

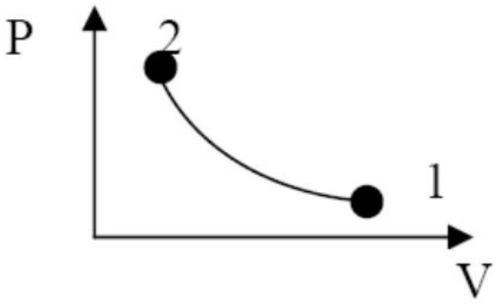


Figure I.14: Open transformation

b-Notion of thermodynamic cycle

A thermodynamic cycle is a series of open transformations or the system undergoes a series of transformations, which returns it to its initial state (**Figure I.15**).

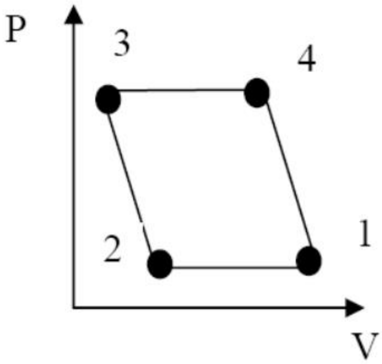
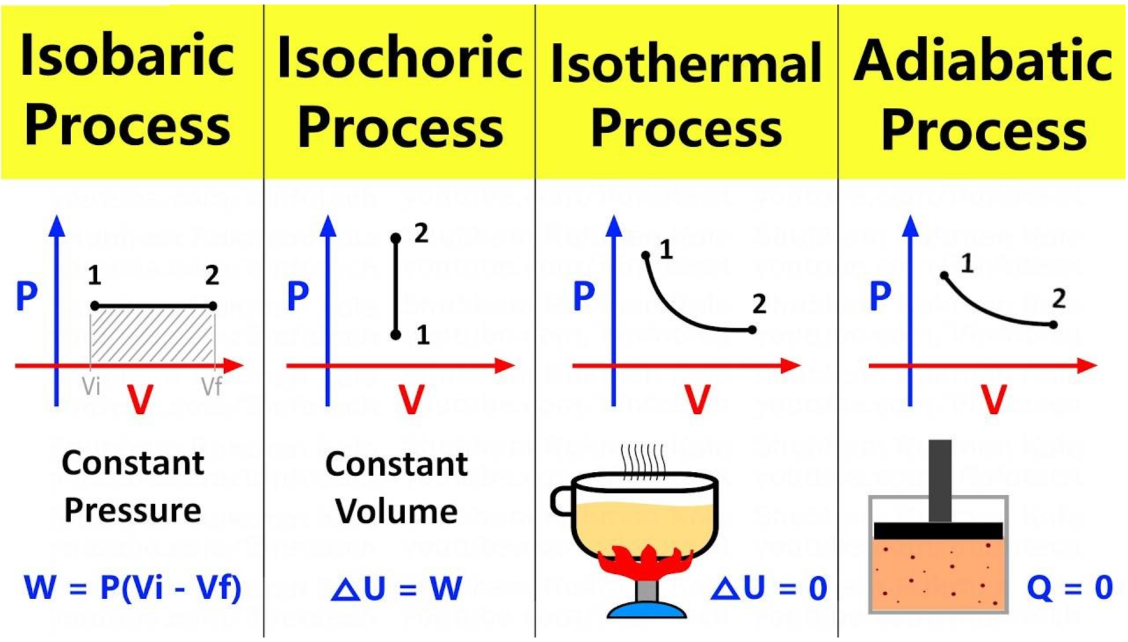


Figure I.15: Cyclic transformation c-Clapeyron diagram

The transformations of an ideal gas isochoric, isobaric and isothermal and adiabatic can be represented on the Clapeyron diagram (P = f(V)) (**Figure I.16**).



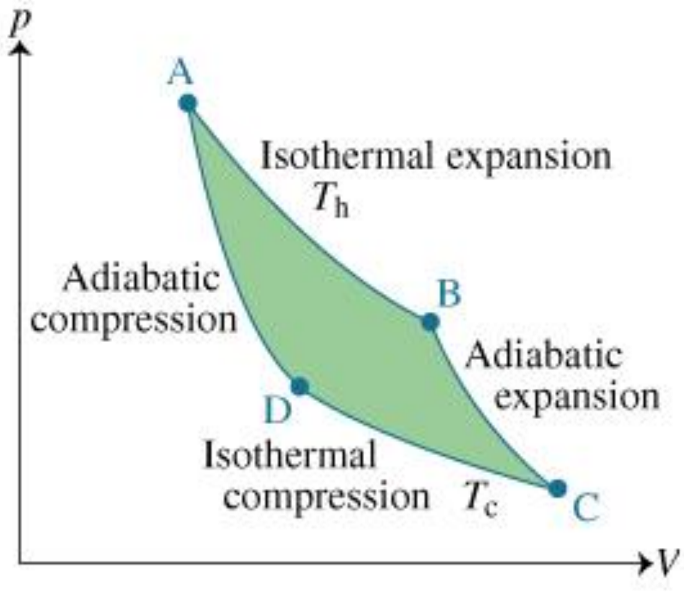


Figure I.16: Clapeyron diagram

d-Amagat diagram

The diagram which represents the product (PV) as a function of P for gases such as: hydrogen, oxygen, nitrogen or carbon monoxide gives a better interpretation of the pressure difference which exists between a ideal gas and a real gas.

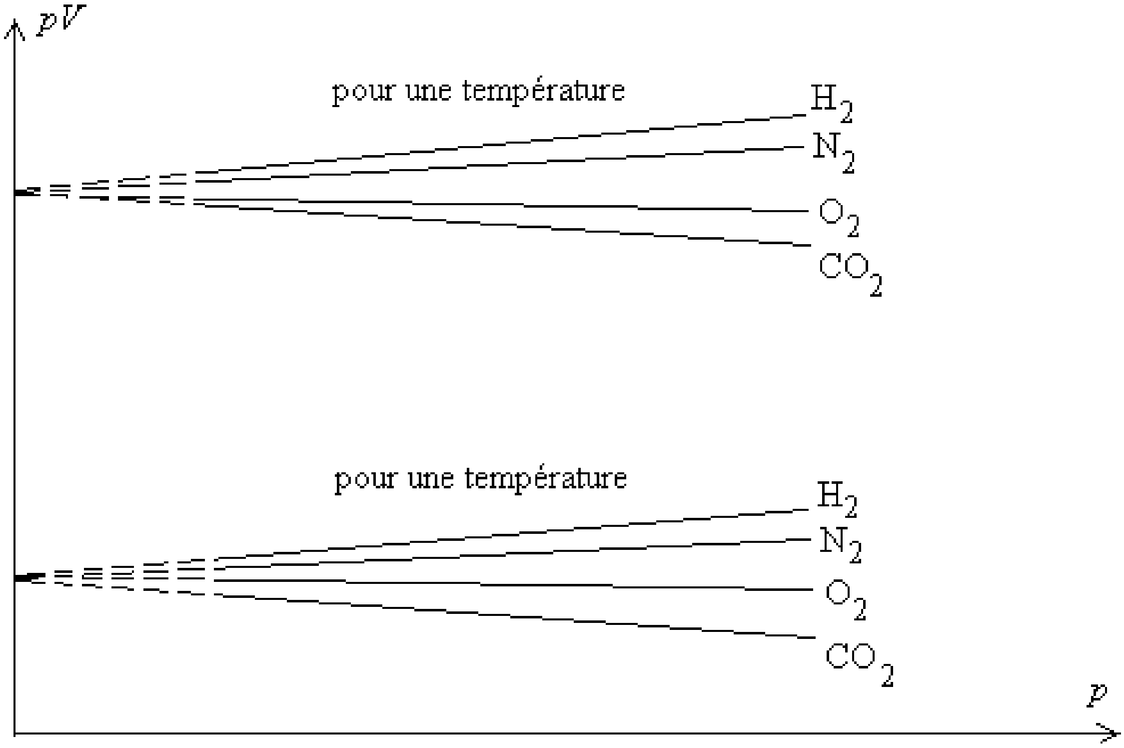


Figure I.17: Amagat diagram

It was found that beyond a pressure of 1 atm, real gases deviate from ideal gases as shown in the Amagat diagram with a straight line. If the pressure $P \rightarrow 0$,

the entire curve converges towards a single point RT. So an ideal gas is the approximation of the real gas in the limit for: P → 0 : lim P→0 (real gas) = ideal gas When the pressure increases we notice that certain gases (H_2, O_2) move away from the right of the ideal gas model.

I.8 Thermodynamic equilibrium

A system is in thermodynamic equilibrium if its thermodynamic variables (P, V, T, etc.) are constant over time and if there is no exchange between this system and its external environment as well as between the different parts of the system. system. Thermodynamic equilibrium includes both mechanical equilibrium, thermal equilibrium and chemical equilibrium. A system is in mechanical equilibrium when there are no uncompensated forces, both within the system and between the system and the external environment. A system is in thermal equilibrium when the temperature is the same at all its points and is also the same as that of the external environment. A system is in chemical equilibrium when it is not the site of a chemical reaction causing a modification of its internal structure. Noticed The systems studied are assumed to be at rest, that is to say, no overall movement, neither translation nor rotation. The gravitational potential energy of the system is assumed to be constant.

I.9 State function

I.9.1 Mathematical notions

1. Differential of a function

with a single variable Let the function of a variable f(x) be the differential:

$$df = \left(\frac{\partial f}{\partial x}\right) dx.$$

2. Multivariable function.

Partial derivatives Let f be a function of two variables x and y, differentiable according to x and y If we provisionally consider y as a constant, f can be derived with respect to x: We then obtain the partial derivative of f with respect

to x, denoted:

$$\left(\frac{\partial f}{\partial x}\right)_y$$

Similarly, by fixing x and differentiating f with respect to y, we obtain the partial derivative of with respect to y, denoted:

$$\left(\frac{\partial f}{\partial y}\right)_x$$

Example

$$f(x,y) = 2\,x^2 + 5y^2 - xy$$

$$\left(\frac{\partial f}{\partial x}\right)_y = 4x - y$$

$$\left(\frac{\partial f}{\partial y}\right)_x = 10y - x$$

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

$$df = (4x - y)dx + (10y - x)dy$$

I.9.2 Différentielle totale exacte (D.T.E)

The equality of the crossed second derivatives makes it possible to recognize the DTEs. The differential form, df (x,y) is totally exact if and only if, we have:

$$\boxed{\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right) = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)}$$

Exemple

$$1\text{-}df = (4x - y)dx + (10y - x)dy$$

$$\left(\frac{\partial f}{\partial x}\right)_y = (4x - y) \Rightarrow \left(\frac{\partial}{\partial y}(4x - y)\right) = -1$$

$$\left(\frac{\partial f}{\partial y}\right)_x = (10y - x) \Rightarrow \left(\frac{\partial}{\partial x}(10y - x)\right) = -1$$

where f (x, y) is a DTE

2-The equation of state of a gas is given by the relation:

$$: P = \frac{RT}{V-b}$$

a-Determine the expressions for the following partial derivatives:

$$\left(\frac{\partial P}{\partial T}\right)_V \text{ et } \left(\frac{\partial P}{\partial V}\right)_T$$

$$(\partial P/\partial T)\ V\text{and } (\partial P/\partial V)\ T$$

b-Prove that dP is an exact total differential

2-a-Partial derivatives

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\left(\frac{RT}{V-b}\right)\right) \Rightarrow \boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{RT}{V-b}\right)\right) \Rightarrow \boxed{\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2}}$$

b-DTE

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \Rightarrow dP = \left(\frac{R}{V-b}\right) dT + \left(-\frac{RT}{(V-b)^2}\right) dV$$

$$\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right) = \frac{\partial}{\partial V}\left(\frac{R}{V-b}\right) \Rightarrow \boxed{\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right) = -\frac{R}{(V-b)^2}}$$

$$\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right) = \frac{\partial}{\partial T}\left(-\frac{RT}{(V-b)^2}\right) \Rightarrow \boxed{\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right) = -\frac{R}{(V-b)^2}}$$

A state function is a quantity which is linked to state variables such as internal energy (U), enthalpy (H), entropy (S)... It is a function of two or several variables, its differential must be exact total and its integral does not depend on the path followed (Figure I.18).

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

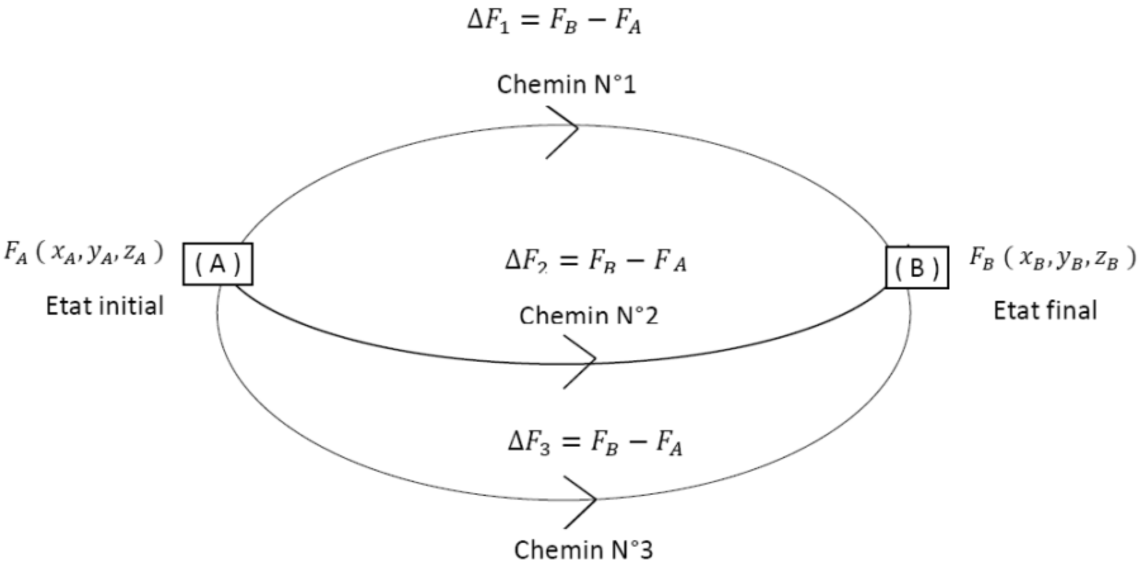


Figure I.18: Definition of a state function

We demonstrate in mathematics that the mixed second derivative does not depend on the order of differentiation.

$$\boxed{\frac{\partial^2 F}{\partial x\,\partial y} = \frac{\partial^2 F}{\partial y\,\partial x}}$$

I.10 Chemical composition of a gas mixture

The chemical composition of a phase or a homogeneous system is defined if we know the relative proportions of all the constituents found there.

These different relative proportions can be expressed in various ways.

I.10.1 Molar fraction

The mole fraction (X) is a quantity used to express the composition of a mixture.

The molar number of a constituent i is equal to the ratio of the number of moles of this constituent i to the total number of moles of the mixture. It is therefore a dimensionless quantity.

$$\boxed{X_i = \frac{n_i}{\sum n_i}}$$

Xi: mole fraction of a gas ni: number of moles of a gas

$$\boxed{n_i = \frac{\text{masse donnée}}{\text{masse molaire}} \text{ ou } \frac{\text{volume donnée}}{\text{volume molaire (22,4 L)}}}$$

The sum of the mole fractions of the constituents of the mixture is equal to unity $\sum Xi = 1$.

I.10.2 Partial pressure

Consider the case where two gases, A and B, are in a container of volume v.

the pressure exerted by gas A, according to:

$$P_A = \frac{n_A RT}{v}$$

where nA is the number of moles of A. Similarly, the pressure exerted by B is

$$P_B = \frac{n_B RT}{v}$$

In the case of a mixture of gases A and B, the total pressure PT is the result of the collisions of the two types of molecules A and B, on the wall of the container. Thus, according to Dalton’s law (**Figure I.19**),

$$P_T = P_A + P_B \Rightarrow P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V} \Rightarrow P_T = \frac{RT}{V}(n_A + n_B) \Rightarrow P_T = \frac{n_T RT}{V}$$

where nT is the number of total moles of gases present.

$$\frac{P_A}{P_T} = \frac{\frac{n_A RT}{V}}{\frac{RT}{V}(n_A + n_B)} \Rightarrow \frac{P_A}{P_T} = \frac{n_A}{n_A + n_B} \Rightarrow \frac{P_A}{P_T} = X_A$$

SO:

$$\boxed{P_i = X_i P_T}$$

Pi: partial pressure

PT: total pressure

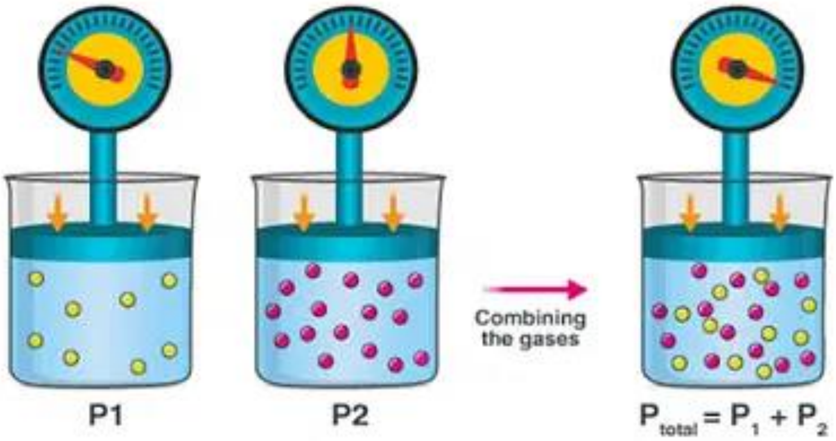


Figure I.19: Dalton partial pressure

Example

A gas mixture of 0.428 g, contained in an enclosure at a pressure of 1.75 atm is consisting (by mass) of 15.6% N2 (g), 46.0% N2O (g) and 38.4% CO2 (g). What is the partial pressure of each of the gases in the mixture? The masses of the three gases in the mixture are:

$$m\ (g) = \frac{\text{pourcentage} \times \text{masse du mélange gazeux}}{100}$$

$$m_{N_2(g)} = \frac{15{,}6 \times 0{,}428}{100} \Rightarrow \boxed{m_{N_2(g)} = 0{,}0668\ g}$$

$$m_{N_2O(g)} = \frac{46{,}0 \times 0{,}428}{100} \Rightarrow \boxed{m_{N_2O(g)} = 0{,}197\ g}$$

$$m_{CO_2(g)} = \frac{38{,}4 \times 0{,}428}{100} \Rightarrow \boxed{m_{CO_2(g)} = 0{,}164\ g}$$

Mole number

$$n_{N_2(g)} = \frac{m_{N_2(g)} \times 1\ \text{mol de}\ N_2}{M_{N_2(g)}} \Rightarrow n_{N_2(g)} = \frac{0{,}0668 \times 1\ \text{mol}}{14 \times 2} \Rightarrow \boxed{n_{N_2(g)} = 2{,}38\ 10^{-3}\text{mol}}$$

$$n_{N_2O(g)} = \frac{m_{N_2O(g)} \times 1\ \text{mol de}\ N_2O}{M_{N_2O(g)}} \Rightarrow n_{N_2O(g)} = \frac{0{,}197 \times 1\ \text{mol}}{14 \times 2 + 16}$$

$$\Rightarrow \boxed{n_{N_2O(g)} = 4{,}48\ 10^{-3}\text{mol}}$$

$$n_{CO_2(g)} = \frac{m_{CO_2(g)} \times 1\ \text{mol de}\ CO_2}{M_{CO_2(g)}} \Rightarrow n_{CO_2(g)} = \frac{0{,}164 \times 1\ \text{mol}}{12 + 16 \times 2}$$

$$\Rightarrow \boxed{n_{CO_2(g)} = 3{,}73\ 10^{-3}\text{mol}}$$

Mole fraction

$$x_{N_2(g)} = \frac{n_{N_2(g)}}{n_{Tot(g)}}$$

$$n_{Tot(g)} = n_{N_2(g)} + n_{CO_2(g)} + n_{N_2O(g)} \Rightarrow \boxed{n_{Tot(g)} = 10{,}59\ 10^{-3}\text{mol}}$$

$$x_{N_2(g)} = \frac{2{,}38\ 10^{-3}}{10{,}59\ 10^{-3}} \Rightarrow \boxed{x_{N_2(g)} = 0{,}225}$$

$$x_{N_2O(g)} = \frac{4{,}48\ 10^{-3}}{10{,}59\ 10^{-3}} \Rightarrow \boxed{x_{N_2O(g)} = 0{,}423}$$

$$x_{CO_2(g)} = \frac{3{,}73\ 10^{-3}}{10{,}59\ 10^{-3}} \Rightarrow \boxed{x_{CO_2(g)} = 0{,}352}$$

Partial pressure

$$P_{N_2(g)} = x_{N_2(g)} \times P_{Tot} \Rightarrow P_{N_2(g)} = 0{,}225 \times 1{,}75 \Rightarrow \boxed{P_{N_2(g)} = 0{,}349\text{ atm}}$$

$$P_{N_2O(g)} = x_{N_2O(g)} \times P_{Tot} \Rightarrow P_{N_2O(g)} = 0{,}423 \times 1{,}75 \Rightarrow \boxed{P_{N_2O(g)} = 0{,}740\text{ atm}}$$

$$P_{CO_2(g)} = x_{CO_2(g)} \times P_{Tot} \Rightarrow P_{CO_2(g)} = 0{,}352 \times 1{,}75 \Rightarrow \boxed{P_{CO_2(g)} = 0{,}616\text{ atm}}$$

I.11 Thermometry

is the field of measuring temperature using instruments called thermometers.If the thermometer is in thermal equilibrium with the body whose temperature is unknown then the temperature measured by the thermometer is that of the body considered.

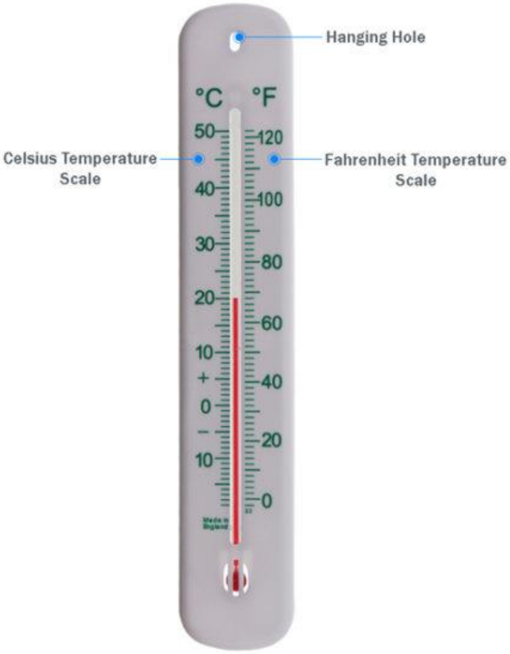
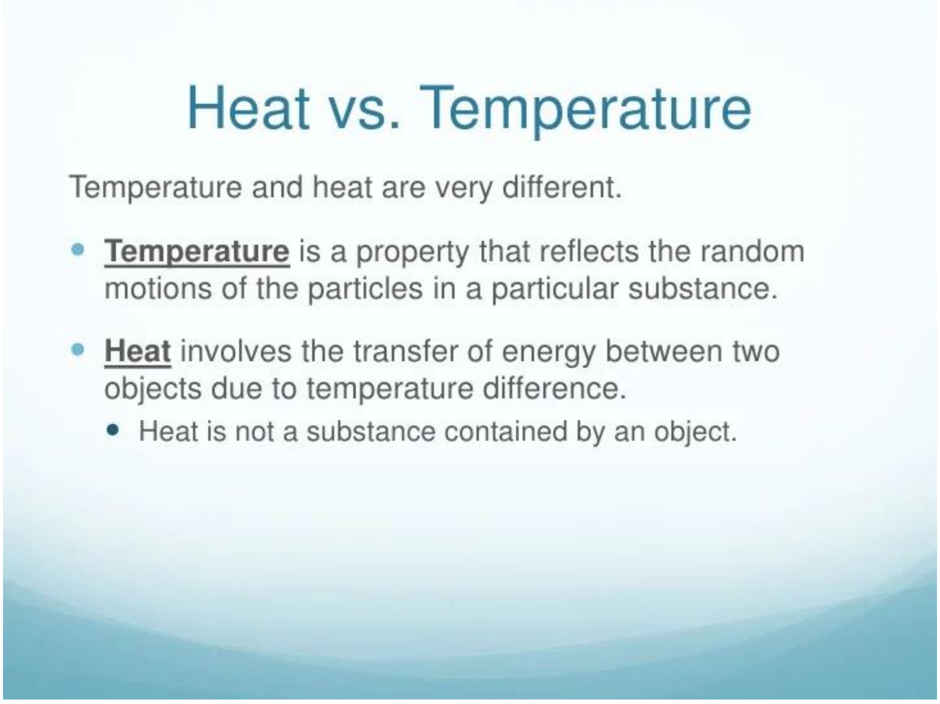


Figure I.20: Descriptive image of the thermometer

I.11.1 Concept of temperature

Temperature is a measurable physical quantity associated with the heat level of a body or a system: it relates heat by involving temperature and quantity what is hot (the mass); it also depends on the nature of the substance (**Figure I.21**).



Heat vs. Temperature

Temperature and heat are very different.

- **Temperature** is a property that reflects the random motions of the particles in a particular substance.
- **Heat** involves the transfer of energy between two objects due to temperature difference.
  - Heat is not a substance contained by an object.

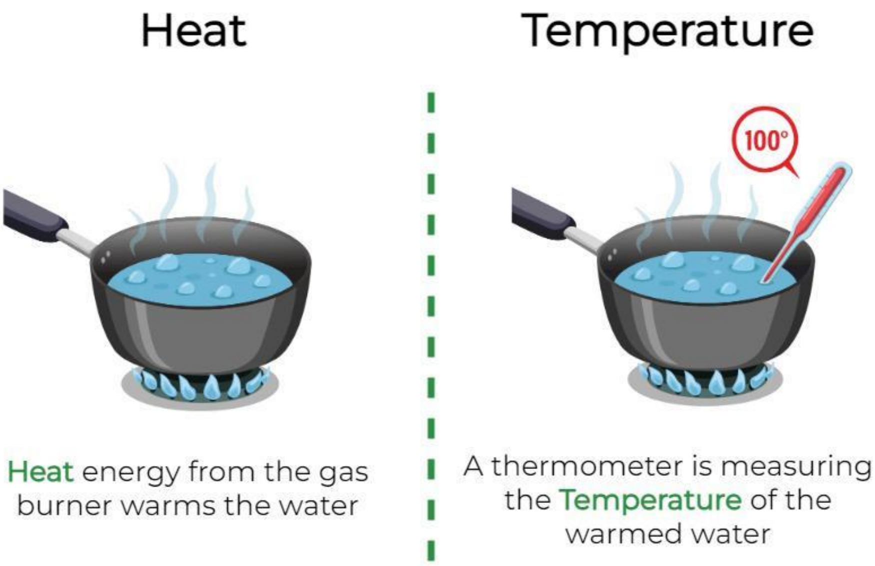


Figure I.21: Physical meaning of temperature

On the microscopic scale, temperature is linked to the variation in the speed of molecules. The higher the temperature of a substance, the greater the speed of the molecules (**Figure I.22**). When we observe two objects: the one whose temperature is higher is the hotter: the molecules which make up the hotter object will move faster than those which make up the colder object.

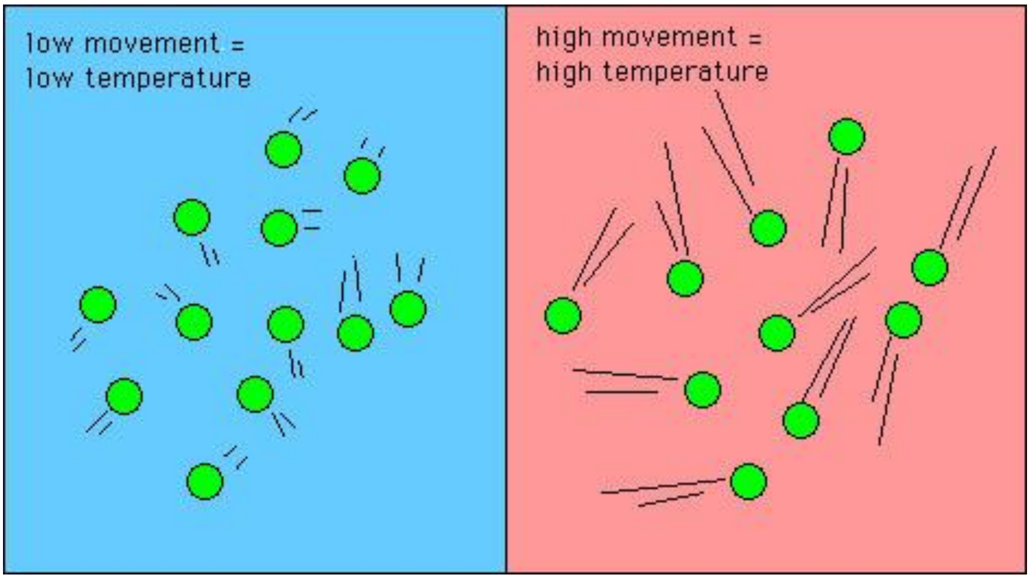


Figure I.22: Thermal agitation phenomenon

I.11.2 Temperature scale

To set a temperature scale on a thermometer, we choose 02 temperatures that can be easily obtained (the boiling and freezing temperature of water). These two temperatures constitute the upper and lower fixed points. The interval between these two fixed points is divided into a number of equal parts called degrees.

I.11.2.1 Centesimal scale

The thermometric degree is the hundredth part of the distance between the term of melting ice and that of boiling water under normal atmospheric pressure. Either: Two fixed points: 0° melting ice, 100° boiling water A linear relationship T ax b We can write:

$$T_0 = 0 \Rightarrow ax_0 + b = 0$$

$$T = 100 \Rightarrow ax_{100} + b = 100$$

$$a = \frac{100}{x_{100} - x_0} \text{ et } b = \frac{100\, x_0}{x_0 - x_{100}} \text{, donc } \boxed{T = \frac{100}{x_{100} - x_0}\, x + \frac{100\, x_0}{x_0 - x_{100}}}$$

Since x_0 and x_{100} are known, the determination of T is done by measuring x.

I.11.2.2 Centigrade or Celsius scale

This scale was developed by the Swedish astronomer Albert Celsius (1702-1744), taking into account:

-Melting points of ice (0°C) when the thermometer is placed in melting ice under ambient atmospheric pressure.

-Boiling points of water at 100°C, when the thermometer is placed in boiling water under ambient atmospheric pressure.

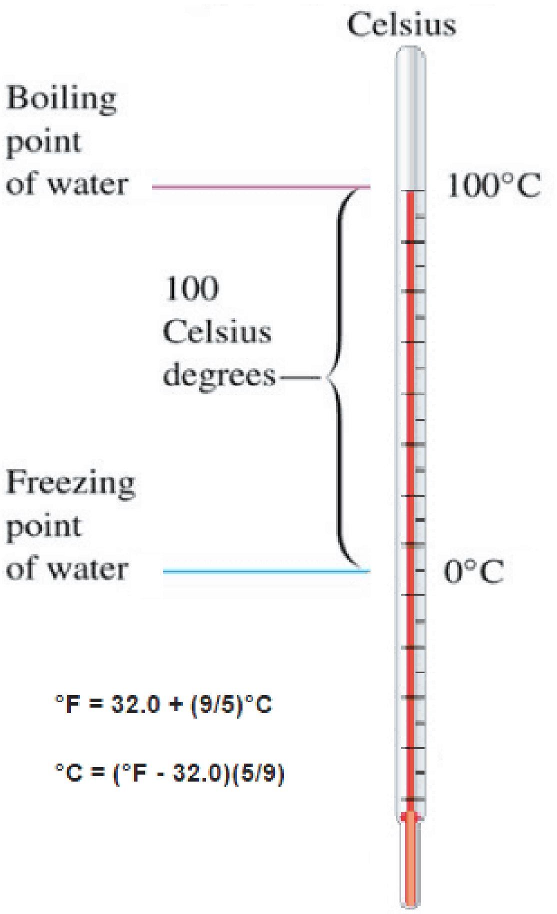


Figure I.23: Celsius scale

I.11.2.3 Absolute or Kelvin scale

This scale was proposed by Lord Kelvin (1824-1907). Experience has shown that there is a limit to the concept of cold. At the temperature – 273.15 °C, and on the microscopic scale, the particles no longer have thermal energy (no molecular agitation) and we cannot go below this temperature which is called absolute zero (0K).

$$T(K) = T(°C) + 273,15$$

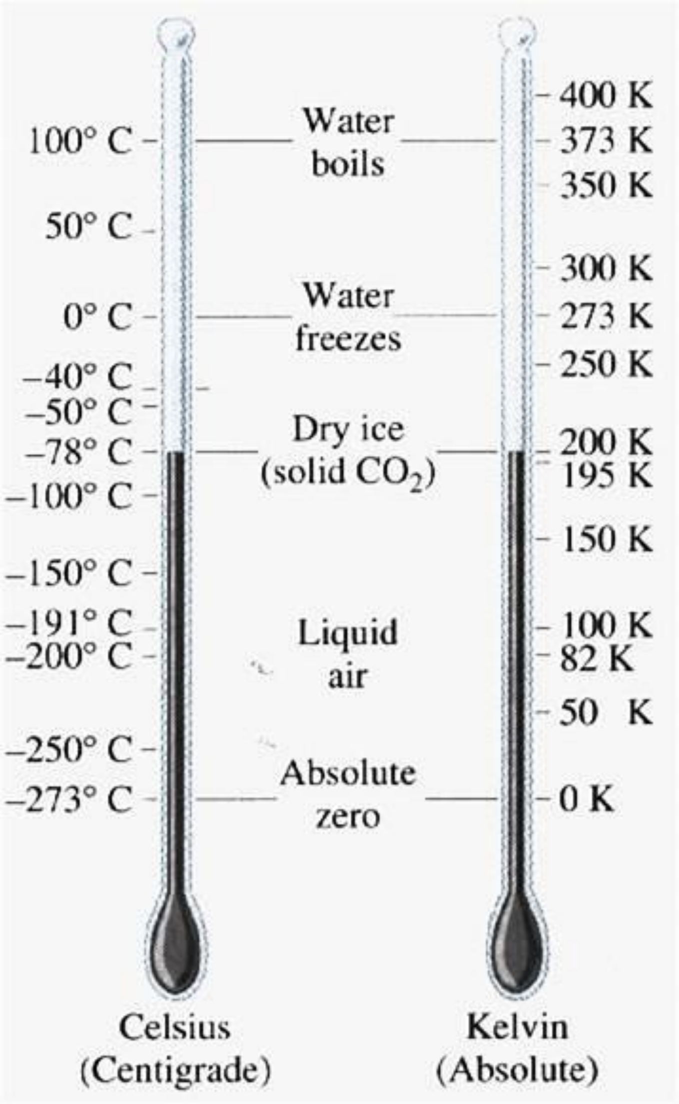


Figure I.24: Comparison between Celsius and Kelvin scales

I.11.2.4 Echelle de Fahrenheit

This scale was proposed by the German physicist Daniel Gabriel Fahrenheit in 1724. It is used in Anglo-Saxon countries. The relationship between temperatures expressed in degrees Celsius and degrees Fahrenheit is of the form: $T(°C)\ 100 = T(°F) - 32180$ that is to say:

$$T(°F) = 1.8\ T(°C) + 32$$

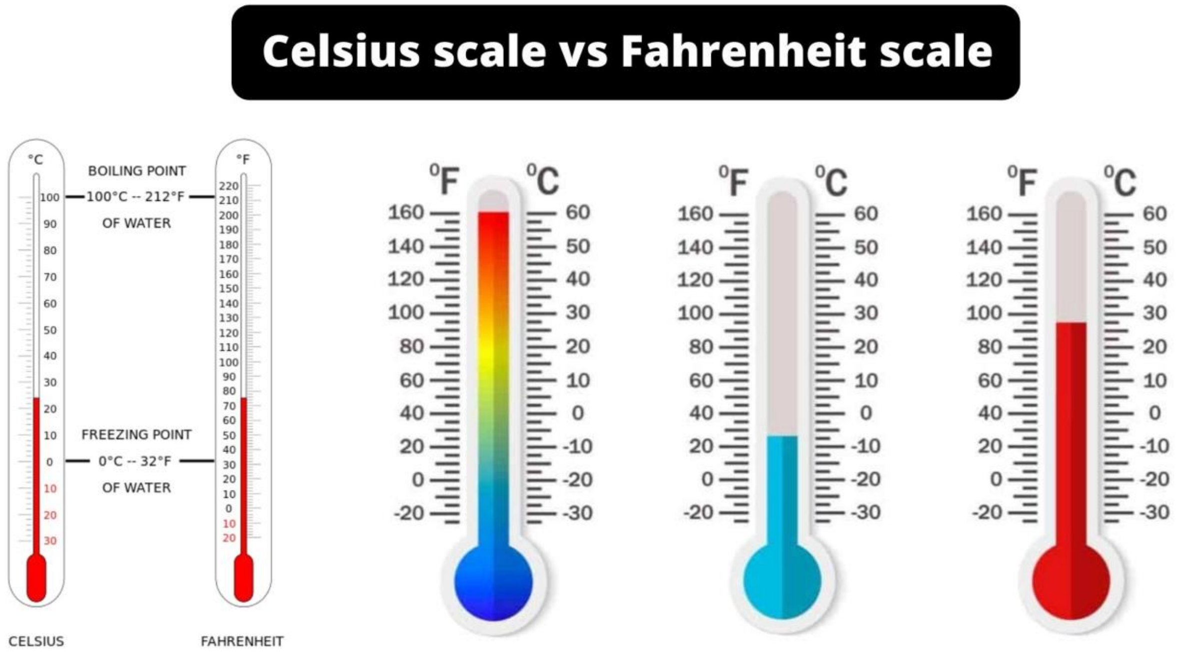
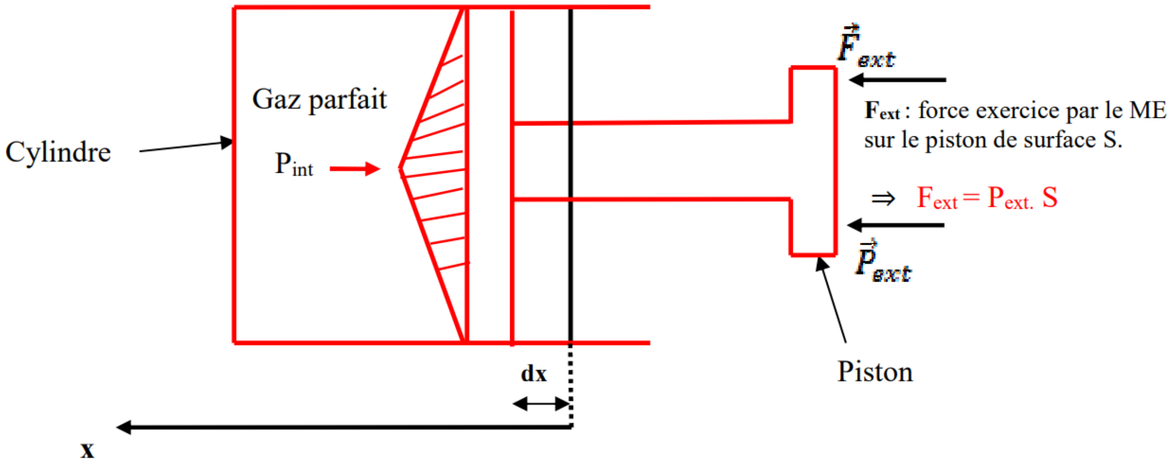


Figure I.25: Comparison between Celsius and Fahrenheit scales

I-12 Work of pressure forces:

For mechanical systems, work is defined as the action of an external force on an object across a distance. as the action of an external force on an object across a distance. It is equal to product of the force (F) multiplied by the displacement (d). The expression for mechanical work is obtained in the simplest case, by considering a perfect gas as the system in a cylinder. a perfect gas as a system in a cylinder closed by a movable piston of cross-section S. When a force is exerted on the piston, it moves to the left. exerts a pressing force F



Fext: The force exerted by the external environment on the piston with surface area S ⇒ Fext= Pext × S

For an elementary displacement dx of the piston under the effect of the force Fext, the

elementary work δW is equal to a

$$|\delta W| = |\overrightarrow{F_{ex}} \times \overrightarrow{dx}|$$

$$|\delta W| = |P_{ext} \times S \times dx|$$

$$|\delta W| = |P_{ext} dV| \quad \text{avec} \quad dV = S \times dx$$

During compression, the system receives work:

$\delta W > 0$

$$\text{Compression: } V_f < V_i \Rightarrow dV < 0$$

$$\text{donc } \delta W = -P_{ext} dV$$

During expansion, the system supplies work:

$$\delta W < 0$$

$$\text{Detente: } V_f > V_i \Rightarrow dV > 0$$

$$\text{donc } \delta W = -P_{ext} dV$$

The relation $\delta W = -P_{ext} dV$

is applicable whatever the shape of the container and the nature of the system transformation. For a finite transformation from an initial state to a final state:

$$W_{i \to f} = \int_i^f -P_{ext}\, dV = -\int_{V_i}^{V_f} P_{ext}\, dV$$

Units of work:

$$[W] = Pa \times m^3 = Joul$$

$$[W] = L \times atm \text{ avec } 1L = 10^{-3} m^3 \text{ et } 1atm = 1{,}013 \times 10^5 Pa$$
$$\Rightarrow 1L \times atm = 1{,}013 \times 10^{-2} Joul$$

$$[W] = Cal \text{ avec } 1Cal = 4{,}18 Joul$$

Work of a reversible transformation:

$$On\ a\quad \delta W = -P_{ext}dV$$

$$\text{Transformation réversible} \Rightarrow P_{ext} = P_{int} = P_{G\,P} = \frac{nRT}{V}$$

Reversible isothermal transformation:

$$\begin{array}{lcl} \text{Etat (i)} & \xrightarrow{T=cste} & \text{Etat (f)} \\ P_i & & P_f \\ V_i & & V_f \\ T_i & & T_f = T_i = cste \end{array}$$

$$\text{Isotherme: } T_i = T_f = T = cste \Rightarrow dT = 0$$

$$\text{Transformation réversible} \Rightarrow P_{ext} = P_{int} = P_{G\,P} = \frac{nRT}{V}$$

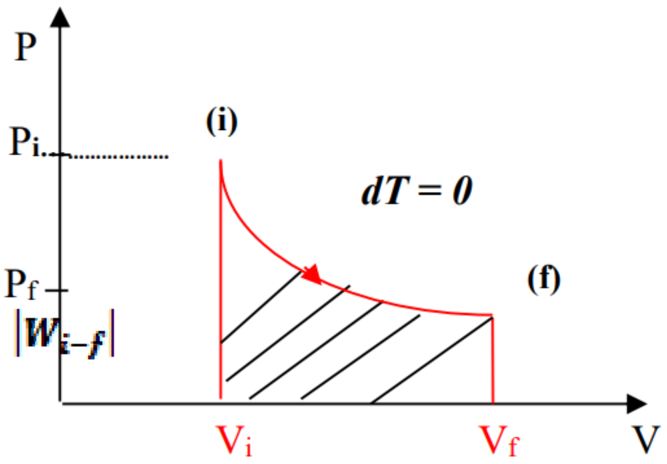
$$W_{i\to f} = -\int_{V_i}^{V_f} P_{ext}dV = -\int_{V_i}^{V_f} P_{int}\,dV = -\int_{V_i}^{V_f}\frac{nRT}{V}dV = -nRT\int_{V_i}^{V_f}\frac{dV}{V}$$

$$W_{i\to f} = -nRT\ln\frac{V_f}{V_i} = -nRT_i\ln\frac{V_f}{V_i} = -nRT_f\ln\frac{V_f}{V_i}$$

$$dT = 0 \Rightarrow P_iV_i = P_fV_f = cste$$

$$\frac{V_f}{V_i} = \frac{P_i}{P_f} \Rightarrow \quad W_{i\to f} = -nRT\ln\frac{P_i}{P_f} = -nRT_i\ln\frac{P_i}{P_f} = -nRT_f\ln\frac{P_i}{P_f}$$

In the Clapeyron diagram (P, V), work $W_{i\to f} = -\int_{V_i}^{V_f} P_{ext} \cdot dV$ is represented by the area between the curve, the volume axis and the parallels to the pressure $P = f(V)$ axis passing through the abscissae Vi and Vf.



Reversible isothermal expansion

$$\text{Etat (i)} \xrightarrow{dV=0} \text{Etat (f)}$$

$$\begin{array}{ll} P_i & P_f \\ T_i & T_f \\ V_i & V_f = V_i = \text{cste} \end{array}$$

$$\text{Isochore : } V_i = V_f = V = \text{cste} \Rightarrow dV = 0$$

$$\text{Réversible} \Rightarrow P_{ext} = P_{int} = P_{G\,p}$$

$$\delta W = -P_{ext}\,dV \Rightarrow \int_i^f \delta W = -\int_{V_i}^{V_f} P_{ext}\,dV = -\int_{V_i}^{V_f} P_{G\,p}\,dV \quad \text{avec } dV = 0$$

$$W_{i\rightarrow f} = 0 \text{ Joul}$$

Reversible isobaric transformation

$$\text{Etat (i)} \xrightarrow{dP=0} \text{Etat (f)}$$

$$\begin{array}{ll} P_i & P_f = P_i = \text{cste} \\ V_i & V_f \\ T_i & T_f \end{array}$$

Isobare: $P_i = P_f = P = \text{cste}$

Réversible ⇒ $P_{ext} = P_{int} = P_{GP} = P_i = P_f$

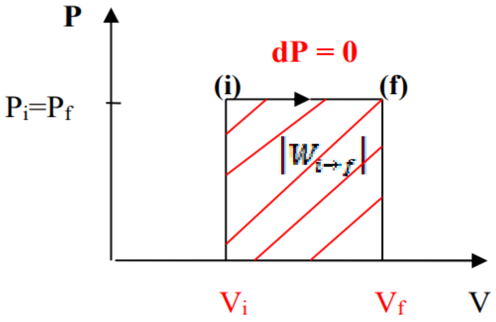
$$W_{i\to f} = -\int_{V_i}^{V_f} P_{ext}\,dV = -\int_{V_i}^{V_f} P_i\,dV$$

$$W_{i\to f} = -P_i\int_{V_i}^{V_f} dV = -P_i\,(V_f - V_i)$$

$$W_{i\to f} = -P_i(V_f - V_i) = -P_f(V_f - V_i) = -nR(T_f - T_i)$$

$$|\,W_{i\to f}\,| = S = \Delta P \times \Delta V = P_i\,(V_f - V_i)$$

$$W_{i\to f} = -P_i\,(V_f - V_i)$$



Reversible adiabatic transformation

$$\text{Etat (i)} \xrightarrow{Q=0} \text{Etat (f)}$$

$$\begin{array}{cc} P_i & P_f \\ V_i & V_f \\ T_i & T_f \end{array}$$

$$\text{Adiabatique: } Q = 0\text{Joul}$$

$$\text{Réversible} \Rightarrow P_{ext} = P_{int} = P_{GP} = \frac{cste}{V^{\gamma}}$$

$$W_{i\to f} = -\int_{V_i}^{V_f} P_{ext}\, dV = -\int_{V_i}^{V_f} P_{GP}\, dV = -\int_{V_i}^{V_f} \frac{cste}{V^{\gamma}} dV \quad / \quad cste = P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

$$W_{i\to f} = -\int_{V_i}^{V_f} cste \frac{dV}{V^{\gamma}} = -cste \int_{V_i}^{V_f} \frac{dV}{V^{\gamma}}$$

$$\int x^n dx = \frac{1}{n+1} x^{n+1} \quad \text{avec } x = V \text{ et } n = -\gamma$$

$$W_{i\to f} = -\frac{cste}{1-\gamma}\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right) = \frac{cste}{\gamma - 1}\left(V_f^{1-\gamma} - V_i^{1-\gamma}\right)$$

$$W_{i\to f} = \frac{1}{\gamma - 1}\left(P_f V_f^{\gamma} \times V_f^{1-\gamma} - P_i V_i^{\gamma} \times V_i^{1-\gamma}\right) = \frac{1}{\gamma - 1}\left(P_f V_f^{\gamma+1-\gamma} - P_i V_i^{\gamma+1-\gamma}\right)$$

$$\mathbf{W_{i\to f} = \frac{1}{\gamma - 1}(P_f V_f - P_i V_i)}$$

Work of an irreversible (spontaneous) transformation:

$$\text{Variation brutale de P:}\quad P_i \rightarrow P_f$$

$$\text{Irréversible} \Rightarrow P_{ext} \neq P_{G\,P}$$

At the initial instant, the external pressure is equal to Pf, and during the transformation, the gas works against this pressure. gas works against this pressure

$$P_{ext} = P_f = \text{cste}$$

$$(W_{i\rightarrow f})_{irré} = -\int_{V_i}^{V_f} P_{ext}\, dV = -\int_{V_i}^{V_f} P_f\, dV = -P_f\,(V_f - V_i)$$

$$(W_{i\rightarrow f})_{irré} = -P_f(V_f - V_i)$$

$$\text{On sait que: } V_f = \frac{nRT_f}{P_f} \text{ et } V_i = \frac{nRT_i}{P_i}$$

$$(W_{i\rightarrow f})_{irré} = -P_f\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right) = -nR\, P_f\left(\frac{T_f}{P_f} - \frac{T_i}{P_i}\right) = -nR\left(T_f - \frac{P_f\, T_i}{P_i}\right)$$

I-13 Heat or quantity of heat I-13 Heat or quantity of heat

Heat is characterized by a change in system temperature, or a change in the physical state of the system's matter. change in the physical state of matter in the system.

I-13-1 Temperature variation:

Heat is the quantity of energy that is exchanged between two bodies without any change in phase. This exchange results in a change in the temperature of the two bodies. For an elementary transformation, the amount of heat exchanged is proportional to Dt

$$\delta Q = m\,C\,dT$$

a-Calorific capacity:

The ratio of heat quantity δQ to temperature change temperature dT called the heat capacity C.

$$C = \frac{\delta Q}{dT}, \qquad C \text{ en } J\,K^{-1} \text{ ou } Cal\,K^{-1}$$

C: heat required to raise or lower the temperature of the system in question by 1K (1°C). considered.

$$\delta Q = C\,dT \quad \rightarrow \quad (3)$$

b- Heat capacity or specific heat:

$$c = \frac{\delta Q}{m\, dT} \qquad c \text{ en } J\, Kg^{-1}\, K^{-1} \text{ ou } J\, g^{-1} K^{-1}$$

C: This is the heat required to raise or lower by 1°C (1K) the temperature of 1Kg (1g) of a system.

$$\delta Q = m\, c\, dT \quad \rightarrow \quad (4)$$

$$(3) = (4) \Rightarrow \quad C = m\, c$$

The heat quantity for a finite transformation

$$\int_i^f \delta Q = \int_{T_i}^{T_f} C\, dT = \int_{T_i}^{T_f} m\, c\, dT$$

$$Q_{i\to f} = \int_{T_i}^{T_f} C\, dT = \int_{T_i}^{T_f} m\, c\, dT$$

$$\text{Si } c = \text{cste} \quad \Rightarrow \quad Q_{i\to f} = m\, c\, (T_f - T_i)$$

$$\text{Si } c \neq \text{cste} \quad \Rightarrow \quad Q_{i\to f} = \int_{T_i}^{T_f} m\, c\, dT$$

If the quantity of matter is given in number of moles (n):

$$Q_{i\to f} = \int_{i}^{f} n\, c'\, dT \qquad \text{avec } c' : \text{Capacité thermique molaire } (J\,mol^{-1}\,K^{-1})$$

Application example:

a hot water tank contains 160Kg of water at 20°C. Calculate the amount of heat required to raise the water temperature to 60°C.

$$c_{eau} = 4200\ JKg^{-1}K^{-1} = cste, \qquad T_i = 20°C \text{ et } T_f = 60°C$$

$$Q_{i\to f} = \int_{T_i}^{T_f} m\, c_{eau}\, dT = m\, c_{eau}(T_f - T_i) = 160Kg \times 4200JKg^{-1}K^{-1}(333K - 293K)$$

$$Q_{i\to f} = 26{,}88 \times 10^{6}\ J > 0 \Rightarrow \text{transformation endothermique}$$

Note: For perfect gases

- Transformation isochore $\Rightarrow V = cste$

$$Q_{i\to f} = Q_V = \int_{T_i}^{T_f} m\, C_V\, dT = \int_{T_i}^{T_f} n\, C'_V\, dT$$

- Transformation isobare $\Rightarrow P = cste$

$$Q_{i\to f} = Q_P = \int_{T_i}^{T_f} m\, C_p\, dT = \int_{T_i}^{T_f} n\, C'_p\, dT$$

- Transformation adiabatique

$$Q_{i\to f} = 0\ J$$

- Transformation isotherme

$Q_{i\to f}$ avec le 1^{er} principe de la thermodynamique

I-13-2- Change of physical state:

❖ Physical state transformations take place at constant temperature (T) and pressure (P).

❖ The latent heat of change of physical state is the quantity of heat that enables heat that transforms a:

a- One unit mass of a body

$$L = \frac{Q}{m} \Rightarrow Q = m\,L \ \text{ avec } L \text{ en } J\,Kg^{-1} \text{ ou } J\,g^{-1}$$

b- Mole unit of a body:

$$L = \frac{Q}{n} \Rightarrow Q = n\,L \text{ avec } L \text{ en } Jmol^{-1}$$

Latent heats of change of state: Lfus, Lsub, Lvap, ...

With:

Lfus: Latent heat of fusion.

Lvap: Latent heat of vaporization.

Lsub: Latent heat of sublimation

$$L_{Soli} = -L_{fus}, \quad L_{Liqu} = -L_{Vap} \text{ et } L_{Cond} = -L_{Sub}$$

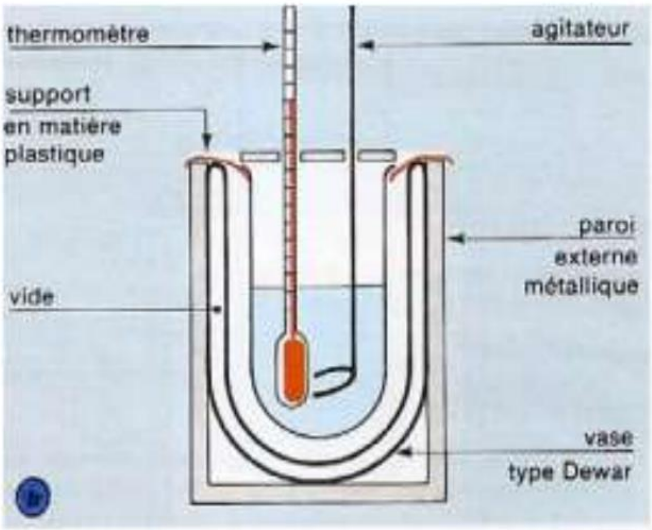
I-16 Calorimetry

Calorimetry is the part of thermodynamics concerned with measuring heat quantities.

The quantities of heat required to raise a body's temperature, to change its state, or the amount of heat given off by a body as it cools (or changes from a gaseous to a liquid state). cooling (or changing from a gaseous to a liquid state, or from a liquid to a solid state). The experiments take place in a calorimeter. The calorimeter is an isolated system that exchanges no energy with the outside environment (neither work nor heat). However, there are heat transfer between the different parts of the calorimeter (components under study, accessories, etc.). Since there is no heat exchange with the outside, this implies that the sum of the heat exchanged Qi within the calorimeter is zero:

$$\sum_{i=1}^{n} Q_i = 0 \Rightarrow Q_{cedée} + Q_{reçue} = 0$$

There is a system that gives off heat $Q_{cédée} < 0$ and another that receives this amount of heat. $Q_{reçue} > 0$.



I-16-1-Determining the equilibrium temperature Teq=Tf :

A mass m1 of water at temperature T1 is immersed in a calorimeter with a suitable heat capacity C cal. a metal cylinder of mass m2 and temperature T2 (with T2 > T1).

The final temperature of the assembly is Teq =?

$$\sum Q_i = 0 \Leftrightarrow Q_{cedé} + Q_{reçue} = 0$$

$T_2 > T_1 \Rightarrow$ *le métal céde de la chaleur à l'ensemble(calorimétre + eau)*

L'ensemble(calorimétre + eau)reçoit de la chaleur du métal

$$Q_{cedée} = Q_{mét} = m_2 C_{mét}(T_{eq} - T_2)$$

$$Q_{reçu} = Q_{Calo} + Q_{eau} = (C_{cal} + m_1 C_{eau})(T_{eq} - T_1)$$

$$\sum_{i=1} Q_i = Q_{cédée} + Q_{reçue} = C_{mét}\ (T_{eq} - T_2) + (C_{cal} + m_1 C_{eau})(T_{eq} - T_1) = 0$$

$$T_{eq}(C_{cal} + m_2 C_{mét} + m_1 C_{eau}) = m_2 C_{mét} T_2 + (C_{cal} + m_1 C_{eau}) T_1$$

$$T_{eq} = \frac{m_2 C_{mét} T_2 + (C_{cal} + m_1 C_{eau}) T_1}{C_{cal} + m_2 C_{mét} + m_1 C_{eau}}$$

Avec

$C_{mét}$: Capacité thermique massique du métal

C_{eau}: Capacité thermique massique de l'eau

❖ Calorimeter water value 'µ':

In the calorimeter, heat exchange also takes place with its accessories. The µ is the mass of water that exchanges the same amount of heat as the accessories. water value of the calorimeter.

Avec: $C_{Cal} = \mu \, C_{eau}$

C_{cal}: Capacité calorifique du calorimétre en JK^{-1}

C_{eau}: Capacité thermique massique de l'eau en $J\,Kg^{-1}K^{-1}$ ou en $J\,g^{-1}K^{-1}$

μ: Valeur en eau en Kg ou en g.

Exercises:

Exercise 1:

Calculate the perfect gas constant R in J $Kg^{-1}K$

-1 for one mole of the following

gases; H_2, O_2, N_2 and CO_2 under standard conditions of temperature and pressure.

conditions.

Data: M(H) = 1g mol^{-1}, M(O) = 16g mol 1, M(N) = 14g mol^{-1} and M(C) = 12g mol^{-1}

Exercise 2:

From the equation of state for a perfect gas:

P V = n R T

Where R is the perfect gas constant (8.314 J $mol^{-1}K^{-1}$), and n is the number of moles of the gas.

1-Demonstrate that this equation can be written as P = ρ. R.T/M, where ρ is the density of the gas, and M is the molar mass (Kg/mol).

2- Rewrite the equation of state for a perfect gas, introducing the number of gas molecules

as well as the expression of the constant k = R/Ɲa called Boltzmann's constant, where Ɲa is the Avogadro number.

Exercise 3: The pressure of a perfect gas is equal to 2 atm.

pressure in; Bar, Pascal, mmHg, torrs and N/m^2.

Exercise 4: Calculate the volume occupied by 3.6 g of oxygen at 27°C and a pressure of 2 atm?

Data: M(O) = 16g mol^{-1} and R = 0.082 l atm $mol^{-1}K^{-1}$

Exercise 5:

A quantity of 10 g of CO_2 occupies a volume of 5 liters at a pressure of 740 torr. Determine the gas temperature.

Exercise 6:

What will become of the temperature (in °C) of a sample of methane (CH_4), if a volume of 1 liter at 735 torr and 25°C is compressed to 809 torr and then occupies a volume of 0.9 liters.

Exercise 7:

A car tire is inflated to 27°C at 2 bars. After the car has been driven, the tire pressure is 2.2 bar. Assuming the volume of the tire to be constant, and

considering the air in the tire as a perfect gas, calculate the temperature inside the tire.

Exercise 8:

A mass of oxygen occupies a volume of 3litres at a pressure of 2 atm. Determine the volume occupied by the same mass of gas at normal pressure, with temperature remains constant.

Exercise 9:

One mole of a perfect gas occupies a volume of 200 cm^3 at 100°C. Assuming the pressure of the gas is constant, calculate its volume at 25°C.

Exercise 10:

A gas mixture containing 0.15 g hydrogen (H_2) g, 0.7 g nitrogen (N_2)g and 0.34 g ammonia (NH4)g at a total pressure of 1 atm and a temperature of 25°C.

Calculate:

1- The mole fraction of each gas.

2- The partial pressure of each gas.

3- The volume occupied by each gas and the total volume of the mixture.

Exercise 11:

Consider two rigid-walled containers, one containing hydrogen and the other methane, the other methane, we have

	P (atm)	T (K)	V (L)
H_2	5	250	10
CH_4	40	300	40

1- Calculate the masses of hydrogen and methane contained in each vessel.

2- Heat the two containers to a temperature of 350K. Calculate the pressure of H_2 and CH_4.

3- Using a tap, connect the two containers.

a- What happens?

b- Calculate the partial pressures of each gas and deduce the total pressure.

Exercise 12:

Mix a volume $V_1 = 3$ liters of carbon dioxide (CO_2) at a pressure

$P_1 = 4$ atm with a volume $V_2 = 1$ liter of oxygen (O_2) at a pressure $P_2 = 6$ atm.

The temperature of each gas has the same value T = 300 K.

1- Calculate the number of moles of each gas.

2- Calculate the total pressure P of the mixture. Check Dalton's law.

3- Calculate the density of the mixture in Kg/m^3 and in g/ l

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Online resources

• Khan Academy : Plateforme pédagogique avec des cours vidéo sur la thermodynamique.

• MIT OpenCourseWare : Cours gratuits en thermodynamique proposés par le MIT.

• Thermodynamics and Statistical Mechanics by UC Berkeley (YouTube) : Série de cours en ligne.