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Thermodynamics Course

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Foreword

This introductory course is designed primarily for first-year Science and Technology (ST) students, but is also suitable for anyone seeking a basic understanding of thermodynamics.

To promote effective learning, the course is structured into six chapters. Each chapter presents key concepts followed by practice exercises with detailed solutions.

The content is based on a comprehensive review of textbooks and online resources, some of which are listed in the bibliography.

Syllabus

CHAPTER V: Second Law of Thermodynamics

CHAPTER VI: Third Law, Absolute Entropy, Free Energy and Free Enthalpy

Introduction

Thermodynamics derived from "therme" (heat) and "dynamis" (power), is a fundamental branch of science emerged at the end of the 17th century, with the object to study exchanges of matter and energy through a system and its environment. It is particularly interested in the transformations of heat into work and vice versa.

Understanding thermodynamics is crucial for anyone pursuing a career in science, technology, engineering, or mathematics because it provides the framework for analyzing and predicting the behavior of systems ranging from microscopic molecules to the largest power plants.

Thermodynamics is also the macroscopic description of the properties of matter in terms of specific physical quantities. To express these quantities, thermodynamics uses mathematical notions such as differentials.

Throughout this course, we will delve into the following fundamental concepts:

System and surroundings, thermodynamic properties (temperature (T), pressure (P), volume (V), internal energy (U), enthalpy (H), and entropy (S)), the laws of thermodynamics (zero law, first law, second law and third law), thermodynamic processes (isothermal, adiabatic, isobaric and isochoric processes) and finally thermodynamic cycles.

Thermodynamics can initially seem abstract, but with a solid grasp of the fundamental principles, this powerful framework can be applied to solve real-world problems and gain a deeper understanding of the world surrounding.

CHAPTER I : General Thermodynamics

1 Mathematical tool

1.1 Partial derivatives

Given a function f(x) with a single variable x, the differential of f is defined by:

$$\boldsymbol{f'(x) = \lim_{\Delta x \to 0} \frac{f(x+\Delta x)-f(x)}{\Delta x} = \frac{df(x)}{dx}}$$

Given a function f(x, y) with two variables x and y, the differential of f is defined by:

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

$\left(\frac{\partial f}{\partial x}\right)$: The partial derivative of f with respect to x assuming y is constant.

$\left(\frac{\partial f}{\partial y}\right)$: The partial derivative of f with respect to y assuming x is constant.

1.2 Mathematical condition of a state function

A state function, in mathematical terms, is an exact differential. The differential form df(x, y) is exact if and only if:

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

2 Definition of thermodynamic systems

A thermodynamic system is a specific, defined region of the universe, separated from its surroundings by a boundary, which may be either a physical surface or an imaginary demarcation.

Depending on whether a system can exchange energy and matter with the surroundings or not, we distinguish three types of systems:

- Open system: this type of system can exchange both energy and matter with its surroundings.

  Example: a pot of boiling water on a stove.

- Closed system: this type of system can exchange energy with its surroundings, but it cannot exchange matter.

  Example: a battery.

- Isolated system: this type of system cannot exchange either energy or matter with its surroundings. This is an idealized concept, as truly isolated systems are difficult to create in practice.

  Example: insulated thermos.

- If the system is open, it cannot be isolated.
- By sign convention, anything received by a system is counted as positive, and anything given out by the system is counted as negative.

3 A thermodynamic system description

3.1 System state

The state of a thermodynamic system is defined by a collection of macroscopic properties, such as mass (m), temperature (T), pressure (P), and volume (V). The specific variables chosen to describe the system depend on the nature of the studied problem.

There are two types of variables:

- Extensive variables: variables proportional to the amount of matter in the system.

  Example: mass (m), volume (V), etc.

- Intensive variables: variables independent of the amount of matter in the system.

  Example: pressure (P), temperature (T), concentration, density, etc.

3.2 Equation of state

A thermodynamic system is defined by a set of state variables, related to each other by a relationship called the equation of state.

- For a gas considered being ideal, the equation of state is called the **« Ideal Gas Law »** often written as: **PV = nRT**

Where:

P = Pressure (usually in Pascals or atmospheres)

V = Volume (usually in cubic meters or liters)

n = Number of moles of gas

R = Ideal gas constant (8.314 $J.mol^{-1}.K^{-1}$ or 0.0821 $L \cdot atm.mol^{-1}.K^{-1}$).

T = Temperature (in Kelvin)

- The Ideal Gas Law is an approximation that works well under certain conditions (low pressure, high temperature). Real gases deviate from this ideal behavior, and more complex equations of state are needed to accurately describe them.

- For a real gas, we can cite the ***« Van der Waals »*** equation:

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

a and b characteristic constant of each gas.

- Equations of state are not limited to gases. They exist for liquids, solids, and systems that are even more complex.

3.3 State function

During a thermodynamic transformation, a system can go from state (1), called the initial state, to state (2), called the final state, by following different paths.

A state function is a function whose change during a transition of a system from one state to another depends only on the initial and final states of the system, and not on the path taken between those states

Example: internal energy (U), enthalpy (H), and entropy (S) are state functions. However, heat (Q) and work (W) are not state functions.

4 Evolution and thermodynamic system equilibrium states

4.1 Thermodynamic equilibrium

A system is in equilibrium when all its state variables remain constant over time.

There are different types of equilibrium, including:

- Thermal equilibrium: temperature is uniform throughout the system and does not change (T = constant).
- Mechanical equilibrium: pressure is uniform (P = constant).
- Chemical equilibrium: the chemical composition is stable, and there is no net reaction occurring.

- A system must be in all types of equilibrium to be in full thermodynamic equilibrium.

4.2 Different thermodynamic transformations

When a system transitions from an initial equilibrium state (i) to another final equilibrium state (f), we say that it has undergone a thermodynamic transformation.

The different possible transformations are as follows:

- Isothermal (T = constant):

Examples: melting ice at 0°C.

- Isochoric (V = constant):

Example: heating a sealed metal can.

- Isobaric (P = constant):

Example: boiling water in an open pot.

- Adiabatic (dQ = 0):

Example: expansion of a gas in an engine cylinder,

- Cyclic: the system goes through a series of transformations and returns to its original state, allowing the cycle to repeat.
- Isothermal/Isobaric (external): the system itself may change temperature or pressure, the environment surrounding stays at a constant temperature or pressure.
- Infinitesimal: very small changes to the system so it is always close to equilibrium.
- Reversible & Irreversible: one of the most important distinctions in thermodynamics:
  - Reversible: idealized processes that occur infinitely slowly and are always in equilibrium. They represent the theoretical limit of efficiency. No real-world process is perfectly reversible.
  - Irreversible: real-world processes that occur spontaneously and are not in equilibrium. They always increase the entropy of the universe. Friction, rapid expansion, and chemical reactions are examples of irreversible processes.

5 The ideal gases laws

5.1 Boyle-Mariotte law

For an ideal gas, if the temperature and the number of moles are constant the product PV = constant (isothermal transformation). As the volume decreases, the pressure increases, and vice versa.

Between two states, the equation is: $P_1V_1 = P_2V_2$

5.2 Gay-Lussac's law

For an ideal gas, if the volume is constant and the number of moles is constant, the pressure is directly proportional to the absolute temperature. As the temperature increases, the pressure increases proportionally.

P/T = constant (isochoric transformation).

Between two states, the equation is: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

5.3 Charles law

For an ideal gas, if the pressure and number of moles are constant the volume is directly proportional to the absolute temperature. As the temperature increases, the volume increases proportionally.

V/T = constant (isobaric transformation).

Between two states, the equation is: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

5.4 Avogadro's law

The number of moles of a gas contained within a given volume is the same, regardless of the type of gas, at constant temperature and pressure.

One mole of gas contains Avogadro's number 6.02×10^{23} of particles and occupies a volume called molar volume, under standard conditions of temperature and pressure (STP).

- Standard conditions (STP) mean:
  - Older definition (commonly used): 0°C (273.15 K) and 1 atm (101.325 kPa).
  - IUPAC standard (more recent): 0°C (273.15 K) and 100 kPa (0.9869 atm or 1 bar).
- The molar volume of an ideal gas is slightly different depending on which standard is used:
  - At 0°C and 1 atm: Vm ≈ 22.414 L/mol.
  - At 0°C and 100 kPa: Vm ≈ 22.711 L/mol.

5.5 Dalton's law

The total pressure exerted by a mixture of ideal gases is the sum of the partial pressures exerted by each gas in the mixture.

$$\boldsymbol{P = \sum_{i=1}^{n} P_i}$$

The partial pressure of a gas in a mixture is the pressure that the gas would exert if it occupied the same volume alone at the same temperature.

$$\boldsymbol{P_i = X_i \times P}\ ;\quad X_i \text{ : molar fraction.}$$

5.6 Thermoelastic coefficients

5.6.1 Isobaric expansion coefficient *(α)*

The expansion coefficient *(α)* quantifies how much a substance expands per degree of temperature increase, specifically when the pressure is constant. (α) is expressed in K^{-1}.

$$\boldsymbol{\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P}$$

5.6.2 Isochoric pressure variation coefficient *(β)*

The isochoric pressure variation coefficient *(β)* quantifies how much the pressure of a substance changes per degree of temperature increase, when the volume is constant. (β) is expressed in K^{-1}.

$$\boldsymbol{\beta = \frac{1}{P}\left(\frac{dP}{dT}\right)_V}$$

5.6.3 Isothermal compressibility coefficient (χ_T)

The isothermal compressibility coefficient quantifies how much a substance's volume decreases per unit increase in pressure, when the temperature is constant. The larger the coefficient, the more compressible the substance. (χ_T) is expressed in Pa^{-1}.

$$\boldsymbol{\chi_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T}$$

- Gases have a much higher compressibility than liquids or solids. While steel has a very low compressibility.

The three coefficients also verify the relationship:

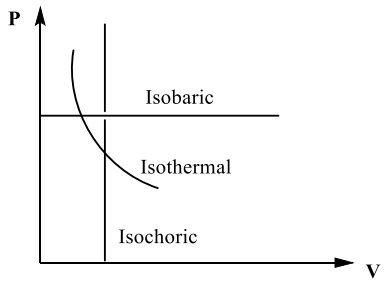
$$\boldsymbol{\frac{\alpha}{\beta \cdot \chi_T} = P}$$

For an ideal gas: $\alpha = \beta = \frac{1}{T}$; $\chi_T = \frac{1}{P}$.

6 Graphical representation of ideal gas transformations

6.1 Clapeyron diagram

The Clapeyron diagram is a Pressure-Volume (P-V) diagram. It provides a visual representation of how the pressure and volume of a gas change during a thermodynamic process, and it allows calculating the work done during the process.

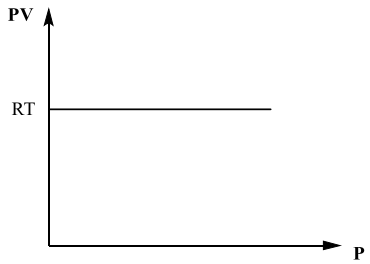


Feature I.1: Clapeyron diagram

- The area under the curve representing a transformation on a P-V diagram represents the work done during the process.

6.2 Amagat diagram

The Amagat diagram allows for the representation of the product PV as a function of pressure (P).



Feature I.2: Amagat diagram

- The Amagat diagram is a valuable tool for understanding and predicting the behavior of real gases, particularly when ideal gas assumptions are not valid. It provides a visual representation of the compressibility factor as a function of pressure at constant temperature, highlighting the deviations from ideal behavior and providing insight into the intermolecular forces at play.

First chapter exercises

Exercise 01:

I. Partial derivatives

Consider the function f (x, y) = $x^2y - 2y^3$.

1- Calculate the first order partial derivatives of the function f.

2- Calculate the expression: $x\left(\frac{\partial f}{\partial x}\right)_y + y\left(\frac{\partial f}{\partial y}\right)_x$.

II. State function

According to the ideal gas law, volume varies as a function of temperature and pressure; thus, we have V = (T, P). In this case, is the volume function a state function?

Exercise 02: Ideal gas

1- Give the equation of state of an ideal gas.

2- Under standard conditions (T = 0°C and P = 1 atm), one mole of gas occupies a volume of 22.4 L. Calculate the value of the ideal gas constant R when:

a) The pressure is in (atm) and the volume is in (L).

b) The pressure is in (Pa) and the volume is in (m^3).

c) The pressure is in (atm) and the volume is in (cm^3).

3- Give the energy equivalent of one liter-atmosphere in Joules and in calories.

Data: 1atm = 1,0132. 10^5 Pascal; 1calorie = 4,18 joules.

Exercise 03: Mixture of ideal gases

A gaseous mixture of nitrogen N_2 and oxygen O_2 is considered ideal. The pressure of the mixture is P_0 = 385 x 10^5 Pa at T_0 = 25°C. (R = 8.314 $J.mol^{-1}.K^{-1}$).

1- Calculate the new pressure P_1 when the mixture is cooled to T_1 = 10°C at constant volume.

2- Calculate the total amount of substance (number of moles) of the gaseous mixture if the volume is 10 L.

All the oxygen is removed from the mixture. The new measured pressure is P_2 = 250 x 10^5 Pa.

3- Calculate the mole fractions of nitrogen and oxygen in the initial mixture.

4- Calculate the partial pressures of oxygen O_2 and nitrogen N_2 at the final temperature.

Exercise 04: Thermoelestic coefficients

I. Ideal gas

One mole of ideal gas obeys to the equation PV = RT.

1- What is the equation for n moles?

2- Prove that $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$. (*)

3- Find the relation between the thermoelestic coefficients α, β, and χ.

4- What are the units and expressions of α, β, and χ for an ideal gas?

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P ; \ \beta = \frac{1}{P}\left(\frac{dP}{dT}\right)_V ; \ \chi_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T$$

II. Real gas

One mole of Van der Waals gas obeys the equation $\left(p + \frac{a}{V^2}\right)(V - b) = RT$.

a and b are constants.

1- What is the equation for n moles?

2- What are the units of a and b constants?

3- Determine α and β coefficients for one mole of Van der Waals gas.

Exercise 05: Concepts.

1- Indicate which of the following quantities are intensive or extensive:
Volume, density, pressure, temperature, energy, electric charge, mole fraction.

2- Which of the following systems are isolated, closed, or open?
- Hot water in a beaker - Tea in a thermos - A radiator
- Mercury in a thermometer - An electric battery - A living being

3- Among the two following transformations, determine which one is reversible, justify your answer:
- A spring undergoing slow, very large elongations.
- A spring undergoing slow, small elongations.

Exercises solutions

Exercise 01:

I. partial derivatives

1- The first order partial derivatives of f (x, y) = $x^2y - 2y^3$:

$\left(\frac{\partial f}{\partial x}\right)_y = 2xy$ and $\left(\frac{\partial f}{\partial y}\right)_x = x^2 - 6y^2$

2- Calculating the expression $x\left(\frac{\partial f}{\partial x}\right)_y + y\left(\frac{\partial f}{\partial y}\right)_x$:

$$x\left(\frac{\partial f}{\partial x}\right)_y + y\left(\frac{\partial f}{\partial y}\right)_x = 2x^2y + yx^2 - 6y^3 = 3(x^2y - 2y^3) = 3.f(x,y).$$

II. State function

In mathematical terms, a state function is an exact total differential.

According to the ideal gas law, we have: PV = nRT, which gives us V = nRT/P.

The volume function V (P, T) is an exact total differential if the second derivatives are equal. $\left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right]_T$

We have $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$ $\left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial T}\left(-\frac{nRT}{P^2}\right)_T\right]_P = -\frac{nR}{P^2}$

And $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$ $\left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial P}\left(\frac{nR}{P}\right)_P\right]_T = -\frac{nR}{P^2}$

Based on the results, the second derivatives are equal; therefore, the volume is a state function.

Exercise 02: Ideal gases

1- The equation of state for an ideal gas is $\boldsymbol{PV = nRT}$.

2- According to the equation of state of ideal gases $R = \frac{PV}{nT}$

a) Pressure in (atm) and volume in (L):

- $R = \frac{1atm\ 22,4l}{1mol\ 273,15K} = 0{,}082\ l.atm.mol^{-1}.K^{-1}$

b) Pressure in (Pa) and volume in (m^3): *1atm=1,0135 10^5 Pa ; 1J=1Pa*1m^3*

- $R = \frac{1{,}0135.10^5 \text{Pa}\ 22{,}4.10^{-3}\text{m}^3}{1mol\ 273{,}15K} = = 8{,}31\ Pa.m^3.mol^{-1}.K^{-1} = 8{,}31\ J.mol^{-1}.K^{-1}$

c) Pressure in (atm) and volume in (cm^3):

- $R = \frac{1atm\ 22{,}4.10^3 cm^3}{1mol\ 273{,}15K} = 82\ atm.cm^3.mol^{-1}.K^{-1}$

3- The energy equivalent of one liter-atmosphere:

- In Joules:

R = 0,082 $l.atm.mol^{-1}.K^{-1}$ = 8,31 $J.mol^{-1}.K^{-1}$ $\Rightarrow 1l.atm = \frac{8{,}31\ J.mol^{-1}K^{-1}}{0{,}082 mol^{-1}K^{-1}}$

$$1l.atm = 101.34J$$

- In calories: $1l.atm = \frac{101{,}34}{4{,}18} = 24.24$ cal

Exercise 03: Mixture of ideal gases

1- New pressure P_1 :

According to ideal gas law:

At T_0 we have: $P_0V = nRT_0$ and at T_1 we have: $P_1V = nRT_1 \Rightarrow \frac{P_1}{P_0} = \frac{T_1}{T_0}$

$\Rightarrow P_1 = 385.10^5 \frac{273{,}15 + 10}{273{,}15 + 25} = 366.10^5$ Pa

2- Total amount of substance:

At T_0 we have : $P_0V = n_{tot}RT_0 \Rightarrow n_{tot} = \frac{P_0V}{RT_0}$

$\Rightarrow n_{tot} = \frac{385.10^5.10.10^{-3}}{8{,}314.(273{,}15 + 25)} = 155{,}3$ moles

3- Molar fractions :

The ideal gas law is applied to nitrogen only.

$P_{N2}.V = n_{N2}.R.T_1 \Rightarrow n_{N2} = \frac{P_{N2}V}{RT_1}$

$\Rightarrow\ n_{N2} = \frac{250.10^5.10.10^{-3}}{8{,}314.(273{,}15 + 10)} = 106{,}2$ moles

- $X_{N2} = \frac{n_{N2}}{n_{tot}} = \frac{155{,}3}{106{,}2} = 0{,}68$

- $X_{O2} = 1 - X_{N2} = 0{,}32$

4- Partial pressure:

Dalton's law $P = \sum_{i=1}^{n} P_i$ and $P_i = X_i \times P$

Pressure at last temperature T_1 is $P_1 = 366.10^5$ Pa

$\Rightarrow$ $P_{N2} = 0{,}68.\ 366.10^5 = 248{,}88.10^5$ Pa

$\Rightarrow$ $P_{O2} = 0{,}32.\ 366.10^5 = 117{,}12.10^5$ Pa

Exercise 04: Thermoelastic Coefficients

I. Ideal gas

1- The equation of state for an ideal gas for n moles is PV= nRT.

2- Partial derivatives:

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

- $V = \frac{nRT}{P} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$

- $T = \frac{PV}{nR} \Rightarrow \left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{nR}$

$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = \left(-\frac{nRT}{V^2}\right)\left(\frac{nR}{P}\right)\left(\frac{V}{nR}\right) = -\frac{nRT}{PV} = -1$ (the relation holds).

3- Relation between thermoelastic coefficients :

We have $\left(\frac{\partial V}{\partial T}\right)_P = \alpha.V$ and $\left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V} = \frac{1}{\beta.P}$ and $\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T} = -\frac{1}{V\chi_T}$

Using the relation (*****) we find:

$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 = (\alpha.V)\left(\frac{1}{\beta.P}\right)\left(-\frac{1}{V\chi_T}\right) \Rightarrow \frac{\alpha}{\beta.\chi_T} = P$

4- Units and expressions of thermoelastic coefficients :

- According to the definition units are:

[α] = K^{-1} ; [β] = K^{-1} ; $[\chi_T] = Pa^{-1}$.

- The coefficients expressions are:

- $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{nR}{P}\right) = \frac{1}{T}$

- $\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{P}\left(\frac{nR}{V}\right) = \frac{1}{T}$

- $\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{V^2}{nRT}\right) = \frac{1}{P}$

II. Real gas

1- The equation of state for a Van der Waals gas for n moles:

For n moles we have $V = n.V_m$, V_m (molar volume).

$\Rightarrow \left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

1) a and b units:

V is the molar volume its unit is m^3/mol.

- a is a constant and ($\frac{a}{V^2}$) is a pressure ⇒ $[\frac{a}{V^2}] = Pa$ ⇒ a = $Pa.m^6/mol^2$.
- The constant b dimension is that of a molar volume ⇒ b = m^3/mol.

2- α and β coefficients of a Van der Waals gas:

- $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$, to determine α we need to calculate $\left(\frac{\partial V}{\partial T}\right)_p$

  $\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{\left(P+\frac{a}{V^2}\right)-(V-b)\frac{2a}{V^3}} \Rightarrow \alpha = \frac{R}{V\left(\left(P+\frac{a}{V^2}\right)-(V-b)\frac{2a}{V^3}\right)}$

- $\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$, to determine β we need to calculate $\left(\frac{\partial P}{\partial T}\right)_V$

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

Exercise 05: Concepts.

1- Extensive properties are proportional to the mass of a system, while intensive properties are independent of the mass of a system. Thus:

Extensive properties: number of moles, volume, energy, electric charge.

Intensive properties: density, pressure, temperature, mole fraction.

2- A system is closed, open, or isolated depending on whether or not it can exchange energy and matter. Thus:

- Hot water in a beaker (open system)
- Tea in a thermos (isolated system)
- A radiator (closed system)
- Mercury in a thermometer (closed system)
- Electric battery (closed system)
- A living being (open system)

3- A reversible transformation is a transformation that can be carried out in the opposite direction, or where the system passes through the same equilibrium states as in the direct direction.

Therefore:

- A spring undergoing slow, small elongations is a reversible transformation. The spring retains its elasticity, and by following the same path as in the forward direction, it can return to the initial state.
- A spring undergoing slow, very large elongations) is an irreversible transformation. A significant elongation causes the spring to lose its elasticity, and consequently, returning to the initial state is impossible by following the same path as in the forward direction.

CHAPTER II : Temperature, Heat, Calorimetry and Work

1 Temperature concept

Temperature reflects the degree of molecular motion in matter. The higher the temperature of an object, the greater the speed of its molecules. Temperature is not an intrinsic property of matter itself; it is a measure of the average kinetic energy of the molecules that make up the substance.

1.1 The zero law of thermodynamics

The zero law of thermodynamics establishes the concept of thermal equilibrium and provides a basis for measuring temperature.

The zero law states that if two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other.

Example: If A has the same temperature as C and B has the same temperature as C, then A and B must have the same temperature as each other, even if you never directly compared A and B.

1.2 Thermometry

Thermometry is the science and practice of measuring temperature. It is not just about the instruments themselves (thermometers), but also about the principles, techniques, and calibration methods used to obtain accurate and reliable temperature readings.

Thermometry involves more than just using a thermometer. It also encompasses understanding different temperature scales and how to convert between them.

1.2.1 Temperature scales

Different scales are used to measure temperature. The most recognized scales:

- Degrees Celsius (°C): The centigrade scale, based on the freezing point of pure water, which is 0 degrees Celsius (°C), and the boiling point, which is 100 degrees Celsius.
- Degrees Kelvin (K): A scale that assigns a value of zero to the lowest possible temperature. Absolute zero corresponds to -273.15 °C. T (K) = °C + 273.15. At absolute zero, all molecular motion ideally ceases.
- Degrees Fahrenheit (°F): This scale is based on the freezing point of water, which is 32 °F, and the boiling point, which is 212 °F. T(°F) = 32 + 1.8T(°C)

- The Celsius scale is convenient for everyday use. The Kelvin scale is crucial in scientific applications, especially in thermodynamics and statistical mechanics. ***Example:*** the ideal gas law (PV = nRT) works correctly only when T is in Kelvin.

1.2.2 Different types of Thermometers

The operation of a thermometer is linked to temperature variations resulting from several physical phenomena. ***Examples:***

- Volume variation ⇒ mercury thermometers

  This type relies on the principle of thermal expansion. Most substances expand when heated and contract when cooled. Liquid-in-glass thermometers use a liquid (traditionally mercury, but now often alcohol or other colored organic liquids) contained within a glass bulb connected to a narrow glass tube (capillary).
- Variation of electrical resistance ⇒ resistance thermometers

  Resistance thermometers typically use a metal (platinum, copper, nickel) as the sensing element, while thermistors use semiconductors. The relationship between resistance and temperature is usually calibrated and can be linear or non-linear, depending on the material.
- Variation of a potential difference ⇒ thermocouple

  The thermoelectric effect (also known as the Seebeck effect) states that a temperature difference between two dissimilar electrical conductors or semiconductors creates a voltage difference between them.
- Magnetic variation of paramagnetic dipoles ⇒ magnetic thermometer

  This type is used for very low temperatures (typically below 1 Kelvin). It exploits the temperature dependence of the magnetic susceptibility of a paramagnetic material. Paramagnetic materials have atoms with unpaired electrons, which create small magnetic dipoles.

2 Heat concept

2.1 Heat

Heat represented by the symbol (Q), is a quantity of energy exchanged in a disordered form due to molecular agitation, expressed in Joules *[J]* or Calories *[Cal]*.

Heat is a process function; it describes energy in transit and only exists when there is a temperature difference between two objects or systems.

There are two states of heat:

2.1.1 Sensible heat

Sensible heat is the heat energy that, when added to or removed from a substance, results in a change in its temperature without changing its phase. It is proportional to the amount of matter and related to the change in temperature (ΔT).

$Q = m\ C\ \Delta t$ or $Q = n\ C\ \Delta t$

Q = heat energy transferred (in Joules or Calories)

m = mass of the substance (in kg or grams)

C = specific heat capacity of the substance (in $J.kg^{-1}.K^{-1}$ or $cal.g^{-1}.°C^{-1}$)

ΔT = change in temperature (in K or °C)

2.1.2 Latent heat

Latent heat is the heat energy absorbed or released during a phase change of a substance (melting, freezing, boiling, condensation, sublimation, deposition) without a change in temperature. It is proportional to the amount of matter and the latent heat associated with the change.

$Q = m\ L$ or $Q = n\ L$

Q = heat energy transferred (in Joules or Calories)

m = mass of the substance (in kg or grams)

L = latent heat of transformation (in J/kg or cal/g)

There are three types of latent heats (Ls, Lv and Lf) associated respectively with sublimation, vaporization and fusion. Each substance has specific latent heat values that represent the amount of energy required to change the phase of (1kg or 1g) of substance.

- If $Q > 0 \Rightarrow$ the thermodynamic system has received heat (Endothermic process).
- If $Q < 0 \Rightarrow$ the thermodynamic system has lost heat (Exothermic process).
- If $Q = 0 \Rightarrow$ the thermodynamic system is isolated (no heat exchange).

2.2 Thermal heat capacity

Heat capacity (C) is a measure of a system's ability to store thermal energy. Specific heat capacity is a property of a substance that indicates how much heat energy is required to raise the temperature of (1kg or 1 g) of that substance by 1 degree Celsius or 1 Kelvin.

Heat capacity is an extensive property measured in [$J.K^{-1}$] or [$cal.K^{-1}$]. Different substances have different specific heat capacities.

Different thermal heat capacities:

- Mass-specific heat capacity Cm, measured in [$J.\ Kg^{-1}.\ K^{-1}$].
  Useful for comparing the heat storage capacity of different materials based on their mass.
- Molar heat capacity Cn, measured in [$J.\ mole^{-1}.\ K^{-1}$].
  It helps to understand the relationship between heat capacity and the molecular structure of a substance.
- Isobaric mass or molar heat capacity Cp (calculated at constant pressure).
  The heat capacity relevant to many everyday processes that occur at atmospheric pressure.
- Isochoric mass or molar heat capacity Cv (calculated at constant volume).
  The heat capacity relevant to processes that occur in a closed, rigid container where the volume cannot change.

2.2.1 Thermal heat capacity for ideal gases

For ideal gases, Cp and Cv are related by an equation called Mayer's relation

$$C_p - C_v = R$$

Mayer's relation is only valid for ideal gases, that obeys the ideal gas law (PV = nRT) and has no intermolecular forces. Real gases can deviate from this relationship, especially at high pressures and low temperatures.

The values of Cv and Cp for ideal monatomic gases are constant and do not depend on temperature (as long as the gas remains ideal and at temperatures where electronic excitation is negligible). While for ideal diatomic gases, Cv and Cp depends on temperature due to the activation of rotationnel and vibrationnel modes.

For a monoatomic gas $C_v = \frac{3}{2}R$; $C_p = \frac{5}{2}R$ their ratio is $\gamma = \frac{C_p}{C_v} = \frac{5}{3}$

For a diatomic gas $C_v = \frac{5}{2}R$; $C_p = \frac{7}{2}R$ their ratio is $\gamma = \frac{C_p}{C_v} = \frac{7}{5}$

From $\begin{cases} \gamma = \frac{C_p}{C_v} \\ C_p - C_v = R \end{cases} \Rightarrow C_v = \frac{R}{(\gamma-1)}$ $and\ C_p = \gamma C_v = \frac{\gamma R}{(\gamma-1)}$

2.3 Calculation of the amount of heat

Heat is not a state function; it depends on the path followed. For an ideal gas, the amount of heat is calculated according to the transformation undergone.

The equation for the heat Q exchanged during a finite transformation between states (1) and (2):

$$Q = \int_1^2 dQ = \int_1^2 mCdT = mC\int_1^2 dT = mC(T_2 - T_1) = mC\Delta T$$

- Isochoric transformation (V = constant) ⇒ Q = m C_v ΔT.
  The heat added to the system goes into increasing its internal energy, which is directly proportional to the temperature change.
- Isobaric transformation (P = constant) ⇒ Q = m C_p ΔT.
  Some of the heat added goes into increasing the internal energy of the gas, and some goes into doing work as the gas expands against the constant pressure.
- Isothermal transformation (T = constant) ⇒ $Q = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{P_1}{P_2}$.
  All the heat added to the system is converted into work done by the system.
- Reversible adiabatic transformation ⇒ (dQ = 0).
  No heat is transferred.

3 Calorimetry

Calorimetry is the science and art of measuring the quantity of heat absorbed or released during physical or chemical processes. It is a branch of thermodynamics concerned with the accurate measurement of heat transfer.

Calorimetry allows us to determine specific heat capacities (C), latent heats (L) and calorific values using thermally insulated containers called calorimeters.

The fundamental principle of calorimetry is based on the principle of equality of heat exchange between systems. When two systems exchange only heat, the amount of heat gained (Q1 > 0) by one system is equal to the amount of heat lost by the other system (Q2 < 0) and the sum of all heat exchanges within the calorimeter must be zero $\sum_i Q_i = 0$ (Law of conservation of energy).

3.1 Different types of calorimeters

A calorimeter is a thermally insulated container designed to measure heat transfer. The goal is to minimize heat exchange between the calorimeter and its surroundings.

Examples:

- Coffee cup calorimeter: simple, inexpensive; measures heat transfer at constant pressure using temperature changes in water, ideal for solution-based reactions.
- Bomb calorimeter: measures heat released during combustion at constant volume, more accurate but complex, used for caloric content and fuel studies
- DSC (Differential Scanning Calorimeter): measures heat flow changes during material transitions (melting, etc.) by comparing a sample to a reference, revealing thermal properties.

3.2 Water equivalent of a calorimeter (μ)

The water equivalent of a calorimeter (μ) is the mass (in kg) of water that would have the same heat capacity as the calorimeter.

$$\mu = \frac{C_{cal}}{C_m}$$

C_{cal}: heat capacity of calorimeter in $J.K^{-1}$.

C_m: heat capacity of water in $J.Kg^{-1}.K^{-1}$.

3.3 Calculation of equilibrium temperature

The equilibrium temperature, Teq, is obtained from the energy balance of two systems in contact at different temperatures. After heat transfer reaches thermal equilibrium, the two systems have the same temperature, Teq.

Adiabatic system:

$$\sum Q = 0 \Rightarrow Q1 + Q2 = 0$$

We have $Q_1 = m_1 C_1 (T_{eq} - T_1)$ and $Q_2 = m_2 C_2 (T_{eq} - T_2)$

$$\Rightarrow \quad T_{eq} = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2}$$

C_1 and C_2 heat capacities of system 1 and 2 in $J.Kg^{-1}.K^{-1}$.

m_1 and m_2 masses of system 1 and 2 in *Kg*.

T_1 and T_2 temperatures of system 1 and 2 in *K*.

4 Work

Work represented by the symbol (W), is a quantity of energy exchanged in an organized manner due to a change in volume of a deformable system, measured in Joules [J] or Calories [Cal].

$$\partial W = - P\, dV.$$

For a finished transformation: $W = \int \partial W = \int -PdV$.

For a reversible transformation the work exchanged is:

$$W_{rev} = \int -PdV = -\int \frac{nRT}{V} dV = -nRTln\, \frac{V_2}{V_1}$$

For an irreversible transformation the work exchanged is:

$$W_{irrev} = \int -PdV = -P \int dV = -P(V_2 - V_1)$$

- The negative sign by convention is used for understanding the direction of energy flow.

- Expansion ($\Delta V > 0$) leads to negative work ($W < 0$) ⇒ the system loses energy (work done on the surroundings).
- Compression ($\Delta V < 0$) leads to positive work ($W > 0$) ⇒ the system gains energy (work is done on the system by the surroundings).

4.1 Work calculation

Work is not a state function (it depends on the path taken). For an ideal gas, the calculation of work depends on the transformation undergone.

- Isochoric transformation (V = constant) ⇒ W = 0
  No volume change, therefore no pressure-volume work.
- Isobaric transformation (P = constant) ⇒ $W = -P(V_2 - V_1)$

- Isothermal transformation (T = constant) ⇒ $W = nRT\ln\frac{V_1}{V_2} = nRT\ln\frac{P_2}{P_1}$

  The relationships due to Boyle's Law, $P_1V_1 = P_2V_2$.

- Adiabatic reversible transformation ⇒ $W = \int nC_v dt = \frac{nRT_2 - nRT_1}{(\gamma - 1)} = \frac{P_2V_2 - P_1V_1}{(\gamma - 1)}$

  Cv is the molar heat capacity at constant volume and γ = Cp/Cv is the adiabatic index.

Second chapter exercises

Exercise 01: Course questions

1- Give the expression for the work of a force, and show that the work of a force and the product PdV have the same dimension.
2- Give the expression for the elementary (infinitesimal) heat, as well as the dimensions in the International System (SI) of heat and absolute temperature T.
3- Is it possible to add heat to a system without changing its temperature?
Is it possible to change the temperature of a system without adding heat to it?

Exercise 02: Heat

One mole of nitrogen, considered as an ideal gas, is heated from 20°C to 100°C.

1- Calculate the amount of heat Q received by this system in these cases:

a) When the transformation is isochoric.

b) When the transformation is isobaric.

2- Is heat a state function?

Data: C_p (N_2, g) = 33 J.mol^{-1}.K^{-1}; R = 8,31 J.mol^{-1}.K^{-1}.

Exercise 03: Work

An ideal gas, undergoes a reversible transformation from the initial state (1) (P_1 = 1 bar; V_1 = 3 L) to the final state (2) (P_2 = 3 bar; V_2 = 1 L), following three different paths (a, b, and c).

a) An isochoric transformation followed by an isobaric transformation.

b) An isobaric transformation followed by an isochoric transformation.

c) A direct rectilinear transformation (isothermal).

1- Calculate the work done in the three cases and state whether it is released (done by the system) or received (done on the system).
2- Represent the three transformations in Clapeyron coordinates (P-V diagram).
3- What do you conclude?

Exercise 04: Calorimetry, thermometr heat capacity

A calorimeter contains m_1 = 250 g of water at T_1 = 18°C. A mass m_2 = 300 g of water at a temperature T_2 = 80°C is added.

1- What would be the thermal equilibrium temperature Teq of the system if the heat capacity of the calorimeter and its accessories were negligible?
2- An actual thermal equilibrium temperature is measured, Teq = 50°C. Determine the heat capacity C of the calorimeter and its accessories

Data: $C_{water} = 4185\ J.kg^{-1}.K^{-1}$.

Exercise 05: Calorimetry, final equilibrium state

A mass m_1 = 500 g of iron is taken out of a freezer at a temperature T_1 = -30°C. This mass is immersed in a calorimeter containing a mass m_2 = 200 g of water at a temperature T_2 = 4°C.

1- Determine the final equilibrium state of the system (final temperature, mass of the different substances present in the calorimeter).
The heat capacity of the calorimeter is negligible.
Data: $C_{water} = 4185\ J.Kg^{-1}.K^{-1}$; $C_{Fe} = 460\ J.Kg^{-1}.K^{-1}$; $L_f = 3{,}34.10^5\ J.Kg^{-1}$.

Exercise solutions

Exercise 01: Course questions

1- The elementary (infinitesimal) work of a force F that displaces its point of application by $d\ell$ is $\delta W = F.d\ \ell$

- Pressure P is a force (F) exerted on an area (S) : $P = \frac{F}{S} \Rightarrow [P] = \frac{[F]}{[S]}$
- Volume V is an area multiplied by a length: V= S.L ⇒ [V]=[S].[L]
- The dimension of the product [PdV] is $\frac{[F]}{[S]}$ [S]. [L] = [F][L]
- Work unit is $J = Kg.m^2.s^{-2}$ and [F] = N = $Kg.m.s^{-2}$

Therefore, work and the product PdV have the same unit.

2- The expression for the elementary (infinitesimal) quantity of heat:"

$\delta Q = C_v\, dT + \ell\, dV$

$\delta Q = C_p\, dT + \hbar\, dP$

$\delta Q = \lambda\, dP + \mu\, dV$

- In the International System of Units (SI), the unit of heat Q is Joule (J), and the unit of temperature T is Kelvin (K).

3-

- During phase changes, the addition of heat can change either the volume or the pressure or both. Therefore, it is indeed possible to add heat to a system without changing its temperature.
- Temperature (T) varies with volume (V) or with pressure (P) (adiabatic compression or expansion). Therefore, it is indeed possible to change the temperature of a system without adding heat to it.

Exercise 02: Heat

1- Calculation of the amount of heat

a) Isochoric transformation (volume constant) :

$Q_v = n\, C_v\, \Delta T = n\, C_v\, (T_2 - T_1)$.

According to Mayer's relation: $C_p - C_v = R \Rightarrow C_v = C_p - R$

$\Rightarrow C_v = (33\text{-}8{,}31) = 24{,}69$ J.mol^{-1} K^{-1} and $Q_v = 1\ (24{,}69)\ (100\text{-}20) = 1975{,}2$ J

b) Isobaric transformation (pressure constant) :

$Q_p = n\, C_p\, \Delta T = n\, C_p\, (T_2 - T_1)$.

$\Rightarrow Q_p = 1\ (33)\ (100 - 20) = 2640$ J

2- According to the result, the quantity of heat changes depending on the transformation undergone. Consequently, heat is not a state function; it depends on the path taken.

Exercise 03: Work

1- Calculation of work

a) Isochoric then isobaric transformation:

$W_a = W_v + W_p$; $W_v = 0$ (isochoric) and $W_p = - P_2\ (V_2 - V_1)$ (isobaric)

$W_a = - 3.10^5\ (1-3)\ 10^{-3} = 600$ J

b) Isobaric then isochoric transformation:

$W_b = W_p + W_v$; $W_p = - P_1\ (V_2 - V_1)$ (isobaric) and $W_v = 0$ (isochoric).

$W_b = - 10^5\ (1-3)\ 10^{-3} = 200$ J

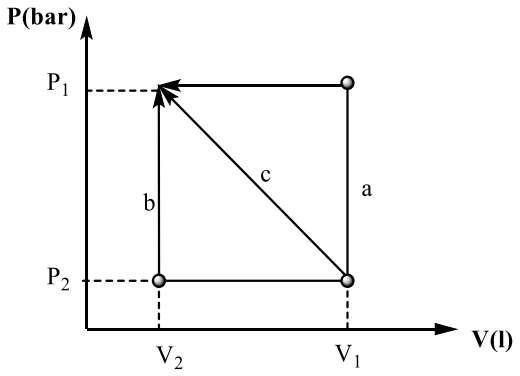
c) Isothermal transformation:

$$W_c = -nRT\ ln\frac{V_2}{V_1} = \ nRT\ ln\frac{V_1}{V_2} = \ P_1V_1\ ln\frac{V_1}{V_2}$$

$W_c = 10^5.\ 3.10^{-3} \ln 3 = 327$ J

- The work calculated following the three paths is positive; therefore, it is work received by the system from the external environment."

2- The Clapeyron diagram represents the evolution of the transformations by plotting pressure (P) on the y-axis (ordinate) and volume (V) on the x-axis (abscissa). $P\ = \ f(V)$



3- Conclusion: the value of the work changes depending on the transformation undergone; therefore, work is not a state function, it depends on the path taken.

Exercise 04: Calorimetry, thermometr heat capacity

1- Thermal equilibrium temperature:

- Cold water: $T_1 = 18°C$, $m_1 = 250$ g.

The temperature of the cold water will rise to Teq, and the cold water will absorb a quantity of heat $Q_1 > 0$; $Q_1 = m_1 C_w (T_{eq} - T_1)$.

- Hot water: $T_2 = 80$ °C, $m_2 = 300$ g.

The hot water will lose a quantity of heat $Q_2 < 0$; $Q_2 = m_2 C_w (T_{eq} - T_2)$.

- The system is isolated $\Rightarrow Q_1 + Q_2 = 0$

  $\Rightarrow m_1 C_w (T_{eq} - T_1) + m_2 C_w (T_{eq} - T_2) = 0 \Rightarrow T_{eq} = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2}$

  $T_{eq} = \frac{250.10^{-3}.18 + 300.10^{-3}.80}{250.10^{-3}+300.10^{-3}} = 51{,}8°C$

2- Calorimeter heat capacity :

- For the (cold water + calorimeter and its accessories) system: $T_1 = 18$ °C.

The system absorbs a quantity of heat $Q_1 > 0$; $Q_1 = (m_1 C_w + C) (T_{eq} - T_1)$.

- Hot water $T_2 = 80$ °C; $m_2 = 300$ g.

Hot water will lose a quantity of heat $Q_2 < 0$; $Q_2 = m_2 C_w (T_{eq} - T_2)$.

- Isolated system $\Rightarrow Q_1 + Q_2 = 0$

  $\Rightarrow (m_1 C_w + C) (T_{eq} - T_1) + m_2 C_w (T_{eq} - T_2) = 0$

  $\Rightarrow C = \frac{m_1 Cw (T_{eq} - T_1) + m_2 Cw (T_{eq} - T_2)}{T_1 - T_{eq}}$

  $C = \frac{250.10^{-3}.4185.(50-18) + 300.10^{-3}.4185.(50-80)}{18-50} = 130{,}8$ J.K^{-1}

Exercise 05: Calorimetry, final equilibrium state

Final equilibrium state:

We suppose $T_f = T_{eq} = 0°C$.

- Iron: $T_1 = -30°C$; $m_1 = 500$ g.

Q_1 is the amount of heat absorbed to go from T_1 = -30°C to T_f = 0°C

$Q_1 = m_1 C_{Fe} (T_f – T_1) = m_1 C_{Fe} (0 - T_1)$

$Q_1 = 500.10^{-3}.460. (0-(-30)) = 6900$ J; $Q_1 > 0$.

- (Calorimeter + water): T_2 = 4 °C ; m_{water} = 200 g.

  Q_2 is the amount of heat lost by the system. T_2 = 4°C à T_f = °0 C

  $Q_2 = m_2 C_w(T_f – T_2) = m_2 C_w (0 - T_2)$

  $Q_2 = 200.10^{-3}.4185. (0-4) = -3348$ J; $Q_2 < 0$.

  We observe that |Q1| > |Q2|. This means that some of the water will freeze. A portion of the water will be in liquid form, and a portion will be in the form of ice at 0°C.

  Calorimetric equation: $\sum Q = 0 \Rightarrow Q_1 + Q_2 + Q_s = 0$

  $Q_s \Rightarrow$ Latent heat required for the solidification of water. Same latent heat of fusion but with a negative sign

  $Q_s = m L_s = - m L_f$.

  $\Rightarrow Q_1 + Q_2 + Q_s = 0 \Rightarrow Q_1 + Q_2 – m'_2 L_f \Rightarrow m'_2 = \frac{Q_1+Q_2}{L_F}$

  $m'_2 = \frac{6900-3348}{3{,}34.10^5} = 10{,}6.10^{-3}$ kg

  Final equilibrium state:

  500g of iron, 10,6g of ice and m’ = 200-10,6 = 189,4g of water at T_{eq} = 0°C.

CHAPTER III : First Law of Thermodynamics

1 First law statement

Various statements of the first law of thermodynamics are possible:

- The first law is the principle of energy conservation.
- Energy is conserved and does not degrade; however, it exchanges with the external environment.
- Energy is exchanged with the external environment through thermal transfer (heat) and mechanical transfer (work).
- The energy of an isolated system is conserved, that is, constant.
- The change in internal energy is equal to the sum of the energies exchanged with the external environment.

We can summarize the statement of the First Law of Thermodynamics as follows:

« The change in internal energy (ΔU) of a closed system during a transformation is equal to the sum of the amount of heat (Q) exchanged by the system and the work (W) done by or on the system, with the external environment ».

1.1 General expression of the first law

The change in internal energy (ΔU) between a state (1) and a state (2) depends only on the states (1) and (2) and is equal to the algebraic sum of the work (W) and the heat (Q) exchanged by the system with the external environment.

$$\Delta U = W + Q$$

1.2 Differential expression of the first law

- For a defined transformation:

$$\Delta U = U_2 - U_1 = \int dW + \int dQ = W + Q$$

- For an elementary (infinitesimal) transformation:

$$dU = \partial W + \partial Q$$

  - dU is an exact differential, and ∂W and ∂Q are differential forms.

2 Internal Energy

Represented by the symbol (U), internal energy is the total energy contained within a system, measured in Joules [J] or in Calories [Cal].

Internal energy is a state function also an extensive and additive variable, which can change due to energy exchanges with the external environment in the form of heat (Q) and work (W). Changes in internal energy are governed by the first law of thermodynamics.

2.1 Differential expression of internal energy

Internal energy (U) is a state function that does not depend on the path followed. Mathematically, dU is an exact total differential.

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy \text{ And } \left[\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right]_y$$

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

3 Calculation of the change in internal energy (ΔU)

a) Joule's first law

The internal energy (U) is a function only of the temperature (T). Any changes in internal energy (ΔU) are solely caused by changes in temperature (ΔT).

$$U = f(T)$$

If the temperature of an ideal gas remains constant (isothermal process), its internal energy also remains constant (ΔU = 0).

b) Isochoric transformation (V = constant)

V = constant ⇒ dV = 0; W = 0 ⇒ $Q_v = \Delta U = n\, C_v\, \Delta T$

At constant volume, all the heat added to the system goes directly into increasing its internal energy.

For an ideal gas, the change in internal energy is related to the molar heat capacity at constant volume (Cv) and the change in temperature (ΔT).

c) Isobaric transformation (P = constant)

$\Delta U = Q_p + W = n\, C_p\, \Delta T - P\Delta V = n\, C_v\, \Delta T$.

The heat added at constant pressure is related to the molar heat capacity at constant pressure (Cp) and the change in temperature (ΔT).

$\Delta U = n\, Cp\, \Delta T - P\Delta V$

Since the gas is ideal, we can use the ideal gas law:

$PV = nRT \Rightarrow P\Delta V = nR\Delta T$

$\Delta U = n\, Cp\, \Delta T - nR\Delta T$

$\Delta U = n\, (Cp - R)\, \Delta T$

According to Mayer's relation, for an ideal gas:

$C_p - C_v = R$ or $C_v = C_p - R$

$\Rightarrow \Delta U = n C_v \Delta T$

The change in internal energy depends only on the temperature change and the heat capacity at constant volume, irrespective of the process. The heat added is used both to increase the temperature and to do work (expand the volume).

d) Isothermal transformation (T = constant)

According to Joule's first law

$\Delta U = W + Q = 0 \Rightarrow W = - Q$

In an isothermal process, of an ideal gas, internal energy is zero and the work done on the system is equal in magnitude but opposite in sign to the heat added to the system.

e) Adiabatic transformation (Q = 0)

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

An adiabatic process, no heat exchange and the change in internal energy is equal to the work done on the system. All the work goes directly into changing the internal energy of the system.

f) Relation between Q_p and Q_v

The relationship between Qp (heat transferred at constant pressure) and Qv (heat transferred at constant volume) is a direct consequence of the first law of thermodynamics and highlights the different ways energy is partitioned in these two common types of thermodynamic processes.

According to first law $\Delta U = Q + W \Rightarrow Q_p = \Delta U - W = Q_v - W = Q_v + P\Delta V$

The relationship $Q_p - Q_v = P\Delta V$ is most easily applied when dealing with ideal gases.

4 Reversible adiabatic transformation

A reversible adiabatic transformation is a process where no heat is exchanged, and the process occurs slowly enough to be considered reversible. For an ideal gas, the relationship between pressure and volume during such a transformation is governed by Laplace's law, also known as Poisson's equation or the adiabatic equation of state.

$$PV^{\gamma} = constant \; ; \gamma = \frac{C_p}{C_v} .$$

γ (gamma): is the adiabatic index (also known as the heat capacity ratio or the isentropic exponent.

$C_v = \frac{R}{(\gamma-1)}$ and $C_p = \frac{\gamma R}{(\gamma-1)}$; C_v and C_p: calorific capacities.

Using the ideal gas law (PV = nRT), Laplace's law can be expressed in other equivalent forms:

$$TV^{\gamma-1} = constant\ ;\ P^{1-\gamma}T^{\gamma} = constant\ ; TP^{\frac{1-\gamma}{\gamma}} = constant.$$

In an adiabatic process, by definition, (Q = 0). Therefore, according to the first law of thermodynamics ΔU = W.

- For a reversible transformation work exchanged is:

$$W_{rev} = \int -PdV = -\int \frac{const}{V^{\gamma}}dV = -const\int \frac{1}{V^{\gamma}}dV = -const\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]$$

$$= -const\left[\frac{{V_2}^{-\gamma+1}-{V_1}^{-\gamma+1}}{-\gamma+1}\right] = \frac{const{V_2}^{-\gamma+1}-const{V_1}^{-\gamma+1}}{\gamma-1} = \frac{P_2{V_2}^{\gamma}{V_2}^{-\gamma+1}-P_1{V_1}^{\gamma}{V_1}^{-\gamma+1}}{\gamma-1}$$

$$W_{rev} = \frac{P_2V_2-P_1V_1}{\gamma-1} \Rightarrow \frac{nRT_2-nRT_1}{\gamma-1}$$

- For an irreversible transformation, Laplace's law does not hold but the first law of thermodynamics still applies:

$$\Delta U = W_{irrev} = \int nC_v dT = \frac{nR(T_2-T_1)}{\gamma-1} = \frac{nRT_2-nRT_1}{\gamma-1};\ \ C_v = \frac{R}{(\gamma-1)}$$

5 Enthalpy

5.1 Enthalpy function

Enthalpy represented by the symbol (H), is the total heat content of a thermodynamic system, measured in Joules (J) or Calories (cal). It is important to note that enthalpy is related to heat content, but it is not simply "heat."

Enthalpy is a state function defined by the equation:

$$H = U + PV$$

U: internal energy; P: pressure of the system; V: volume of the system.

Enthalpy is particularly useful for analyzing processes that occur at constant pressure (isobaric processes).

If a process occurs at constant pressure, the change in enthalpy (ΔH) is equal to the heat transferred to or from the system:

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

From the first law of thermodynamics:

$\Delta U = Q + W = Q - P\Delta V$

Substituting this into the enthalpy equation:

$\Delta H = (Q - P\Delta V) + P\Delta V = Q$

Therefore, at constant pressure: $\Delta H = Q_p = nC_p\Delta T$.

The change in enthalpy directly represents the heat absorbed or released by the system at constant pressure.

5.2 Differential expression of enthalpy

Isobaric transformation: $Q_p = \Delta H = H_2 - H_1$.

The total differential of enthalpy expresses how a small change in enthalpy (dH) is related to small changes in temperature (dT) and pressure (dP).

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

At constant pressure $dH = \left(\frac{\partial H}{\partial T}\right)_P dT = dQ_p = nC_p dt.$

C_p : molar heat capacity at constant pressure

- If $\Delta H < 0 \Rightarrow$ the system releases heat to the surroundings (exothermic process).
- If $\Delta H > 0 \Rightarrow$ the system absorbs heat from the surroundings (endothermic process).

5.3 Joule's second law

The enthalpy of an ideal gas depends only on its temperature.

$$H = f(T)$$

Enthalpy is a state function and an extensive property, therefore this law is only valid when the number of moles (n) of the gas remains constant.

Third chapter exercises

First law of thermodynamics

Exercise 01:

A greenhouse containing 812 g of air is heated to prevent freezing in winter. The temperature of the air increases from 2°C to 16°C.

The heated air is considered an ideal gas.

1- Calculate the change in internal energy of the air during this heating.
2- Calculate the amount of heat received by the gas, if the gas performed 546.4 J of work.

Data: M_{air} = 29 g /mole; R = 8,32 S.I.; γ (air) = C_P /C_v = 1,4.

Exercise 02:

One mole of an ideal gas is characterized by $P_0 = 2.10^5$ Pa, V_0 = 14 L in the initial state. This mole of gas successively undergoes the following transformations:

a) An isobaric expansion that doubles its volume.

b) An isothermal compression that returns it to its initial volume.

c) An isochoric cooling that returns it to the initial state (P_0, V_0).

1- At what temperature does the isothermal compression occur? Deduce the maximum pressure reached.
2- Represent the transformation cycle in the Clapeyron diagram (P-V diagram).
3- Calculate the work, the heat, and the change in internal energy during each transformation.
4- Give the balance of the transformation cycle.

Data: R = 8,314 J.mol^{-1}.K^{-1}; $C_p = \frac{7}{2}R$; $C_v = \frac{5}{2}R$.

Reversible adiabatic transformation

Exercise 03:

A horizontal cylinder of invariable volume is divided into two compartments, C_1 and C_2, each filled with $V_0 = 2$ L of helium (ideal gas). The two compartments are separated by a mobile piston that moves without friction, and the entire assembly is thermally insulated (adiabatic). At the initial state, C_1 and C_2 are characterized by $P_0 = 1$atm and $T_0 = 273$ K. The gas in compartment C_1 receives heat from the external environment using a heating resistor.

1- Determine the pressures, volumes, and temperatures of compartments C_1 and C_2 when the pressure of the gas contained in C_1 becomes $P_1 = 3P_0$.
2- Determine the change in internal energy of the gas in C_1 and C_2, and the energy supplied by the heating resistor. *Data*: $\gamma = 5 / 3$.

Exercise 04:

A closed cylinder, whose walls are adiabatic, is divided into two compartments, C_1 and C_2. The two compartments contain air and are separated by a piston that is initially fixed. The air contained in C_1 is in the state (P_0, V_0, T_0), and the air in C_2 is in the state ($2P_0$, V_0, T_0). When the piston is released and equilibrium is established:

1- Determine the final pressure P_1 as a function of P_0 and γ.
2- Calculate the pressures, volumes, and temperatures of the gas in each compartment. *Data*: $P_0 = 1$atm; $V_0 = 2$ l; $T_0 = 300$ K; $\gamma = 7 / 5$.

Exercise 05:

2 g of helium (monatomic ideal gas) are enclosed in a container closed by a mobile piston under conditions (P_1, V_1). The enclosed gas undergoes a reversible adiabatic compression that brings it to conditions (P_2, V_2). Given that: $P_1 = 1$ bar; $V_1 = 10$ L; $P_2 = 3$ bar.

1- Calculate the final volume V_2.
2- Calculate the work exchanged by the gas with the external environment.
3- Find the change in internal energy of the gas.
4- Deduce the change in temperature of the gas without calculating its initial temperature.

Data: $\gamma = C_p/C_v = 5/3$; $R = 8{,}314$ J.K^{-1}.mol^{-1}.

Exercises solutions

First law of thermodynamics

Exercise 01:

1- The change in internal energy:

The change in internal energy of n moles of an ideal gas is $\Delta U = n C_v \Delta T$.

Air is an ideal gas: γ (air) = $\frac{C_p}{C_v}$ and $C_p - C_v = R$ so $C_v = \frac{R}{(\gamma-1)}$

$\Rightarrow \Delta U = n \frac{R}{(\gamma-1)} \Delta T$

For air $n = \frac{m}{M} = \frac{812}{29}$

$\Rightarrow \Delta U = \frac{812}{29} \frac{8,32}{(1,4-1)} (16 - 2) = 8153,6$ J

2- The amount of heat received by the air

According to the first law of thermodynamics $\Delta U = W + Q$

$\Rightarrow Q = \Delta U - W$

The work is provided so it is negative, W = - 546,4 J

$\Rightarrow Q = 8153,6 - (-546,4) = 8700$ J

Exercise 02:

1- The temperature at which the isothermal compression occurs:

- Initial state $P_0 = 2.10^5$ Pa, $V_0 = 14$ l.

  According to ideal gas law $T_0 = \frac{P_0 V_0}{R} = 336,78$ K

- At the end of the isobaric expansion, the volume doubles, the state of the gas becomes $P_1 = P_0$, $V_1 = 2V_0$ and $T_1 = \frac{P_1 V_1}{R} = \frac{2P_0 V_0}{R} = 2T_0 = 673,56$ K

- After isothermal compression, the state of the gas is characterized by V_0, $T_2 = 2T_0$ and $P_2 = \frac{P_1 V_1}{V_0} = 2P_0$.

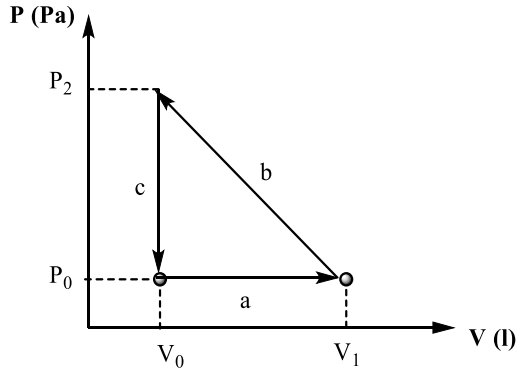
  So:

  The temperature is $T_2 = 2T_0 = 673,56$ K.

  The maximum pressure reached is $P_2 = 2P_0 = 4\ 10^5$ Pa.

2- Representation of the transformation cycle in the diagram (P, V):

The (P, V) diagram is the Clapeyron diagram which represents the evolution of the transformations by plotting the pressure (P) on the ordinate and the volume (V) on the abscissa.



3- Calculation of W, Q and ΔU:

a) Isobaric expansion

$W_a = - P_0 (2 V_0 - V_0) = - P_0 V_0 = -2.10^5 .14 = - 2800$ J

$Q_a = C_P (T_1 - T_0) = \frac{7}{2} 8,314 (673,56 - 336,78) = 9800$ J

$\Delta U_a = W + Q = - 2800 + 9800 = 7000$ J

b) Isothermal compression

$W_b = R T_1 ln \frac{P_2}{P_0} = 2 R T_0 \ln 2 = 3881,61$ J

$Q_b = R T_1 ln \frac{V_2}{V_1} = - 2 R T_0 \ln 2 = - 3881,61$ J

$\Delta U_b = 0$ J (T = constant, Joule's first law).

c) Isochoric cooling

$W_c = 0$ J (V = constant).

$Q_c = C_V (T_0 - T_1) = \frac{5}{2} 8,314 (336,78 - 673,56) = -7000$ J

$\Delta U_c = Q_c = -7000$ J

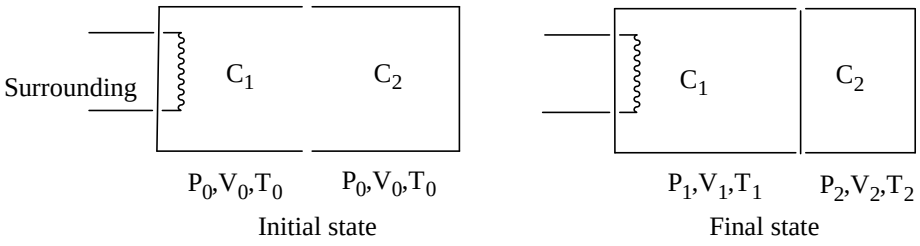
4- The cycle report:

- Work : $W_{cycle} = W_a + W_b + W_c = 1081,61$ J
- Heat : $Q_{cycle} = - W = - 1081,61$ J
- The variation of the internal energy ΔU is zero because it is a state function and the transformation is cyclical (return to the initial state).

  W is positive, Q is negative ⇒ the system has received work which it has returned to the external environment in the form of heat.

Reversible adiabatic transformation

Exercise 03:



1- Pressures, volumes and temperatures of $C_1$and C_2:

a) Pressures

Mechanical equilibrium ⇒ $P_1 = P_2 = 3P_0 = 3$atm.

b) Volumes

- In C_2 compartment, the gas undergoes reversible adiabatic compression, so we can apply Laplace's law $PV^{\gamma} = constant$

$$P_0 V_0{}^{\gamma} = P_2 V_2{}^{\gamma} \Rightarrow V_2 = \left(\frac{P_0}{P_2}\right)^{\frac{1}{\gamma}} V_0 = \frac{1}{3}^{\left(\frac{3}{5}\right)} 2 = 1{,}03\text{l}$$

- The total volume is conserved $V_1 + V_2 = 2V_0 \Rightarrow V_1 = 2V_0 - V_2 = 4 - 1{,}03 = 2{,}97$l

c) Temperatures

According to Laplace's law $TP^{\frac{1-\gamma}{\gamma}} = constant$

$$T_0 P_0{}^{\frac{1-\gamma}{\gamma}} = T_2 P_2{}^{\frac{1-\gamma}{\gamma}} \Rightarrow T_2 = T_0 \left(\frac{P_2}{P_0}\right)^{\frac{\gamma-1}{\gamma}} = 273(3)^{\frac{2}{5}} = 423{,}7\text{ K}$$

According to ideal gas law PV = nRT

We have $\begin{cases} P_0 V_0 = nRT_0 \\ P_1 V_1 = nRT_1 \end{cases} \Rightarrow T_1 = T_0 \frac{P_1 V_1}{P_0 V_0} = 273 \frac{3(2{,}97)}{1(2)} = 1216\text{ K}$

2- Internal energy variation

- C_1 compartment

$\Delta U = n C_v \Delta T$ and $C_v = \frac{R}{(\gamma-1)}$

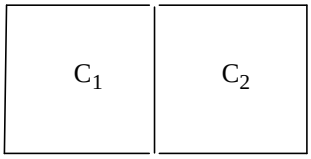
$\Delta U_1 = n \frac{R}{\gamma-1}(T_1 - T_0) = \frac{P_1 V_1 - P_0 V_0}{\gamma-1} = 1040$ KJ

- C_2 compartment

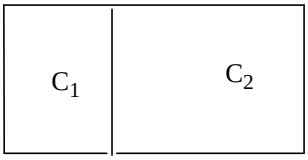
$\Delta U_2 = \frac{P_2 V_2 - P_0 V_0}{\gamma-1} = 164$ KJ

- The energy supplied by the heating resistor $E = \Delta U_1 + \Delta U_2 = 1204$ KJ.

Exercise 04:



Initial state



Final state

The pressure of the gas in compartment C_2 is greater than the pressure of the gas in compartment C_1, so by releasing the piston, it will move to the left.

3- P_1 pressure in function of P_0 and γ:

The gas in compartment C_1 underwent an adiabatic compression, and the gas in compartment C_2 underwent an adiabatic expansion.

According to Laplace's law $PV^{\gamma} = constant$

We have $\begin{cases} P_0V_0{}^{\gamma} = P_1V_1{}^{\gamma} \ (1) \\ 2P_0V_0{}^{\gamma} = P_2V_2{}^{\gamma} \ (2) \end{cases}$

$\frac{(2)}{(1)} \Rightarrow \frac{2P_0V_0{}^{\gamma}}{P_0V_0{}^{\gamma}} = \frac{P_2V_2{}^{\gamma}}{P_1V_1{}^{\gamma}} \Rightarrow (\frac{V_2}{V_1})^{\gamma} = 2$

In the other hand, the volume is conserved $V_1+V_2 = 2V_0 \Rightarrow V_2 = 2V_0-V_1$

So $(\frac{2V_0-V_1}{V_1})^{\gamma} = 2 <=> (\frac{2V_0}{V_1} - 1)^{\gamma} = 2 \Rightarrow \frac{V_0}{V_1} = \frac{1}{2}\left(2^{\frac{1}{\gamma}} + 1\right)$

According to (1) $\Rightarrow P_1 = \left(\frac{V_0}{V_1}\right)^{\gamma} P_0 = \frac{1}{2}\left(2^{\frac{1}{\gamma}} + 1\right)^{\gamma} P_0$

3- Pressures, volumes and temperatures of C_1 and C_2 :

a) Pressures

At equilibrium the pressures are equals $P_1 = P_2$

$P_1 = \frac{1}{2}\left(2^{\frac{1}{\gamma}} + 1\right)^{\gamma} P_0$ = 1,47atm

b) Volumes

- C_1 compartment: $V_1 = \left(\frac{P_0}{P_1}\right)^{\frac{1}{\gamma}} V_0 = \left(\frac{1}{1.47}\right)^{\frac{5}{7}} 2$ = 1,52l
- C_2 compartment: $V_2 = 2V_0 - V_1 = 4-1,52 = 2,48$l

c) Temperatures

According to PV = nRT

- C_1 compartment: $T_1 = T_0 \frac{P_1V_1}{P_0V_0} = 300 \frac{1,47 \times 1,52}{1 \times 2} = 334$K
- C_2 compartment: $T_2 = T_0 \frac{P_2V_2}{2P_0V_0} = 300 \frac{1,47 \times 2,48}{2 \times 1 \times 2} = 274$K

Exercise 05:

1- Final volume V_2:

Reversible adiabatic transformation, we apply Laplace's law:

$$P_1 V_1{}^{\gamma} = P_2 V_2{}^{\gamma} \Rightarrow V_2 = \left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} V_1 = 10\,(\tfrac{1}{3})^{(\frac{3}{5})} = 5{,}16\text{l}$$

2- Work exchanged:

$$W = \frac{(P_2V_2 - P_1V_1)}{\gamma - 1} = \frac{3.10^5.5{,}17.10^{-3} - 10^5 10.10^{-3}}{\frac{5}{3} - 1} = 822\text{ J}$$

3- Internal energy variation:

Adiabatic transformation $\Rightarrow$ Q = 0; $\Delta U = W + Q$

$\Rightarrow \Delta U = W = 822$ J

4- Temperature variation:

$\Delta U = n\, C_v\, \Delta T$ and $C_v = \frac{R}{(\gamma - 1)} \Rightarrow \Delta U = n \frac{R}{(\gamma - 1)} \Delta T \Rightarrow \Delta T = \frac{\Delta U(\gamma - 1)}{nR}$

For helium: $n = \frac{m}{M} = \frac{2}{4} mol$

$\Rightarrow \Delta T = \frac{822\,(\frac{5}{3} - 1)}{\frac{2}{4} \times 8{,}314} = 132$ degrees.

CHAPTER IV : Applications of the First Law of Thermodynamics to Thermochemistry

1 Heat of reaction

The heat of a chemical reaction assumed to be complete and considered as a closed thermodynamic system, is the heat energy exchanged (absorbed or released) with the external environment.

- At constant volume ⇒ $Q_v = \Delta U$.
- At constant pressure ⇒ $Q_p = \Delta H$ (enthalpy).

By convention:

- $\Delta H > 0$ ⇒ endothermic reaction (absorbed heat).
- $\Delta H < 0$ ⇒ exothermic reaction (released heat).

1.1 Relationship between Q_p and Q_v

According to the first law of thermodynamics

$Q_p = \Delta U - W = Q_v - W$

$\Rightarrow Q_p = Q_v + P (V_f - V_i)$

According to ideal gas law $PV = nRT \Rightarrow V = \frac{nRT}{P}$

So $Q_p = Q_v + P (\frac{n_f RT}{P} - \frac{n_i RT}{P}) = Q_v + RT (n_f - n_i) = Q_v + RT\Delta n$

Or $\Delta H = \Delta U + RT\Delta n$

- If the variation in number of moles (Δn) = 0 ⇒ $Q_p = Q_v$

2 Standard state

The standard state of a substance refers to its most stable and common physical form under defined standard conditions (T = 25°C and P = 1atm).

Examples:

- The standard state of oxygen is diatomic gas O_2, not single oxygen atoms.
- The standard state of carbon is graphite (s), not diamond.
- The standard state of water is liquid water.

The standard enthalpy of a reaction (ΔH°_R) is the change in enthalpy under standard conditions. It represents the amount of heat absorbed or released (at constant

pressure) when a reaction converts reactants in their standard states completely to products in their standard states.

2.1 Determination of standard enthalpy

The standard enthalpy of a chemical reaction can be determined using two methods:

- From the standard enthalpies of the secondary reactions.
- From the standard enthalpies of formation of the reactants and products, or from the bond energies of the reactants and products.

3 Standard enthalpy of formation

Standard enthalpy of formation (ΔH°_{f}) is the enthalpy change when one mole of a compound is formed from its elements in their standard states and at (P = 1atm).

Example: $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$; $\Delta H^{\circ}_{f,289}$ (H_2O): Standard enthalpy of formation of $H_2O_{(l)}$ at T = 298K.

- The standard enthalpy of formation of a compound allows comparing its stability with the stability of its simple elements.
- Standard enthalpies of reaction provide a reference point for comparing the heat effects of different reactions and for thermodynamic calculations.

3.1 Standard enthalpy of formation of a simple elements

The standard enthalpy of formation of a simple element, formed from a single type of atoms such as (O_2, O_3, H_2, He...) is zero.

Example: $\Delta H^{\circ}_{f,289}$ (O_2) = 0 Cal/mol.

4 Enthalpy of a chemical reaction

4.1 Hess's law

Hess's law states that the enthalpy change for a chemical reaction is independent of the path taken between the initial and final states.

If a reaction can be carried out in a single step or through a series of steps, the sum of the enthalpy changes associated with the series of steps will be equal to the enthalpy change for the single-step reaction.

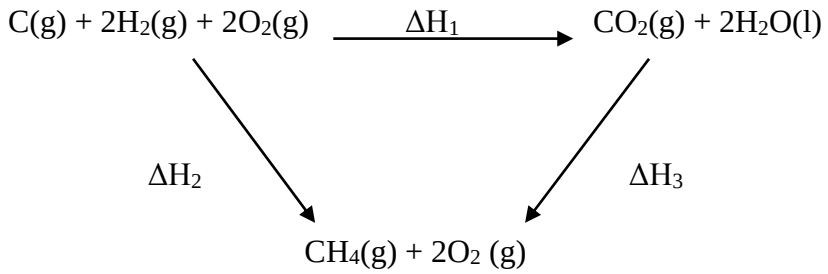
Therefore, for a main chemical reaction, its standard enthalpy is the sum of the standard enthalpies of all intermediate reactions.

$$\Delta H^{\circ}_{R} = \sum \Delta H^{\circ}_{\mathrm{i}}$$

Either, the standard enthalpy of a chemical reaction is equal to the sum of the enthalpies of formation of the products minus those of the reactants.

$$.\Delta H^{\circ}_{R} = \sum \Delta H^{\circ}_{\mathrm{f}}(products) - \sum \Delta H^{\circ}_{\mathrm{f}}(reactants)$$

Example: Calculation of ΔH_1 of the following reaction



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

Or else $\Delta H_1 = (\Delta H^{\circ}_{f}(CO_2)_{(g)} + 2\Delta H^{\circ}_{f}\ (H_2O)_{(l)}) - (\Delta H^{\circ}_{f}C_{(g)} + 2\Delta H^{\circ}_{f}H_{2(g)} + 2\Delta H^{\circ}_{f}O_{2(g)})$. With ΔH°_{f} equals zero for simple elements.

4.2 Kirchhoff's law

Kirchhoff's law states that the enthalpy change (ΔH_R) of a reaction with respect to temperature is equal to the change in heat capacity (ΔC_p) between products and reactants.

Kirchhoff's law allows calculating the enthalpy change of a reaction at a temperature T_2 given the enthalpy change at a temperature T_1, assuming heat capacity is constant or an average value is used.

$$\Delta H_R(T_2) = \Delta H_R(T_1) + \int_{T_1}^{T_2} \Delta C_p dt$$

$$\Delta U_R(T_2) = \Delta U_R(T_1) + \int_{T_1}^{T_2} \Delta C_v dt$$

- If phase transitions occur, the enthalpy changes associated with the transitions must be included in the calculation.

4.3 Bond energy

Covalent bond energy is the energy released when a bond forms between two atoms in a gaseous state at T = 25°C and P = 1atm.

Dissociation energy corresponds to the reverse reaction of covalent bond formation.

- The energy released when forming a bond is equal to the energy required to break it, but the sign is opposite.
  - Bonding energy is released energy ⇒ $\Delta H_l < 0$.
  - Dissociation energy is received energy ⇒ $\Delta H_{Diss} > 0$.

Example: The standard enthalpy of the following reaction can be calculated from the bond energy of the free atoms.

$$6\dot{H}(g) + 2\dot{C}(g) \longrightarrow C_2H_6\,(g)$$

$\Delta H^{\circ}_R = 6\,\Delta H_{(C-H)} + \Delta H_{(C-C)}$

4.3.1 Calculation of heat of reaction from bond energies

Bond energies can be used to estimate the enthalpy change of a reaction (ΔH), particularly in the gaseous phase, by calculating the difference between bond energies of bonds broken in product molecules and bond energies of bonds formed in reactants.

$$\Delta H_R = \sum E_{(products)} - \sum E_{(reactants)}.$$

Fourth chapter exercises

Exercise 01: Hess's law

I. Calculate the standard molar enthalpy of the reduction reaction of iron (III) oxide by aluminum at 25°C. $2Al\ (s) + Fe_2O_3\ (s) \rightarrow 2Fe(s) + Al_2O_3\ (s)$

Data: $\Delta H^\circ_{f,298(Fe_2O_3,s)}$ = -196,5 kcal.mole^{-1} ; $\Delta H^\circ_{f,298(Al_2O_3,s)}$ = -399,1 kcal.mole^{-1}

II. Calculate the standard enthalpy of formation of NH_3 (g) from the standard enthalpies of formation of NO (g) and H_2O (g), in the following reaction:

$2NH_3\ (g) + 5/2\ O_2\ (g) \rightarrow 2NO\ (g) + 3H_2O\ (g)$; $\Delta H^\circ_{r,298}$ = - 109 kcal

Data: $\Delta H^\circ_{f,298(NO,g)}$ = 21,5 kcal.mole^{-1} ; $\Delta H^\circ_{f,298(H_2O,g)}$ = - 58,0 kcal.mole^{-1}

Exercise 02: standard enthalpy

From the standard enthalpies $\Delta H^\circ_{r,298}$ of combustion reactions of CO, H_2 and CH_4:

$CO\ (g) + 1/2O_2\ (g) \rightarrow CO_2\ (g)$; $\Delta H^\circ_{r,298}\ (1)$ = -283 kJ

$H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O\ (g)$; $\Delta H^\circ_{r,298}\ (2)$ = -241, 8 kJ

$CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (g)$; $\Delta H^\circ_{r,298}\ (3)$ = -803, 2 kJ

1- Calculate the standard enthalpy $\Delta H^\circ_{r,298}$ of the following reaction:

$CO\ (g) + 3H_2(g) \rightarrow CH_4(g) + H_2O\ (g)$

2- Is the reaction endothermic or exothermic?

3- What is the internal energy value $\Delta U^\circ_{r,298}$ of this reaction?

Exercise 03: Bond energy

Knowing that the enthalpy of a reaction can be determined from the bond energies of the reactants and products.

I. Calculate the standard enthalpy $\Delta H^\circ_{r,298}$ of the following reaction:

$CH_3CH_2OH \rightarrow CH_2{=}CH_2\ (g) + H_2O\ (g)$

II. Calculate the C-F bond energy in the following reaction:

$CH_4(g) + 4F_2(g) \rightarrow CF_4(g) + 4HF(g)$; $\Delta H^\circ_{r,298}$ = -1923 KJ/mole

Data: values of bond energies at 298K en KJ/mole

E_{C-C} = - 342.5; E_{C-H} = - 412.3; $E_{C=C}$ = - 612.8; E_{C-O} = -356; E_{O-H} = - 426.6;

E_{H-F} = -562.6; E_{F-F} = -153.

Exercise 04: Kirchhoff's law

The combustion reaction of one mole of liquid methanol under one atmosphere and at 298K releases 725.2 kJ of heat to the surrounding environment.

1- Give the balanced combustion reaction of liquid methanol at 298K.
2- Calculate the enthalpy of formation of liquid methanol at 298K.
3- Calculate the enthalpy of this reaction at 60°C.

Data at 298K: $\Delta H^\circ_{f,(H_2O,l)}$ = - 285,8 kJ/mole; $\Delta H^\circ_{f,(CO_2,g)}$ = - 393,51 kJ/mole;

C_p (H_2O, l) = 75,2 J.mole^{-1}.K^{-1}; C_p (O_2) = 34,7 J.mole^{-1}.K^{-1};

C_p (CO_2, g) = 36,4 J.mole^{-1}.K^{-1}; C_p (CH_3OH, l) = 81,6 J.mole^{-1}.K^{-1}.

Exercise 05: Kirchhoff's law

Under standard conditions (T = 25°C and P = 1atm) the combustion enthalpy of methane (CH_4) is $\Delta H^\circ_{r,298}$ = -212,8 kcal.

The enthalpies of the following reactions are given:

C (graphite) + O_2 (g) → CO_2 (g) (1); $\Delta H^\circ_{r,298}$ (1) = - 94,05 kcal

H_2 (g) + 1/2O_2 (g) →H_2O (l) (2); $\Delta H^\circ_{r,298}$ (2)= - 68,3 kcal

1- Write the combustion equation for methane (CH_4).
2- Calculate the standard molar enthalpy of formation of methane gas $\Delta H^\circ_{f,298}\,(CH_4, g)$.
3- At a temperature of 1273 K and under one atmosphere, calculate the molar enthalpy of combustion of methane.

Data: molar heat capacities (assumed constant between 298 and 1273K)

C_p (CH_4, g) = 13,2 al.mole^{-1}.K^{-1}; C_p (O_2, g) = 7,6 cal.mole^{-1}.K^{-1}

C_p (CO_2, g) = 11,2 cal.mole^{-1}.K^{-1}; C_p (H_2O, g) = 9,2 cal.mole^{-1}.K^{-1}

C_p (H_2O, l) = 18,0 cal.mole^{-1}.K^{-1}; $\Delta H^\circ_{vap,373}$ (H_2O, l) = 9,7 kcal.mole^{-1}

Exercise solutions

Exercise 01: Hess's law

I. The standard molar enthalpy of the reduction reaction of iron (III) oxide by aluminum:

$$2Al\ (s) + Fe_2O_3\ (s) \rightarrow 2Fe(s) + Al_2O_3\ (s)$$

According to Hess's law $\Delta H^\circ_R = \sum \Delta H^\circ_f(products) - \sum \Delta H^\circ_f(reactants)$

$\Delta H^\circ_{r,298} = 2\Delta H^\circ_{f,298(Fe,s)} + \Delta H^\circ_{f,298(Al_2O_3,s)} - 2\Delta H^\circ_{f,298(Al,s)} - \Delta H^\circ_{f,298(Al_2O_3,s)}$

The standard enthalpy of formation of a simple element is zero.

$\Delta H^\circ_{f,298(Fe,s)} = \Delta H^\circ_{f,298(Al,s)} = 0$

So $\Delta H^\circ_{r,298} = \Delta H^\circ_{f,298(Al_2O_3,s)} - \Delta H^\circ_{f,298(Al_2O_3,s)}$

$\Delta H^\circ_{r,298} = -399{,}1 - (-196{,}5) = -202{,}6$ kcal

II. The standard molar enthalpy of formation of NH_3 (g):

$2NH_3\ (g) + 5/2\ O_2\ (g) \rightarrow 2NO\ (g) + 3H_2O\ (g)$; $\Delta H^\circ_{r,298} = -109$ kcal

Applying Hess's law:

$\Delta H^\circ_{r,298} = 2\Delta H^\circ_{f,298(NO,g)} + 3\Delta H^\circ_{f,298(H_2O,g)} - 2\Delta H^\circ_{f,298(NH_3,g)}$

$$\Rightarrow \Delta H^\circ_{f,298(NH_3,g)} = \frac{-\Delta H^\circ_{r,298} + 2\Delta H^\circ_{f,298(NO,g)} + 3\Delta H^\circ_{f,298(H_2O,g)}}{2}$$

$$\Delta H^\circ_{f,298(NH_3,g)} = \frac{109 + 2(21{,}5) + 3(-58{,}0)}{2} = -11 \text{ kcal}$$

Exercise 02: Standard enthalpy

1- Calculation of standard enthalpy:

To calculate the standard enthalpy of the reaction $CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$ it is necessary to combine the given reactions.

$CO\ (g) + 1/2O_2\ (g) \rightarrow CO_2\ (g)$; $\Delta H^\circ_{r,298}\ (1) = -283$ kJ

(3) x $[H_2\ (g) + 1/2O_2\ (g) \rightarrow H_2O\ (g)]$; $(3)\Delta H^\circ_{r,298}\ (2) = 3\ (-241, 8)$ kJ

(-1) x $[CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (g)]$; $(-1)\ \Delta H^\circ_{r,298}\ (3) = (-1)\ (-803, 2)$ kJ

$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$; $\Delta H^\circ_{r,298}\ (4)$

$\Delta H^{\circ}_{r,298}(4) = \Delta H^{\circ}_{r,298}(1) + 3\,\Delta H^{\circ}_{r,298}(2) - \Delta H^{\circ}_{r,298}(3)$

$\Delta H^{\circ}_{r,298}(4)$ = -283 + 3 (-241,8) + 803,2 = -206,23 kJ

2- The calculated standard enthalpy $\Delta H^{\circ}_{r,298}(4) =$ -206,23 kJ < 0

⇒ the reaction is exothermic.

3- Internal energy $\Delta U^{\circ}_{r,298}$:

Knowing that $\Delta H^{\circ}_{r,298} = \Delta U^{\circ}_{r,298} +$ RTΔn

Moreover, Δn is the variation of the stoichiometric coefficients of the gaseous products and reactants. $\Delta n = \sum$ ni$(gaseous\ products) - \sum ni(\ gaseous\ reactants)$.

So Δn = 2 - 4 = - 2

⇒ $\Delta U^{\circ}_{r,298} = \Delta H^{\circ}_{r,298} -$ RTΔn

$\Delta U^{\circ}_{r,298}$ = -206,23 – (8,31/1000) (298) (-2) = -201,28 kJ

Exercise 03: Bond energy

I. Calculation of standard enthalpy from bond energies:

$$CH_3CH_2OH \rightarrow CH_2{=}CH_2\ (g) + H_2O\ (g)$$

Knowing that $\Delta H^{\circ}_{r} = \sum E_{(products)} - \sum E_{(reactants)}$

$\Delta H^{\circ}_{r,298} = (E_{C=C} + 4E_{C-H} + 2E_{O-H}) - (E_{C-C} + E_{C-O} + E_{O-H} + 5\,E_{C-H})$

$\Delta H^{\circ}_{r,298}$ = -342,5 + 4 (-412,3) + 2(-426,6) + 342,5 + 356 + 426,6 + 5(412,3)

$\Delta H^{\circ}_{r,298}$ = 341,7 KJ/mole

II. Calculation of the bond energy C-F :

$CH_4(g) + 4F_2(g) \rightarrow CF_4(g) + 4HF(g)$

We have $\Delta H^{\circ}_{r,298} = 4E_{H-F} + 4E_{C-F} - 4E_{F-F} - 4E_{C-H}$ = -1923 KJ/mole

⇒ $E_{C-F} = (\Delta H^{\circ}_{r,298} - 4E_{H-F} + 4E_{F-F} + 4E_{C-H})\ /4$

E_{C-F} = [-1923 – 4(-562.6) + 4(-153) + 4(-412.3)] /4 = - 483.45 KJ/mole

Exercise 04: Kirchhoff's law

1- The combustion equation for liquid methanol:

The amount of heat is supplied to the surrounding therefor $\Delta H^{\circ}_{r,298}$ = -725,2 kJ.

CH_3OH (liquid) + $\frac{3}{2}$ O_2 (g) → CO_2 (g) + 2H_2O (l); $\Delta H^{\circ}_{r,298}$ = -725,2 kJ.

2- The enthalpy of formation of liquid methanol:

According to Hess's law $\Delta H^{\circ}_{R} = \sum \Delta H^{\circ}_{f}(products) - \sum \Delta H^{\circ}_{f}(reactants)$

$\Delta H^{\circ}_{r,298} = \Delta H^{\circ}_{f,298}(CO_2, g) + 2\Delta H^{\circ}_{f,298}(H_2O, l) - \Delta H^{\circ}_{f,298}(CH_3OH, l) - \frac{3}{2}\Delta H^{\circ}_{f,298}(O_2, g)$

And $\Delta H^{\circ}_{f,298}(O_2, g) = 0$ (simple element)

$\Rightarrow \Delta H^{\circ}_{f,298}(CH_3OH, l) = \Delta H^{\circ}_{f,298}(CO_2, g) + 2\Delta H^{\circ}_{f,298}(H_2O, l) - \Delta H^{\circ}_{r,298}$

$\Delta H^{\circ}_{r,298}(CH_3OH, l)$ = - 393,51 + 2 (-285,8) – (-725,2) = 239,91 kJ.mole^{-1}

3- Enthalpy of the reaction at 60°C :

Applying Kirchhoff's law $\Delta H^{\circ}_{r,333} = \Delta H^{\circ}_{r,298} + \int_{298}^{333} \Delta C_p dt$

And $\Delta C_p = \sum n_i C_p(products) - \sum n_i C_p(reactants)$

ΔC_p= C_p (CO_2, g) + 2 C_p (H_2O, l) - C_p (CH_3OH, l) - $\frac{3}{2}$ C_p (O_2, g)

ΔC_p= 36,4 + 2 (75,2) - 81,6 - $\frac{3}{2}$ (34,7) = 53,15 J.mol^{-1}.K^{-1}

$\Rightarrow \Delta H^{\circ}_{r,333} = \Delta H^{\circ}_{r,298} + \int_{298}^{333} \Delta C_p dt$

$\Delta H^{\circ}_{r,333}$ = -725,2 +53,15 (333-298) = -723,33 kJ

Exercise 05: Kirchhoff's law

1- The methane combustion equation:

CH_4 (g) + 2O_2 (g) → CO_2 (g) + 2H_2O (l); $\Delta H^{\circ}_{r,298}$ = -212,8 kcal

2- The standard molar enthalpy of formation of gaseous methane:

Hess's law $\Delta H^{\circ}_{R} = \sum \Delta H^{\circ}_{f}(products) - \sum \Delta H^{\circ}_{f}(reactants)$

From the reactions:

C (graphite) + O_2 (g) → CO_2 (g) (1); $\Delta H^\circ_{r,298}$ (1) = - 94,05 kcal

H_2 (g) + 1/2O_2 (g) →H_2O (l) (2); $\Delta H^\circ_{r,298}$ (2)= - 68,3 kcal

We notice that:

$\Delta H^\circ_{r,298}$ (1) = $\Delta H^\circ_{f,298}(CO_2, g)$ and $\Delta H^\circ_{r,298}$ (2) = $\Delta H^\circ_{f,298}(H_2O, l)$

So $\Delta H^\circ_{r,298} = \Delta H^\circ_{f,298}(CO_2, g) + 2\Delta H^\circ_{f,298}(H_2O, l) - \Delta H^\circ_{f,298}(CH_4, g)$

$\Rightarrow \Delta H^\circ_{f,298}(CH_4, g) = \Delta H^\circ_{f,298}(CO_2, g) + 2\Delta H^\circ_{f,298}(H_2O, l) - \Delta H^\circ_{r,298}$

$\Delta H^\circ_{f,298}(CH_4, g)$ = - 94,05 + 2 (-68,3) – (-212,8) = 17,85 kcal.mole^{-1}

3- The molar enthalpy of combustion of methane at 1273K :

Kirchhoff's law $\Delta H^\circ_{r,1273} = \Delta H^\circ_{r,298} + \int_{298}^{1273} \Delta C_p dt$

At 1273K, all the products are in the gaseous state. Thus, the water has changed phases between 298 and 1273K.

The reaction becomes CH_4 (g) + 2O_2 (g) → CO_2 (g) + 2H_2O (g)

And $\Delta H^\circ_{r,1273} = \Delta H^\circ_{r,298} + \int_{298}^{373} \Delta C_p dt$ + 2$\Delta H^\circ_{vap,373}$ (H_2O, l) + $\int_{373}^{1273} \Delta C'_p dt$

We have $\Delta C_p = \sum n_i C_p(products) - \sum n_i C_p(reactants)$

ΔC_p= C_p (CO_2, g) + 2 C_p (H_2O, l) - C_p (CH_4, g) - 2 C_p (O_2, g)

ΔC_p = 11,2 + 2 (18,0) -13,2 -2 (7,6) = 18,8 cal.mole^{-1}.K^{-1}

$\Delta C'_p$ = C_p (CO_2, g) + 2 C_p (H_2O, g) - C_p (CH_4, g) - 2 C_p (O_2, g)

$\Delta C'_p$ = 11,2 +2 (9,2) -13,2 - 2 (7,6) = 1,2 cal.mole^{-1}.K^{-1}

$\Rightarrow \Delta H^\circ_{r,1273} = \Delta H^\circ_{r,298} + \int_{298}^{373} \Delta C_p dt$ + 2$\Delta H^\circ_{vap,373}$ (H_2O, l) + $\int_{373}^{1273} \Delta C'_p dt$

$\Delta H^\circ_{r,1273}$ = -212,8 + 18,8 (373 - 298)10^{-3} + 2 (9,7) + 1,2 (1273-373)10^{-3}

$\Delta H^\circ_{r,1273}$ = - 190,91 kcal

CHAPTER V : Second Law of Thermodynamics

1 Introduction

The first law of thermodynamics reveals the equivalence between different forms of energy; however, it does not allow predicting the equilibrium state of a system, hence the need for a second law to inform us about the equilibrium state of systems.

The second law of thermodynamics, based on the notion of entropy, allows distinguishing between possible and impossible, reversible and irreversible transformations.

In other words, the first law of thermodynamics is a principle of conservation of energy; the second law is a principle of evolution towards equilibrium.

1.1 Second law statements

The second law of thermodynamics can be expressed in several equivalent ways, each highlighting a different aspect of its implications:

- Heat cannot spontaneously flow from a colder body to a hotter body without external work being performed (Clausius statement).
- Heat cannot be entirely transformed into work. Some heat must always be rejected to a lower-temperature reservoir (Kelvin statement).
- A spontaneous transformation is accompanied by an increase in the overall entropy of the system and the external environment.

2 Entropy concept

2.1 Entropy

The entropy represented by (S) is often described as a measure of the disorder or randomness of a system, expressed in $J.K^{-1}$. It is a state function (depending only on the initial and final states) and a non-conservative extensive property, which allows quantifying the second law by measuring how the amount of energy is stored.

2.2 General expression of the second law of thermodynamics

The total change in entropy of a system can be expressed as the sum of two contributions (the entropy exchanged between the system and the surrounding and the entropy generated within the system itself).

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

$\Delta S_{exchanged}$: the entropy change due to heat transfer (Q) between the system and its surroundings at a specific temperature (T).

$\Delta S_{generated}$: the entropy created due to irreversible processes occurring within the system, such as friction, mixing, chemical reactions, or heat transfer across a finite temperature difference.

For a reversible transformation:

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

For an irreversible transformation:

$$\Delta S > \int_1^2 \frac{dQ_{irr}}{T}$$

Q: quantity of heat exchanged; T: temperature of the external environment.

- A real transformation is irreversible and leads to the creation of entropy.
- In a reversible transformation, the production of entropy is zero.
- A transformation that would result in the production of negative entropy is impossible.

2.3 Calculation of the entropy change (ΔS)

a) Reversible isochoric transformation (V = constant)

$dQ_{rev} = dQ_v = n\,C_v\,dT$; $\Delta S = \int_1^2 \frac{dQ_v}{T} = nC_v \int_1^2 \frac{dt}{T} = nC_v ln\frac{T_2}{T_1}$, (if C_v = constant).

b) Reversible isobaric transformation (P = constant)

$dQ_{rev} = dQ_p = n\,C_p\,dT$; $\Delta S = nC_p ln\frac{T_2}{T_1}$, (if C_p = constant).

c) Reversible isothermal transformation (T = constant)

$\Delta U = 0 \Rightarrow Q = -W$; $\Delta S = \frac{Q_{rev}}{T} = \frac{nRTln\frac{V_2}{V_1}}{T} = nRln\frac{V_2}{V_1} = nRln\frac{P_1}{P_2}$.

d) Reversible adiabatic transformation (Q = 0) :

$dQrev = 0 \Rightarrow \Delta S = \int_1^2 \frac{dQ_{rev}}{T} = 0$

2.4 The entropy of physical state change

During a physical state change (phase transition), the entropy of the system changes because the arrangement of molecules becomes more or less ordered. Latent heat is the heat required to change the physical state of a system.

Example: Melting (solid → liquid): heat is absorbed; the system's entropy increases as the molecules gain freedom of movement.

The entropy change (ΔS) associated with a phase transition can be calculated using the following equation:

Qrev = ΔH ⇒ $\Delta S = \frac{Q_{rev}}{T} = \frac{\Delta H}{T}$

ΔH: latent heat of vaporization, fusion, or sublimation.

T: temperature of the physical state change.

- A larger latent heat or a higher transition temperature results in a greater change in entropy.

2.5 Entropy of a chemical reaction

The entropy change of a chemical reaction at constant temperature and pressure can be calculated using Hess's law. This involves using the standard molar entropies (S°) of the reactants and products (usually 298 K and 1 atm).

$$\Delta S^{\circ} = \sum S^{\circ}(products) - \sum S^{\circ}(reactants)$$

At a new temperature, the entropy change can be determined using Kirchhoff's law:

$$\Delta S^{\circ}(T_2) = \Delta S^{\circ}(T_1) + \int_{T_1}^{T_2} \Delta C_p \frac{dT}{T}$$

2.6 The entropy of solids and liquids

According to the first law dU = dQ + dW

According to the second law dQ = TdS

Else dH = dU + d (PV)

The pressure change for liquids and solids is not significant, so the term d (PV) is neglected. We therefore have:

dU = TdS and dH = TdS

⇒ dS = $\frac{dU}{T} \approx \frac{dH}{T} = nC\frac{dT}{T}$; C : molar heat capacity of the system.

For liquids and solids: $C_v \approx C_p \approx$ constant.

2.7 Entropy of an ideal gas

a) Expression as a function of T and V:

We have dU = dQ + dW = TdS – PdV

Else, dU = n C_v dT and PV = nRT

⇒ dS = $nC_v \frac{dT}{T} + nR \frac{dV}{V}$

b) Expression as a function of T and P:

We have dH = TdS + VdP and dH = n C_p dT

⇒ dS = $nC_p \frac{dT}{T} + nR \frac{dP}{P}$

c) Expression as a function of P and V:

We have PV = nRT ⇒ $\frac{dT}{T} = \frac{dP}{p} + \frac{dV}{V}$

⇒ dS = $nC_v \frac{dP}{P} + nC_p \frac{dV}{V}$

- For a mixture of ideal gases, where the gases do not interact with each other, the entropy of the mixture is the sum of the entropies of each gas, plus the entropy of mixing.

2.8 Evolution criteria for an isolated system

The entropy $\Delta S = S_{exchanged} + S_{generated}$

So $dS_{system} = \frac{\partial Q_{exchanged}}{T} + \partial S_{generated}$

Isolated system (Q = 0) ⇒ $dS_{isolated\ system} = dS_{generated} \Leftrightarrow \Delta S_{isolated\ system} = \Delta S_{generated}$

$$\Delta S_{isolated\ system} \geq 0 \begin{cases} \Delta S_{isolated\ system} > 0 \Rightarrow \text{irreversible transformation} \\ \Delta S_{isolated\ system} = 0 \Rightarrow \text{reversible transformation} \end{cases}$$

- Since there is no heat exchange with the external environment, the entropy of an isolated system can only increase or remain constant.

2.9 Entropy balance

In order to perform an entropy balance, it is necessary to calculate the different terms ΔS, $S_{generated}$, and $S_{exchanged}$, and conclude whether the transformation is reversible or not, possible or not.

a) ΔS is calculated from:

dS = $nC_v \frac{dT}{T} + nR \frac{dV}{V}$ (entropy expressed as a function of volume).

$$\Rightarrow \Delta S = nC_v ln\frac{T_2}{T_1} + nRln\frac{V_2}{V_1}$$

dS = $nC_p \frac{dT}{T} + nR\frac{dP}{P}$ (entropy expressed as a function of pressure).

$$\Rightarrow \Delta S = nC_p ln\frac{T_2}{T_1} + nRln\frac{P_1}{P_2}$$

b) $S_{exchanged}$ is calculated from:

$$S_{exchanged} = \int_1^2 \frac{dQ}{T}$$

c) $S_{generated}$ cannot be calculated directly; it is determined from:

$$S_{generated} = \Delta S - S_{exchanged}$$

- $S_{generated} = 0 \Rightarrow$ reversible evolution.
- $S_{generated} > 0 \Rightarrow$ irreversible evolution.
- $S_{generated} < 0 \Rightarrow$ impossible evolution.

3 Heat engines

3.1 Definition

Heat engines are systems designed to convert thermal energy into mechanical energy, and vice versa.

There are two primary types of heat engines:

a) Single-reservoir (monothermal) engine:

This type of engine exchanges energy with only one thermal reservoir (heat source or sink). According to the second law of thermodynamics, a single-reservoir engine operating in a cycle cannot convert heat entirely into work. As a result, a monothermal machine can only receive work input and release heat.

b) Two-reservoir (dithermal) engine:

This type of engine exchanges energy with two thermal reservoirs at different temperatures: a hot reservoir and a cold reservoir. The heat and work transfers dictate the machine's function, leading to two distinct scenarios:

- $W < 0 \Rightarrow$ (Thermal engine or a power cycle). Heat flows from the hot reservoir to the engine.
- $W > 0 \Rightarrow$ (Refrigerator or a heat pump). Work is required to transfer heat from the cold reservoir to the hot reservoir.

3.2 Applications of the Carnot cycle

The Carnot cycle is a theoretical thermodynamic cycle that operates between two thermal reservoirs at different temperatures: a hot reservoir and a cold reservoir. It is a reversible cycle, meaning that each step can be reversed without any loss of energy, and it represents the maximum possible efficiency for any heat engine operating between these two reservoirs. The Carnot cycle consists of four reversible processes:

a) 1→2: Isothermal expansion
b) 2→3: Adiabatic expansion
c) 3→4: Isothermal compression
d) 4→1: Adiabatic compression

The efficiency (η) of the Carnot cycle is given by the expression: $\eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$

Q_1: the heat rejected to the cold reservoir at temperature T_1.

Q_2: the heat absorbed from the hot reservoir at temperature T_2.

For an irreversible dithermic engine: $\eta < 1 - \frac{T_1}{T_2}$

❖ Carnot refrigerator

The coefficient of performance (COP) for a Carnot refrigerator is expressed as:

$$\varepsilon = \frac{T_2}{T_1 - T_2}$$

❖ Carnot heat pump

The coefficient of performance (COP) for a Carnot heat pump is expressed as:

$$\varepsilon = \frac{T_1}{T_1 - T_2}$$

3.3 Common power cycles

a) Joule cycle (Brayton cycle)

Joule cycle is the ideal thermodynamic cycle for a gas turbine engine. It consists of four reversible processes:

1 → 2: Isentropic compression: no heat transfer occurs during this process.

2 → 3: Isobaric heat addition (constant pressure heating): heat is added to the working fluid, increasing its temperature significantly.

3 → 4: Isentropic expansion: no heat transfer occurs during this process.

4 → 1: Isobaric heat rejection (constant pressure cooling): the gas is cooled in a heat exchanger and then recirculated back to the compressor.

b) Otto cycle

Also known as the Beau de Rochas cycle, is an idealized thermodynamic cycle that describes the functioning of a typical spark-ignition internal combustion engine. It consists of four reversible processes:

1 → 2: Isentropic compression: (Q = 0).

2 → 3: Isochoric heat addition (constant volume combustion).

3 → 4: Isentropic expansion: (Q = 0).

4 → 1: Isochoric heat rejection (constant volume exhaust).

c) Diesel cycle

The Diesel cycle is an idealized thermodynamic cycle that describes the functioning of a typical compression-ignition internal combustion. It is an internal combustion cycle where the ignition of the fuel is achieved through the high temperature reached by compressing the air within the cylinder (spontaneous ignition). It consists of four reversible processes:

1 → 2: Isentropic compression

2 → 3: Isobaric heat addition

3 → 4: Isentropic expansion

4 → 1: Isochoric heat rejection

d) Stirling cycle

The Stirling cycle is a thermodynamic cycle that describes the operation of Stirling engines, which are external combustion engines that can operate on a variety of heat sources. Unlike internal combustion engines, the heat source is external to the engine itself, allowing for the use of solar energy, geothermal energy, biomass, or waste heat. The ideal Stirling cycle consists of four reversible processes:

1 → 2: Isothermal compression

2 → 3: Isochoric heat addition

3 → 4: Isothermal expansion

4 → 1: Isochoric heat rejection

Fifth chapter exercises

Second law of thermodynamics

Exercise 01: Entropy change

I.

Calculate the change in entropy in the following cases:

1- Heating 10 g of an ideal gas from 20 to 100 °C under constant pressure.
2- Heating 10 g of an ideal gas from 20 to 100 °C under constant volume.

Data: $C_p = 29{,}26\ J.Kg^{-1}.K^{-1}$; $C_v = C_p - R$; $R = 8{,}32$ I.S.

II.

2 moles of an ideal gas expand from 30 to 50 liters isothermally and irreversibly.

1- Calculate the change in entropy for this transformation.
2- Calculate the entropy created.
3- Calculate the change in entropy when the expansion is no longer isothermal, and the temperature drops from 300 K to 290 K. *Data*: $C_v = 5\ cal.mole^{-1}.K^{-1}$.

III.

The dissociation reactions of the compounds NO_2 (g) and $CaCO_3$ (s) are given:

$$NO_2\ (g) \rightarrow O_2\ (g) + 1/2\ N_2\ (g)$$
$$CaCO_3\ (s) \rightarrow CO_2\ (g) + CaO\ (s)$$

1- Calculate the standard entropy change at 25°C for the dissociation reaction of NO_2 (g) and $CaCO_3$ (s).
2- Comment the result.

Data:

$\Delta S^\circ_{f,298}\ (NO_2, g) = -14{,}35\ cal.mole^{-1}.K^{-1}$; $S^\circ_{f,298}\ (CO_2, g) = 51{,}1\ cal.mole^{-1}.K^{-1}$;

$S^\circ_{f,298}\ (CaO, s) = 9{,}5\ cal.mole^{-1}.K^{-1}$; $S^\circ_{f,298}\ (CaCO_3, s) = 22{,}2\ cal.mole^{-1}.K^{-1}$.

Exercise 02: Entropy of liquids and solids

I. Entropy of liquids

Two incompressible liquids are brought into contact, L_1 at temperature T_1 and L_2 at temperature T_2 and ($T_1 > T_2$). The two liquids, which have respective heat capacities C_1 and C_2, are isolated from the external environment.

1- Give the expression for the equilibrium temperature Te.

2- Assume the two liquids are identical and $C_1 = C_2 = C$.

   a) Determine the entropy change ΔS_1 of L_1 and ΔS_2 of L_2.

   b) Determine the entropy change of the universe ΔS.

   c) Is the second principle valid?

II. Entropy of solids

A block of iron with mass $m_{Fe} = 50$ g and temperature $T_{Fe} = 400$ K is brought into contact with a block of lead with mass $m_{Pb} = 100$ g and temperature $T_{Pb} = 200$ K, in a rigid enclosure.

1- Establish the equation governing the heat exchange between the two blocks.

2- Deduce the equilibrium temperature of the system.

3- Determine the entropy change of the system, comment.

Data: $C_{Fe} = 447\ J.Kg^{-1}.K^{-1}$; $C_{Pb} = 128\ J.Kg^{-1}.K^{-1}$.

Heat Engines and Cycles

Exercise 03: Heat engine

A heat engine uses one mole of an ideal diatomic gas as its operating fluid. The gas is initially at P = 1.5atm and T = 20°C. The engine performs the following transformations, which form a reversible cycle:

1→2: Adiabatic compression up to a pressure of 20atm.

2→3: Isobaric expansion, which doubles the volume of the gas.

3→4: Isothermal expansion, which returns the gas to its initial volume.

4→1: Isochoric transformation, which returns the gas to its initial pressure.

1- Represent the cycle performed by the engine on the Clapeyron diagram.

2- Calculate the change in internal energy during each transformation.

3- Calculate the efficiency η of the engine. Calculate the number of cycles per minute (N) performed by the machine, given that its power is 73.6 kW.

Data: R = 8,32 I.S.; $\gamma = C_p / C_v$ = 1,4.

Exercise 04: Otto cycle

A quantity of an ideal gas is used to operate a combine harvester. This gas describes the Beau de Rochas cycle, which consists of four transformations (2→3 and 4→1) are adiabatic transformations, and (1→2 and 3→4) are isochoric transformations.

The heat capacity Cv is assumed to be constant throughout the cycle.

1- Express the quantity of heat Q received by the gas during the 1→2 transformation as a function of T_1 and T_2.
2- Determine the work W provided during the cycle as a function of temperature.
3- Determine the cycle efficiency as a function of temperature.
4- Give the expression for the change in entropy for each transformation.

Exercise solutions

Second law of thermodynamics

Exercise 01: Entropy change

I. Calculation of entropy change

1- Entropy change under constant pressure

For an isobaric transformation $\Delta S = \int \frac{dQ_p}{T}$

And $dQ_p = m\ C_p\ dT \Rightarrow \Delta S == \int mC_p \frac{dT}{T} = m\ C_p ln \frac{T_2}{T_1}$

$\Delta S = 10.10^{-3}.29{,}26.\ ln\frac{100}{20} = 0{,}47\ J.K^{-1}$

2- Entropy change under constant volume

For an isochoric transformation $\Delta S = \int \frac{dQ_v}{T}$

And $dQ_v = m\ C_v\ dT \Rightarrow \Delta S = \int mC_v \frac{dT}{T} = m\ C_v ln \frac{T_2}{T_1} = m\ (C_p - R)\ ln \frac{T_2}{T_1}$

$\Delta S = 10.10^{-3}\ (29{,}26 - 8{,}32)\ ln\frac{100}{20} = 0{,}34\ J.K^{-1}$

II. Reversible isothermal transformation

1- The entropy change for a reversible isothermal transformation $dS_{system} = \frac{\delta Q_{syst}}{T}$

We have T = constant $\Rightarrow \Delta U = Q + W = 0 \Rightarrow Q = -W = PdV$.

$\Rightarrow dS = \frac{PdV}{T} = \frac{nRTdV}{TV} = \frac{nRdV}{V}$

So:

a) Entropy of the system: $\Delta S_{system} = nR \int_1^2 \frac{dV}{V} = nRln\frac{V_2}{V_1} = 2{,}2\ ln\frac{50}{30} = 2{,}04\ cal.K^{-1}$

b) Exchanged entropy: $\Delta S_{exchanged} = \frac{Q_{irre}}{T} = \frac{W_{irre}}{T} = P_{final}\frac{\Delta V}{T} = nR\frac{\Delta V}{V_2}$

$$\Delta S_{exchanged} = 2{,}2.\frac{20}{50} = 1.6\ cal.K^{-1}$$

2- Entropy created:

$\Delta S_{created} = \Delta S_{system} - \Delta S_{exchanged} = 2{,}04 - 1{,}6 = 0{,}44\ cal.K^{-1}$

3- Change in entropy when the expansion is no longer isothermal

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

Knowing that: dU = dQ + dW ⇒ dS= $\frac{dU-dW}{T} = n\left(\frac{C_v dT}{T} + \frac{RdV}{V}\right)$

ΔS = $\int_1^2 dS = n\,(C_v\, ln\frac{T_2}{T_1} + Rln\frac{V_2}{V_1})$ = 2 ($5ln\frac{290}{300} + 2ln\frac{50}{30}$) = 1,70 cal.K^{-1}

III. Calculation of the standard entropy change

1- <u>NO_2 (g)</u>

NO_2 (g) → O_2 (g) + 1/2 N_2 (g)

Applying Hess's law: $\Delta S^\circ = \sum S^\circ(products) - \sum S^\circ(reactants)$

$\Delta S^\circ_{r,298} = \Delta S^\circ_{f,298}(O_2, g) + \frac{1}{2}\Delta S^\circ_{f,298}(N_2, g) - \Delta S^\circ_{f,298}(NO_2, g)$

We have $\Delta S^\circ_{f,298}(O_2, g) = \Delta S^\circ_{f,298}(N_2, g) = 0$

So $\Delta S^\circ_{r,298} = -\Delta S^\circ_{f,298}(NO_2, g) = 14{,}35$ cal.mol^{-1}.K^{-1}

2- <u>$CaCO_3$ (s)</u>

$CaCO_3$ (s) → CO_2 (g) + CaO (s)

Hess's law: $\Delta S^\circ = \sum S^\circ(products) - \sum S^\circ(reactants)$

$\Delta S^\circ_{r,298} = S^\circ_{298}(CaO, s) + S^\circ_{298}(CO_2, g) - S^\circ_{298}(CaCO_3, s)$

$\Delta S^\circ_{r,298}$ = 9,5 + 51,1 –22,2 = 38,4 cal.mol^{-1}.K^{-1}

3- According to the results, the entropy change of both reactions are positive, meaning that disorder increases with dissociation.

Exercise 02: Entropy of liquids and solids.

I. Entropy of liquids

1- Equilibrium temperature

Isolated system ⇒ ΔU = 0

L_1 and L_2 are incompressible ⇒ V = constant ⇒ W = 0

There is no exchange of mechanical work between L_1 and L_2, only heat.

$\Delta U = \Delta U_1 + \Delta U_2 = Q_1 + Q_2 = 0$.

At equilibrium: $C_1 (T_e - T_1) + C_2 (T_e - T_2) = 0 \Rightarrow T_e = \frac{C_1T_1 + C_2T_2}{C_1 + C_2}$

2- When the liquids are identical

We have $C_1 = C_2 = C \Rightarrow T_e = \frac{T_1+T_2}{2}$

a) Entropy change ΔS_1 of L_1 and ΔS_2 of L_2:

$\Delta S_1 = \int_{T_1}^{T_e} \frac{\delta Q}{T} = \int_{T_1}^{T_e} \frac{C dT}{T} = C.ln\frac{T_e}{T_1}$

$\Delta S_2 = \int_{T_2}^{T_e} \frac{\delta Q}{T} = \int_{T_2}^{T_e} \frac{C dT}{T} = C.ln\frac{T_e}{T_2}$

b) Entropy change of the universe:

$\Delta S_{univ} = \Delta S_1 + \Delta S_2 = C.ln\frac{T_e}{T_1} + C.ln\frac{T_e}{T_2} = C.ln\frac{{T_e}^2}{T_1.T_2}$

c)

Isolated system, irreversible transformation $\Rightarrow \Delta S > 0$

We have $\Delta S = C.ln\frac{{T_e}^2}{T_1T_2} = \frac{(T_1+T_2)^2}{4T_1T_2} = \frac{(T_1-T_2)^2+4T_1T_2}{4T_1T_2} = 1 + \frac{(T_1-T_2)^2}{4T_1T_2} > 1$

$\Rightarrow \Delta S > 0 \Rightarrow$ the second law is valid.

II. Entropy of solids

1- The equation governing heat exchange between the two blocks:

The system is isolated $\Rightarrow \Delta U = 0$

The blocks are rigid solids $\Rightarrow$ V = constant $\Rightarrow W = 0$

So: $\Delta U = \Delta U_{Fe} + \Delta U_{Pb} = Q_{Fe} + Q_{Pb} = 0$

2- Equilibrium temperature

At equilibrium, we have:

$m_{Fe} C_{Fe}(T_e - T_{Fe}) + m_{Pb} C_{Pb} (T_e - T_{Pb}) = 0 \Rightarrow T_e = \frac{m_{Fe}C_{Fe}T_{Fe}+m_{Pb}C_{Pb}T_{Pb}}{m_{Fe}C_{Fe}+m_{Pb}C_{Pb}}$

$T_e = \frac{50.10^{-3}447.400 + 100.10^{-3}.128.200}{50.10^{-3}.447 + 100.10^{-3}.128} \approx 324K$

3- The entropy change of system

$\Delta S_{system} = \Delta S_{Fe} + \Delta S_{Pb}$

$\Delta S_{Fe} = \int_{T_{Fe}}^{T_e} \frac{\delta Q}{T} = \int_{T_{Fe}}^{T_e} \frac{m_{Fe}C_{Fe}dT}{T} = m_{Fe}C_{Fe}.ln\frac{T_e}{T_{Fe}}$

$\Delta S_{Fe} = 50.10^{-3}.447.ln\frac{324}{400} = -4{,}71$ J.K^{-1}

$\Delta S_{Pb} = \int_{T_{Pb}}^{T_e} \frac{\delta Q}{T} = \int_{T_{Pb}}^{T_e} \frac{m_{Pb}C_{Pb}dT}{T} = m_{Pb}C_{Pb}.ln\frac{T_e}{T_{Pb}}$

$\Delta S_{Pb} = 100.10^{-3}.128.ln\frac{324}{200} = 6{,}18$ J.K^{-1}

$\Delta S_{system} = -4{,}71 + 6{,}18 = 1{,}47$ J.K^{-1}

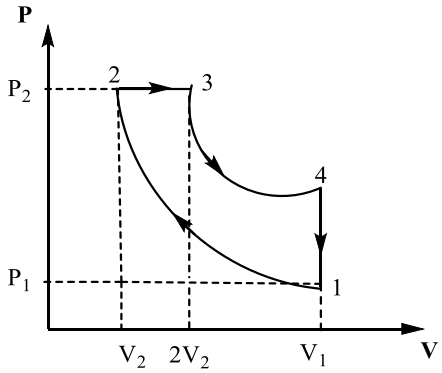
The second principle is verified for this irreversible transformation of an isolated system, because $\Delta S_{sys} > 0$.

Heat engine and cycles

Exercise 03: Heat engine

1- Representation on the Clapeyron diagram (P, V):

The cycle is described in a clockwise direction.



2- Calculation of the change in internal energy:

1→2: Adiabatic compression

Applying Laplace's laws $PV^{\gamma} = constant$ or $TV^{\gamma-1} = constant$

And according to the first law of Joule: $dU = C_v\, dT$.

$\Delta U_{12} = C_v (T_2 - T_1)$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \Rightarrow T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\Delta U_{12} = C_v (T_2 - T_1) = \frac{R}{\gamma-1}T_1\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right]$$

Since $P_1V_1^{\gamma} = P_2V_2^{\gamma} \Rightarrow \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$

So $$\Delta U_{12} = \frac{R}{\gamma-1}T_1\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$$

$$\Delta U_{12} = \frac{8{,}32.293}{0{,}4}\left[\left(\frac{20}{1{,}5}\right)^{\frac{1{,}4-1}{1{,}4}} - 1\right] = 6680\ J$$

2→3: Isobaric expansion

We have $P_2V_2 = RT_2$; $P_3V_3 = RT_3$; $P_2 = P_3$ and $2V_2 = V_3$

$$\Rightarrow \frac{T_3}{T_2} = \frac{V_3}{V_2} = 2 \Rightarrow T_3 = 2T_2$$

Applying the first law of joule

$$\Delta U_{23} = C_v (T_3 - T_2) = \frac{R}{\gamma-1}(2T_2 - T_2) = \frac{RT_2}{\gamma-1}$$

And $$\Delta U_{12} = \frac{R}{\gamma-1}(T_2 - T_1) = \frac{RT2}{\gamma-1} - \frac{RT1}{\gamma-1}) \Rightarrow \frac{RT_2}{\gamma-1} = \Delta U_{12} + \frac{RT1}{\gamma-1} = \Delta U_{23}$$

$\Delta U_{23} = 6680 + \frac{8,32.273}{0,4} = 12774,4$ J

3→4: Isothermal expansion ⇒ $\Delta U_{34} = 0$.

4→1 : Isochoric transformation

$\Delta U_{41} = C_v (T_1 - T_4)$ and $T_4 = T_3 = 2\ T_2$

$\Delta U_{41} = \frac{R}{\gamma-1} (T_1 - 2T_2) = \frac{R}{\gamma-1} T_1 \left(1 - 2\frac{T_2}{T_1}\right)$

And $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$

Thus $\Delta U_{41} = \frac{R}{\gamma-1} T_1 \left(1 - 2\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right)$

$\Delta U_{41} = \frac{8,32.273}{0,4} \left(1 - 2\left(\frac{20}{1,5}\right)^{\frac{1,4-1}{1,4}}\right) = -19453$ J

3- The efficiency η of the machine

The machine is a motor, the efficiency is defined by $\eta = -\frac{W_{cycle}}{Q_c}$

Q_c: the quantity of heat absorbed by the motor ($Q_c > 0$)

- 1→2: adiabatic compression ⇒ $Q_{12} = 0$
- 2→3: Isobaric expansion

$Q_{23} = C_p (T_3 - T_2) = \gamma\ C_v (T_3 - T_2) = \gamma\ \Delta U_{23} = 17884$ J > 0.

- 3→4: Isothermal expansion

$\Delta U_{34} = Q_{34} + W_{34} = 0 \Rightarrow Q_{34} = -W_{34}$

And $W_{34} = \int_{V_3}^{V_4} -PdV = -\int_{V_3}^{V_4} RT_3 \frac{dV}{V} = -RT_3 ln\frac{V_4}{V_3} = -RT_3 ln\frac{V_1}{2V_2} = R2T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} . ln\frac{1}{2}\left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}}$

$-W_{34} = Q_{34} = 2 \times 8,32 \times 293 \times \left(\frac{20}{1,5}\right)^{\frac{1,4-1}{1,4}} . ln\frac{1}{2}\left(\frac{20}{1,5}\right)^{\frac{1}{1,4}} = 11823,93$ J > 0

- 4→1 : Isochoric transformation

V = constant ⇒ $W_{41} = 0 \Rightarrow Q_{41} = \Delta U_{41} = -19453$ J < 0

The absorbed heat is:

$Q_c = Q_{23} + Q_{34} = 17884 + 11823,93 = 29708$ J

The efficiency $\eta = -\frac{W_{cycle}}{Q_c} = -\frac{W_{cycle}}{Q_{23} + Q_{34}}$

Knowing that $W_{cycle} + Q_{23} + Q_{34} + Q_{41} = 0 \Rightarrow W_{cycle} = - Q_{23} - Q_{34} - Q_{41}$

$\Rightarrow \eta = \frac{Q_{23} + Q_{34} + Q_{41}}{Q_{23} + Q_{34}} = \frac{29708 - 19453}{29708} = 0{,}345 = 34{,}5\%$

4- The number of cycles (N) per minute:

The power $P = \frac{|W|}{T} = N \,.\, |W_{cycle}| \Rightarrow N = \frac{P}{|W_{cycle}|}$

$W_{cycle} = - Q_{23} - Q_{34} - Q_{41} = - 17884 - 11823{,}93 + 19453 = - 10255$ J

$\Rightarrow N = \frac{73{,}6 \,.\, 10^{-3}}{10255} = 7{,}17$ *cycle per second (c.p.s)*

N = 7,17. 60 = 431 c.p.m

Exercise 04: Otto cycle

1- The amount of heat received during transformation 1→2 as a function of T_1 and T_2 :

1→2 is an isochoric transformation

If there are n mole of the gas $\Rightarrow Q_{12} = n\, C_v\, (T_2 - T_1)$ and $Q_{12} > 0$

2- W_{Cycle} provided during the cycle as a function of temperatures:

- 1→2 and 3→4 are isochoric transformations

$\Rightarrow$ V = constant $\Rightarrow W_{12} = W_{34} = 0$.

- 2→3 is an adiabatic transformation ($Q_{23} = 0$)

$\Rightarrow W_{23} = \Delta U_{23} = n\, C_v\, (T_3 - T_2)$.

- 4→1 is an adiabatic transformation ($Q_{41} = 0$)

$\Rightarrow W_{41} = \Delta U_{41} = n\, C_v\, (T_1 - T_4)$.

$W_{Cycle} = W_{23} + W_{41} = n\, C_v\, (T_3 - T_2) + n\, C_v\, (T_1 - T_4)$

$W_{Cycle} = n\, C_v\, (T_3 - T_2 + T_1 - T_4)$ and $W_{Cycle} < 0$

3- The efficiency η as a function of temperatures :

$\eta = -\frac{W_{cycle}}{Q_c}$

Q_c: absorbed heat by the cycle $Q_c = Q_{12} > 0$

$W_{Cycle} = n\, C_v\, (T_3 - T_2 + T_1 - T_4)$

Thus: $\eta = -\frac{n\, C_v\, (T_3 - T_2 + T_1 - T_4)}{n\, C_v (T_2 - T_1)} = -\frac{(T_3 - T_2 + T_1 - T_4)}{(T_2 - T_1)} = 1 - \frac{(T_3 - T_4)}{(T_2 - T_1)}$

4- Entropy change for each transformation:

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

- 1→2 : Isochoric transformation: $\Delta S_{12} = nC_v ln\frac{T_2}{T_1}$
- 2→3 : Adiabatic transformation: $\Delta S_{23} = 0$
- 3→4 : Isochoric transformation: $\Delta S_{34} = nC_v ln\frac{T_4}{T_3}$
- 4→1 : Adiabatic transformation: $\Delta S_{41} = 0$

CHAPTER VI : Third Law, Absolute Entropy, Free Energy and Free Enthalpy

1 Third law and absolute entropy

1.1 Third law statements

The Third Law of Thermodynamics is stated as follows:

- At T = 0 K (absolute zero), the entropy of a pure crystal is zero.
- At T = 0 K, every pure substance is in a perfectly crystallized form.

1.2 Standard molar absolute entropy of a pure substance

Every pure substance is assigned an absolute entropy, according to the third law of thermodynamics.

To calculate the standard entropy $S°_{298K}$ of a pure substance, a knowledge of the enthalpy variations, the heat capacities of the different states, and a significant amount of calculation is required.

In fact, there are thermodynamic tables in which the standard entropies of different pure substances are listed, measured in $J.K^{-1}.mole^{-1}$ or $cal.K^{-1}mole^{-1}$.

1.3 Standard molar absolute entropy at T Kelvin

The standard molar absolute entropy of a pure substance at a temperature T is calculated from the standard entropy $S°_{298K}$ according to the following relationship:

- V = constant ⇒ $S°_{TK} = S°_{298K} + \int_{298}^{T} nC_v \frac{dT}{T}$
- P = constant ⇒ $S°_{TK} = S°_{298K} + \int_{298}^{T} nC_p \frac{dT}{T}$

1.4 The entropy change of a chemical reaction

The entropy change that accompanies a chemical reaction at constant pressure and temperature is given as follows:

$$\Delta S^{\circ}_{R} = S_{final} - S_{initial}$$

At temperature T:

$$\Delta S^{\circ}_{T} = \sum S_{T}(products) - \sum S_{T}(reactants)$$

At T = 298 K (standard conditions):

$$\Delta S^{\circ}_{298} = \sum S_{298}(products) - \sum S_{298}(reactants)$$

1.5 The entropy change of a chemical reaction at temperature T

The entropy change of a chemical reaction at a temperature T can be calculated by applying Kirchhoff's law:

- P = constant ⇒ $\Delta S^{\circ}_{T} = \Delta S^{\circ}_{298} + \int_{298}^{T} \Delta n C_p \frac{dT}{T}$

  $\Delta n C_p = \sum nC_p(products) - \sum nC_p(reactants)$

- V = constant ⇒ $\Delta S^{\circ}_{T} = \Delta S^{\circ}_{298} + \int_{298}^{T} \Delta n C_v \frac{dT}{T}$

  $\Delta n C_v = \sum nC_v(products) - \sum nC_v(reactants)$

- It is necessary to consider the entropy created when the system undergoes a change in physical state.

2 Free energy and free enthalpy

2.1 Introduction

For an isolated system, the entropy function allows us to predict the direction of the transformation. However, this is not straightforward for a non-isolated system, and more specifically for chemical reactions, because it is necessary to consider the entropy variations of the system and the external environment.

Two new state functions: free energy (F) and free enthalpy (G), are defined to predict the direction of change in chemical transformations

2.2 Free energy

Free energy represented by (F), also called the Helmholtz function, is a function defined at constant temperature and volume. It allows predicting the direction of change in a transformation.

The free energy is a state function measured in [*J*] or [*Cal*], defined by:

$$\Delta F = U - T\Delta S.$$

ΔU: change in internal energy; ΔS: change in entropy; T: temperature.

- ΔF < 0 ⇒ spontaneous reaction (forward direction).
- ΔF > 0 ⇒ reaction cannot be spontaneous (reverse direction).
- ΔF = 0 ⇒ equilibrium state.

2.3 Free enthalpy

Free enthalpy represented by (G), also called the Gibbs function or thermodynamic potential, is a function defined at constant temperature and pressure to study the spontaneity of chemical reactions and predict their directions.

Free enthalpy is a state function measured in [*J*] or [*Cal*], defined by:

$$\Delta G = \Delta H - T\Delta S.$$

ΔH: change in enthalpy; ΔS: change in entropy; T: temperature.

- ΔG < 0 ⇒ spontaneous reaction (forward direction).
- ΔG > 0 ⇒ reaction cannot be spontaneous (reverse direction).
- ΔG = 0 ⇒ equilibrium state.

2.3.1 Calculation of free enthalpy

The change in free enthalpy that accompanies a chemical reaction can be calculated using the following expression:

At T = 298 K (standard conditions):

$$\Delta G^{\circ}_{298} = \sum \Delta G^{\circ}_{298}(products) - \sum \Delta G^{\circ}_{298}(reactants)$$

At T temperature:

$$\Delta G^{\circ}_{T} = \Delta H^{\circ}_{T} - T\Delta S^{\circ}_{T}$$

ΔH°_{T} *and* ΔS°_{T} are calculated using Kirchhoff's law.

2.4 Chemical equilibriums

2.4.1 Law of mass action, equilibrium constant

The law of mass action, also called equilibrium law or Guldberg-Waage's law, is a law that applies to closed systems at equilibrium.

At equilibrium, ΔG = 0, so the equilibrium law is represented by the relationship:

$$\Delta G = \Delta G^{\circ} + RT\ lnK = 0 \text{ and } K = e^{\frac{-\Delta G^{\circ}}{RT}}$$

K is the equilibrium constant, which depends on temperature and stoichiometric coefficients. The constant K has no dimension or unit.

- For a chemical reaction in equilibrium

$$aA + bB \underset{2}{\overset{1}{\rightleftharpoons}} cC + dD$$

The equilibrium constant: $K = \frac{aC^c.aD^d}{aA^a.aB^b}$

- In a gas phase ($a_i = P_i$) :

The equilibrium constant becomes: $K_p = \frac{PC^c.PD^d}{PA^a.PB^b}$

2.4.2 Van't Hoff relationship

The equilibrium constant K depends on the temperature: $\ln K = \frac{-\Delta G^\circ}{RT}$

- P = constant $\Rightarrow \frac{d(lnK_p)}{dT} = \frac{\Delta H^\circ}{RT^2}$ (isobaric relation of Van't Hoff).
- V = constant $\Rightarrow \frac{d(lnK_p)}{dT} = \frac{\Delta U^\circ}{RT^2}$ (isochoric relation of Van't Hoff).

2.4.3 Displacement Law of Equilibrium

The displacement law of equilibrium, or Le Chatelier's law, states that a change in an equilibrium factor leads to a new equilibrium.

- An increase in pressure pushes the equilibrium toward a decrease in volume, and thus a decrease in the number of moles.
- An increase in temperature pushes the equilibrium toward an endothermic reaction.

2.4.4 A complementary aspect of the study of equilibriums

1) Coefficient or degree of dissociation

The dissociation coefficient (α) describes the state of progress at equilibrium of a single-reactant chemical reaction, defined by the relationship:

$$\alpha = \frac{n_0 - n_t}{n_0} \text{ And } 0 \leq \alpha \leq 1$$

n_0 : Number of initial moles; $n_0 - n_t$: Number of dissociated moles.

2) Progress of a chemical reaction

The progress of a chemical reaction (ζ) is defined by the relationship:

$$\zeta = \frac{n_t - n_0}{\upsilon}$$

n_0 : Number of initial moles; n_t : Number of moles at time T;

υ : Stoichiometric coefficient (for a reaction product $\upsilon > 0$, for a reactant $\upsilon < 0$).

3) Variance of a system in equilibrium

The variance of a system in equilibrium is the number of independent intensive parameters that can be modified without disrupting the equilibrium.

The variance is calculated using Gibbs' theorem (phase rule):

$$\upsilon = C + p - \varphi$$

C: Number of independent components (C = N – R).

N: Number of components; R: Number of relationships between components.

φ: The phase number.

p: Number of intensive parameters.

Sixth chapter exercises

Exercise 01: Absolute entropy

Calculate:

1- The standard molar absolute entropy of water at 25°C.

Data: $S^{\circ}_{273}(H_2O, s)$ = 10,26 cal.mole^{-1}.K^{-1}; $\Delta H^{\circ}_{fusion,273}(H_2O, s)$=1440 cal.mole^{-1}

C_p (H_2O, l) = 11,2 +7,17.10^{-3} T cal.mol^{-1}.K^{-1}.

2- The standard molar entropy of formation of water at 25°C.

Data: $S^{\circ}_{298}(H_2, g)$ = 31,21 cal.mole^{-1}.K^{-1} ; $S^{\circ}_{298}(O_2, g)$ = 49,00 cal.mole^{-1}.K^{-1}.

3- The standard entropy change accompanying the water formation reaction, using absolute standard molar entropies.

$$2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l)$$

Exercise 02: Free enthalpy

Consider the following reaction:

$$2NO\ (g) + 5H_2\ (g) \rightarrow 2NH_3\ (g) + 2H_2O\ (l)$$

1- Calculate the free energy at 25°C.
2- Calculate the free energy of this reaction at 200°C.
3- Discuss the spontaneity of the reaction.

Data:

$\Delta G^{\circ}_{f,298}(NO, g)$ = 50,33 cal.mole^{-1}; $\Delta G^{\circ}_{f,298}(NH_3, g)$ = -3,99 cal.mole^{-1}; $\Delta G^{\circ}_{f,298}(H_2O, l)$ = -56,70 cal.mole^{-1}; $\Delta H^{\circ}_{f,298}(NO, g)$ = 20,69 cal.mole^{-1}; $\Delta H^{\circ}_{f,298}(NH_3, g)$ = -11,04 cal.mole^{-1}; $\Delta H^{\circ}_{f,298}(H_2O, l)$ = - 68,31 cal.mole^{-1};

$S^{\circ}_{298}(NH_3, g)$ = 46,04 cal.mole^{-1}.K^{-1}; $S^{\circ}_{298}(H_2O, l)$ = 16,75 cal.mole^{-1}.K^{-1};

S°_{298} (NO, g) = 21,47 cal.mole^{-1}.K^{-1}; $S^{\circ}_{298}(H_2, g)$ = 31,21cal.mole^{-1}.K^{-1};

C_p (NH_3, g) = 8,50 cal.mole^{-1}.K^{-1}; C_p (H_2O, g) = 17,99 cal.mole^{-1}.K^{-1};

C_p (NO, g) = 7,14 cal.mole^{-1}.K^{-1}; C_p (H_2, g) = 6,89 cal.mole^{-1}.K^{-1}.

Chemical equilibrium

Exercise 03: Equilibrium displacement

Consider the following equilibriums

1- CO_2 (g) + H_2 (g) <=> H_2O (l) + CO (g) ; $\Delta H^\circ = -0{,}68$ kcal

2- Fe_3O_4 (s) + 4C (s) <=> 3Fe (s) + 4CO (g) ; $\Delta H^\circ = 161{,}36$ kcal

3- SO_2 (g) +1/2 O_2 (g) <=> SO_3 (g) ; $\Delta H^\circ = -23{,}49$ kcal

4- N_2 (g) + O_2 (g) <=> 2NO (g) ; $\Delta H^\circ = 43{,}20$ kcal

Predict:

a) The effect of an increase in temperature.

b) The effect of an increase in pressure.

Exercise 04: Equilibrium constant

1.15 g of N_2O4 (s) are introduced into a container at a temperature of 25°C. The compound vaporizes completely and dissociates partially according to the reaction:

$$N_2O_4\ (g) \rightarrow 2NO_2\ (g)$$

At equilibrium, the total pressure is 0.4 atm.

1- Calculate the degree of dissociation α.

2- Deduce the number of moles of the two gases in the mixture at equilibrium.

3- Calculate the equilibrium constant Kp.

4- Calculate the standard molar free energy of formation of N_2O_4 (g). Knowing that $\Delta G^\circ_{f,298}\ (NO_2, g)$ = 52,3 KJ.mole^{-1}

Data: R = 8,31 I.S; M(N) = 14 g.mole^{-1} ; M(O) = 16 g.mole^{-1}.

Exercise 05: System variance

The constant Kp relative to the following equilibrium is equal to $3{,}14.10^{-4}$ at a temperature of 900 K and $3{,}52.10^{-3}$ at a temperature of 1000 K:

$$2\ SO_3\ (g) <=> O_2\ (g) + 2\ SO_2\ (g)$$

1- Calculate the system variance.

2- Is the reaction exothermic or endothermic in this temperature range?

3- Assume that the reaction remains constant in this temperature range; calculate the enthalpy change $\Delta H°_T$.

Exercise solutions

Exercise 01: Absolute entropy

1- Standard molar absolute entropy of water at 25°C:

H_2O (s) → H_2O (l) → H_2O (l)

273K 273K 298K

$S^\circ_{298}(H_2O, l) = S^\circ_{273}(H_2O, s) + \Delta S^\circ_{(fusion)} + \Delta S^\circ_{(heating)}$

$S^\circ_{298}(H_2O, l) = S^\circ_{273}(H_2O, s) + \frac{\Delta H^\circ_{fusion,273}}{T_{fusion}} + \int_{273}^{298} nC_p(H_2O, l)\frac{dT}{T}$

$S^\circ_{298}(H_2O, l) = 10{,}28 + (1440/273) + 11{,}2 \ln(298/273) + 7{,}17.10^{-3}(298-273)$

$S^\circ_{298}(H_2O, l) = 16{,}71$ cal.mole^{-1}.K^{-1}

2- Standard molar entropy of water formation at 25°C:

H_2 (g) → $\frac{1}{2}$ O_2 (g) → H_2O (l)

$\Delta S^\circ_{f,298}(H_2O, l) = S^\circ_{298}(H_2O, l) - S^\circ_{298}(H_2, g) - 1/2\ S^\circ_{298}(O_2, g)$

$\Delta S^\circ_{f,298}(H_2O, l) = 16{,}17 - 31{,}21 - 1/2\ (49{,}00)$

$\Delta S^\circ_{f,298}(H_2O, l) = -\ 39{,}00$ cal.mole^{-1}.K^{-1}

3- Standard entropy change using the absolute standard molar entropies:

$2H_2$ (g) + O_2 (g) → $2H_2O$ (l)

$\Delta S^\circ_{r,298} = 2\ S^\circ_{298}(H_2O, l) - 2\ S^\circ_{298}(H_2, g) - S^\circ_{298}(O_2, g)$

$\Delta S^\circ_{r,298} = 2.(16{,}71) - 2\ (31{,}21) - 49{,}00 = -\ 78$ cal.mole^{-1}.K^{-1}

Exercise 02: Free enthalpy

$2NO$ (g) + $5H_2$ (g) → $2NH_3$ (g) + $2H_2O$ (l)

1- Free enthalpy at 25°C :

$\Delta G^\circ_{r,298} = \sum \Delta G^\circ_{298}(products) - \sum \Delta G^\circ_{298}(reactants)$

$\Delta G^\circ_{r,298} = 2\ \Delta G^\circ_{f,298}(H_2O, l) + 2\ \Delta G^\circ_{f,298}(NH_3, g) - 2\ \Delta G^\circ_{f,298}(NO, g)$

$\Delta G^\circ_{r,298} = 2\ (-56{,}70) + 2\ (-3{,}99) - 2\ (50{,}33)$

$\Delta G^\circ_{r,298} = -\ 222{,}04$ Cal

2- Free enthalpy at 200°C :

To calculate the free enthalpy at 498K we apply the following relationship:

$$\Delta G^{\circ}_{r,498} = \Delta G^{\circ}_{298} - \int \Delta S^{\circ}_{498} dT$$

- The entropy change at 498K

$\Delta S^{\circ}_{498} = \Delta S^{\circ}_{298} + \int_{298}^{498} \Delta C_p \frac{dT}{T} = \Delta S^{\circ}_{298} - \Delta C_p ln \frac{T_1}{T_2}$

And $\Delta S^{\circ}_{298} = \sum \Delta S^{\circ}(products) - \sum \Delta S^{\circ}(reactants)$

ΔS°_{298} = 2 S°_{298} (H_2O, l) + 2 S°_{298} (NH_3, g) – 2 S°_{298} (NO, g) – 5 S°_{298} (H_2, g)

ΔS°_{298} = 2 (16,75) + 2 (46,04) – 2 (21,47) – 5 (31,21)

ΔS°_{298} = - 73,41 cal.K^{-1}

- Calculation of ΔC_p

$\Delta C_p = \sum \Delta C_p(products) - \sum \Delta C_p(reactants)$

ΔC_p= 2 C_p (H_2O, g) + 2 C_p (NH_3, g) – 2 C_p (NO, g) - 5 C_p (H_2, g)

ΔC_p= 2 (17,99) + 2 (8,50) – 2 (7,14) – 5 (6,89)

ΔC_p= 4,25 cal.K^{-1}

$\Rightarrow \Delta S^{\circ}_{498} = \Delta S^{\circ}_{298} - \Delta C_p ln \frac{T_1}{T_2}$

ΔS°_{498} = -73,41 – 4,25 ln $\frac{298}{498}$ = -71,22 cal.K^{-1}

$\Rightarrow \Delta G^{\circ}_{r,498} = \Delta G^{\circ}_{298} - \int \Delta S^{\circ}_{498} dT$

$\Delta G^{\circ}_{r,498}$ = - 222,04 – (-71,22) (498-298)

$\Delta G^{\circ}_{r,498}$ = 140,21 Cal

3- Spontaneity of the reaction:

At 298, $\Delta G^{\circ}_{r,298} < 0 \Rightarrow$ the reaction is spontaneous

At 498, $\Delta G^{\circ}_{r,498} > 0 \Rightarrow$ the reaction is not spontaneous

Chemical equilibrium

Exercise 03: Equilibrium displacement

Knowing that:

a) An increase in temperature shifts the equilibrium toward the endothermic reaction.

b) An increase in pressure shifts the equilibrium toward the direction where the number of moles decreases

1- CO_2 (g) + H_2 (g) <=> H_2O (l) + CO (g) ; $\Delta H^\circ = -0{,}68$ kcal

$$\Delta H^\circ < 0$$

If the temperature increases, the equilibrium shifts in the reverse direction.

If the pressure increases, the equilibrium shifts in the direct direction.

2- Fe_3O_4 (s) + 4C (s) <=> 3Fe (s) + 4CO (g) ; $\Delta H^\circ = 161{,}36$ kcal

$$\Delta H^\circ > 0$$

Unlike the first equilibrium:

If the temperature increases, the equilibrium shifts in the direct direction.

If the pressure increases, the equilibrium shifts in the reverse direction.

3- SO_2 (g) +1/2 O_2 (g) <=> SO_3 (g) ; $\Delta H^\circ = -23{,}49$ kcal

$$\Delta H^\circ < 0$$

By increasing the temperature, the equilibrium shifts in the reverse direction (2).

By increasing the pressure, the equilibrium shifts in the direct direction, direction (1).

4- N_2 (g) + O_2 (g) <=> 2NO (g) ; $\Delta H^\circ = 43{,}20$ kcal

$$\Delta H^\circ > 0 \text{ and } \Delta n \text{ (gaz)} = 0$$

If the temperature increases, the equilibrium shifts in the direct direction.

If the pressure increases, the equilibrium does not change; pressure is no longer a factor in the equilibrium, because Δn (gas) = 0.

Exercise 04: Equilibrium constant

1- The degree of dissociation α:

We have	N_2O_4 (g)	→	$2NO_2$ (g)
At T = 0	n_0		0
At equilibrium	n_0 (1-α)		2 $n_0\alpha$

Knowing that: $\sum n_i = n_0 (1+\alpha)$ and n = m/M

$\sum n_i = n_0 (1+\alpha) = \frac{PV}{RT} \Rightarrow (1+\alpha) = \frac{PV}{RTn_0}$

Thus $\alpha = \frac{PV}{RTn_0} - 1$

$\alpha = \frac{0,4.1}{0,082.298.1,25.10^{-2}} - 1 = 0,31$

2- The number of moles at equilibrium::

- N_2O_4 (g):

n (N_2O_4, g) = n_0 (1 - α)

n (N_2O_4, g) = $8,63.10^{-3}$ moles

- NO_2 (g) :

n (NO_2, g) = 2 $n_0\alpha$

n (NO_2, g) = $7,7.10^{-3}$ moles

3- Equilibrium constant Kp:

$K_P = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{4\alpha^2}{1-\alpha^2} P_t$

$K_p = \frac{4(0,31)^2}{1-(0,31)^2} \times 0,4 = 0,168$atm

4- The standard molar free enthalpy of formation of N_2O_4 (g):

$\Delta G^\circ_{298} = \sum \Delta G^\circ_{298}(products) - \sum \Delta G^\circ_{298}(reactants)$

$\Delta G^\circ_{298} = 2\,\Delta G^\circ_{f,298}(NO_2, g) - \Delta G^\circ_{f,298}(N_2O_4, g)$

$\Rightarrow \Delta G^\circ_{f,298}(N_2O_4, g) = 2\,\Delta G^\circ_{f,298}(NO_2, g) - \Delta G^\circ_{298}$

At equilibrium $\Delta G_T = \Delta G^\circ_{298} + RT\ ln\ K_p = 0$

Thus $\Delta G^\circ_{298} = -RT\ ln\ K_p$ = - 8,2.298 ln (0,168)

ΔG°_{298} = 4417,34 J

$\Rightarrow \Delta G^\circ_{f,298}(N_2O_4, g) =$ (2.52,3) - 4,417 = 100,18 kJ.mole^{-1}

Exercise 05: System variance

1- System variance:

$$2\ SO_3\ (g) <=> O_2\ (g) + 2\ SO_2\ (g)$$

Applying Gibbs's theorem:

$$\upsilon = C + p - \varphi$$

C: number of independent components and C = N – R

N: number of components; for this equilibrium, N = 3.

R: number of relationships between components; in this case, R = 1.

φ: number of phases; for this single-phase equilibrium, φ = 1.

p: number of intensive parameters; p = 2 (pressure and temperature).

Thus $\upsilon = N - R + p - \varphi$

υ = 3 -1 + 2 -1 = 3; the system is trivariant.

2- Reaction nature:

According to Le Chatelier's law, increasing temperature drives the equilibrium toward the direction where the reaction is endothermic.

Kp = 3,14.10^{-4} at T = 900 °C

Kp = 3,52.10^{-3} at T = 1000 °C

The equilibrium constant Kp increases as the temperature increases, meaning that the equilibrium shifts toward direction 1.

- ✓ Therefore, the reaction is endothermic in direction 1.

3- Change in enthalpy $\Delta H°_T$:

In this temperature range [900°C - 1000°C], $\Delta H°_T$ is constant.

According to Van't Hoff relationship:

$$\frac{d(lnK_p)}{dT} = \frac{\Delta H^\circ_T}{RT^2}$$

$$lnK_{p_{T_2}} = lnK_{p_{T_1}} + \frac{\Delta H^\circ_T}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$lnK_{p_{T_2}} = lnK_{p_{T_1}} + \frac{\Delta H^\circ_T}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\Delta H^\circ_T = \left(\frac{T_1 T_2}{T_1 - T_2}\right) R ln \frac{K_{p_2}}{K_{p_1}}$$

ΔH°_T = 72,17 kcal

Bibliography

[1] : BRUNET Éric, HOCQUET Thierry, LEYRONAS Xavier, *Thermodynamics Course,* Science Sorbonne university, 2019.

[2] : FOUSSARD Jean-Noël, JULIEN Edmond, MATHE Stéphane, DEBELLEFONTAINE Hubert, *The base of thermodynamics, Course and exercise with solutions,* Paris : Dunod, 2015.

[3] : OUARGLI-SAKER Rachida, *Thermodynamics Course*, university of science and technology of Oran Mohamed BOUDIAF, 2015-2016.

[4] : CHABANE Mustapha, *Fundamental Notions in Thermodynamics,* university center Salhi Ahmed of Naama, 2016-2017.

[5] : *Thermodynamics Bases,* SM3004, course, Bordeaux 1 university, Science Technology.

[6] : BERTIN Michel, FAROUX Jean-Pierre, RENAULT Jacques, *Thermodynamics physics Course*, Dunod university.

[7] : PERROT Olivier, *Thermodynamics Course,* Saint-Omer Dunkerque, 2010-2011.

[8] : NABIH Khadija, RHALIB KNIAZEVA Albina, CHERKAOUI EL MOURSLI Fouzia, *Exercises and Problems with solutions of Chemical Thermodynamics,* Mohammed V de Rabat university.