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Course handout in Thermodynamics

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Preface

Thermodynamics is a fundamental branch of physical chemical sciences that provides the essential framework for understanding energy, matter, and the laws governing their interactions. Its principles extend far beyond the study of heat and temperature, offering powerful tools for interpreting natural phenomena, explaining chemical and physical transformations, and designing efficient technological systems.

This course handout has been designed to introduce students to the core concepts of thermodynamics in a structured and progressive manner. It aims to build a strong foundation by combining theoretical principles with practical applications, preparing students for advanced studies in chemistry, physics, and engineering.

- **Chapter I** establishes the general concepts of thermodynamics, beginning with definitions of systems and state functions, the distinction between intensive and extensive properties, and the behavior of gases. The study of both ideal and real gases is included, along with fundamental notions of energy exchanges, heat transfer, and mechanical work.
- **Chapter II** presents the First Law of Thermodynamics, focusing on internal energy and enthalpy. The chapter highlights energy conservation, transformations at constant volume and pressure, and applications to ideal gases through different thermodynamic processes.
- **Chapter III** explores the Second Law of Thermodynamics, introducing entropy as a central concept. It discusses reversible and irreversible transformations, entropy variations in ideal gases, and the significance of the Carnot cycle. The chapter also integrates statistical perspectives, linking entropy with disorder and introducing the Third Law of Thermodynamics.
- **Chapter IV** applies the first two laws to chemical reactions and thermochemistry, covering reaction heats, standard enthalpies of formation, calorimetric methods, Hess's law, and Kirchhoff's relation. It also examines bond energies and their role in determining reaction enthalpies.
- **Chapter V** addresses the concepts of free enthalpy and free energy, essential for predicting the spontaneity of chemical and physical processes. It introduces Gibbs and Helmholtz functions, as well as their applications to pure substances and mixtures through the notion of chemical potential.

Through this course handout, the student will develop not only a theoretical understanding of thermodynamics but also an ability to apply its principles to practical problems in science and engineering. The material is presented with clarity and coherence, encouraging both comprehension and critical thinking.

It is hoped that this work will serve as a reliable guide and reference, fostering curiosity, rigor, and appreciation for the unifying power of thermodynamics in explaining the behavior of matter and energy.

Symbols and abbreviations

- c: Specific heat
- Cp: Specific heat at constant-pressure
- Cv: Specific heat at constant-volume
- Δ : Change in a quantity
- η: Efficiency
- F: Helmholtz free energy
- f : Formation
- fus: Fusion
- G: Gibbs free energy
- g : Gas phase
- γ: (gamma): Heat capacity ratio (Cp/Cv)
- H: Enthalpy
- k: Boltzmann constant
- l : Liquid phase
- M : Molar mass
- m: Mass
- μ: Chemical potential
- n: Number of moles
- P: Pressure
- Q: Heat
- ρ: Density
- R: Ideal gas constant
- S: Entropy
- s :Solid phase
- sub : Sublimation
- $\sum$: Summation
- T: Thermodynamic temperature
- U: Internal energy
- V: Volume
- vap : Vaporization
- W: Work
- x: mole fraction

CHAPTER I
General Concepts in Thermodynamics

CHAPTER II
The First Law of Thermodynamics

CHAPTER III
The Second Law of Thermodynamics

CHAPTER IV
Application of the First and Second Laws to Chemical Reactions – Thermochemistry

CHAPTER V
Free Enthalpy – Free Energy

CHAPTER I

General Concepts in Thermodynamics

I.1.Introduction to thermodynamics

Thermodynamics is the branch of science that studies the relationships between heat, work, energy, and matter. It provides fundamental principles governing energy transfer and conversion in physical and chemical systems. Based on key laws, thermodynamics explains how energy flows and transforms, influencing everything from engines and refrigeration to biological processes. The field is built on concepts such as systems, state variables, and equilibrium, with applications spanning engineering, chemistry, and environmental sciences. Understanding thermodynamics is essential for optimizing energy efficiency and designing sustainable technologies.

I.1.a) Definitions

A thermodynamic system is a specific region in space, real or conceptual, chosen for analysis where energy and matter interactions are studied. Everything outside this system is considered the surroundings, and the boundary between them is called the system boundary. These terms are illustrated in Figure.1. The boundary of a system can be fixed or movable. Note that the boundary is the contact surface shared by both the system and the surroundings.

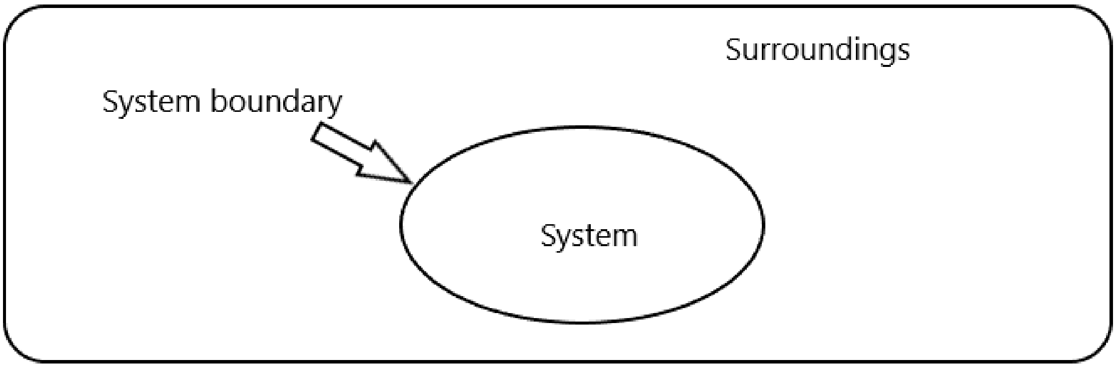


Figure I.1. System, surroundings, and boundary

The system is whatever we want to study. It may be as simple as a free body or as complex as an entire chemical refinery. Systems can be studied from a macroscopic or a microscopic point of view. The macroscopic approach to thermodynamics is concerned with the gross or overall behavior. This is sometimes called classical thermodynamics. No model of the structure of matter at the molecular, atomic, and subatomic levels is directly used in classical thermodynamics. Although the behavior of systems is affected by molecular structure, classical thermodynamics allows important aspects of system behavior to be evaluated from observations of the overall system. The microscopic approach to thermodynamics, known as statistical thermodynamics, is concerned directly with the structure of matter. The objective of statistical thermodynamics is to characterize by statistical means the average behavior of the particles making up a system of interest and relate this information to the observed macroscopic behavior of the system.

Thermodynamic systems are classified into three main types:

I.1.a.1) Open system:

Exchanges both energy and matter with its surroundings (e.g., hot water).

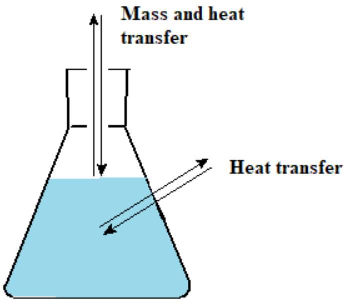


Figure I.2.Hot water in open Erlenmeyer flask

I.1.a.2) Closed system :

Exchanges only energy but not matter with its surroundings (e.g., a sealed, heated container).

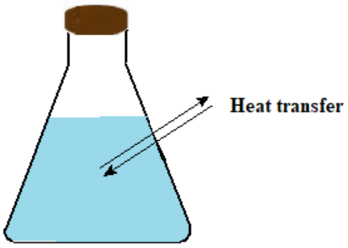


Figure I.3.Hot water in closed Erlenmeyer flask

I.1.a.3) Isolated system:

Does not exchange either energy or matter with its surroundings (e.g., an ideal thermos)

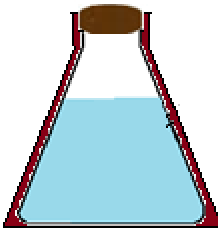


Figure I.4.Hot water in isolated Erlenmeyer flask

I.1.a.4) Thermoelastic systems:

Elasticity, ability of a deformed material body to return to its original shape and size when the forces causing the deformation are removed.

Application 1:

For each of the systems defined below, specify whether it is a closed or open system.

1. The solid material of a burning candle.
2. A running internal combustion engine.
3. An alarm clock that is ringing.
4. Liquid water boiling in a saucepan.
5. The air contained in a sealed inner tube.

Solution: Careful attention must be paid to the definition of the system being considered.

1. ***Open***, because solid material is consumed and released to the surroundings.
2. ***Open***, because air and fuel enter, and burned gases are expelled.
3. ***Closed***, because there is no exchange of matter with the outside.
4. ***Open***, because water changes into vapor and leaves the system.
5. ***Closed***, because the inner tube is sealed.

I.1.a.5) State variables and state functions

State variables (or state properties) are quantities that describe the state of a thermodynamic system at a given moment, regardless of the path taken to reach that state. These variables depend only on the current condition of the system and not on the process it underwent.

It is very useful to classify them and to have at least an approximate understanding of their physical meaning. Somewhat arbitrarily, we will reserve the term *state variable* for physical quantities that can be measured relatively easily using instruments. Below are the main ones, while acknowledging from the outset that their introduction is more subtle than it may first appear.

- ***Volume***: This is a geometric concept; it represents the measure of the Euclidean space occupied by the system under study.

- ***Amount of substance***: This measures the number of particles contained in the system. Chemists use the mole as the unit (1 mol contains 6.02×10^{23} particles). If the system consists of several chemical species, the amount of substance of each species must be specified.
- ***Pressure***: This quantity is essential for describing possible energy exchanges between subsystems, such as between the surface of a solid and a fluid (liquid or gas).
- ***Temperature***: For now, we will adopt a relatively intuitive approach, recognizing it as a property that defines a common equilibrium value when two subsystems are in contact and in thermal equilibrium.

State functions are mathematical expressions that relate state variables to each other. They are properties that depend only on the initial and final states of the system, not on the process or path taken to reach them.

Examples of state functions:

Internal Energy (U), Enthalpy (H), Gibbs Free Energy (G), Entropy (S) and free energy (F)

Since state functions depend only on the state of the system, their differentials are exact differentials, meaning that changes in these properties are independent of the process taken. For example, if a system goes from state A to state B, the change in internal energy $\Delta U = U_B - U_A$ remains the same regardless of how the transition occurred.

The differential of a state function, which depends on several independent variables, is an exact total differential. This means that it can be expressed as the sum of its partial derivatives with respect to each variable. For example, for a function of two variables denoted: *F(x,y).*

$$dF = \left(\frac{\partial F}{\partial x}\right)dx + \left(\frac{\partial F}{\partial y}\right)dy \qquad \text{(I.1)}$$

$\left(\frac{\partial F}{\partial x}\right)$: is the partial derivative of F with respect to xxx, and similarly for y.

For an ideal gas whose state is defined by its temperature T and pressure P, the pressure or temperature is varied from initial values T_i and P_i to final values T_f and P_f. The amount of substance is considered constant. The ideal gas equation provides an explicit expression of the volume as a function of these two parameters:

$$V(T,P) = \frac{nRT}{P} \qquad \text{(I.2)}$$

The volume thus appears as a state function. From this expression, one can calculate the change in the gas volume during the transformation from the initial state to the final state.

For a small infinitesimal variation of pressure and temperature, we can write:

$$dV = \left(\frac{\partial V}{\partial T}\right)dT + \left(\frac{\partial V}{\partial P}\right)dP \Rightarrow dV = \left(\frac{nR}{P}\right)dT + \left(\frac{nRT}{P^2}\right)dP \qquad (I.3)$$

For the differential form dV of the function V(T, P) to be an exact differential, the order of differentiation of V with respect to T and P must be interchangeable; in other words, the mixed second derivatives must be equal, which is indeed the case.

$$\left(\frac{\partial^2 V}{\partial T \partial P}\right) = \left(\frac{\partial^2 V}{\partial P \partial T}\right) = -\frac{nR}{P^2} \qquad (I.4)$$

Non-state functions depend on the path taken to reach a specific state.

Examples include: Work (W) and Heat **(Q)**

These are described by inexact differentials (e.g., δW and δQ).

- The notation d is reserved for the differential of a state function. dX represents the infinitesimal variation of a quantity X that is a state function;
- The notation ∂/∂x is reserved for the partial derivative of the state function with respect to the variable **x**.

I.1.a.6) Intensive and extensive properties

Thermodynamic properties can be placed in two general classes: extensive and intensive. A property is called extensive if its value for an overall system is the sum of its values for the parts into which the system is divided. Mass, volume, energy, and several other properties introduced later are extensive. Extensive properties depend on the size or extent of a system. The extensive properties of a system can change with time, and many thermodynamic analyses consist mainly of carefully accounting for changes in extensive properties such as mass and energy as a system interacts with its surroundings. Intensive properties are not additive in the sense previously considered. Their values are independent of the size or extent of a system and may vary from place to place within the system at any moment. Thus, intensive properties may be functions of both position and time, whereas extensive properties vary at most with time. Specific volume, pressure, and temperature are important intensive properties; several other intensive properties are introduced in subsequent chapters. An easy way to determine whether a property is intensive or extensive is to divide the system into two equal parts with an imaginary partition, as shown in Figure I.5. Each part will have the same value of intensive properties as the original system, but half the value of the extensive properties.

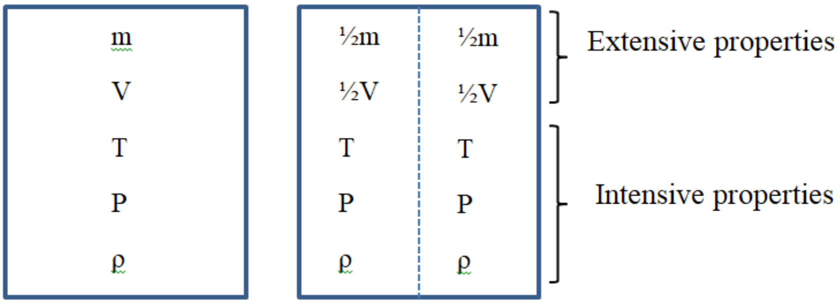


Figure I.5.intensive and extensive properties.

An intensive property is obtained by dividing one extensive property by another. In other words, while extensive properties depend on the size or amount of matter in the system (such as mass, volume, or energy), intensive properties remain independent of the system's size.

For example:

Molar volume (Vm) is defined as the ratio of the total volume (V, an extensive property) to the number of moles (n, also extensive):

$$V_m = \frac{V}{n} \qquad \text{(I.5)}$$

Density (ρ) is defined as the ratio of mass (m, extensive) to volume (V, extensive):

$$\rho = \frac{m}{V} \qquad \text{(I.6)}$$

I.1.a.7) State and thermodynamic equilibrium

Consider a system not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition, or the state, of the system. At a given state, all the properties of a system have fixed values. If the value of even one property changes, the state will change to a different one (Figure I.6).

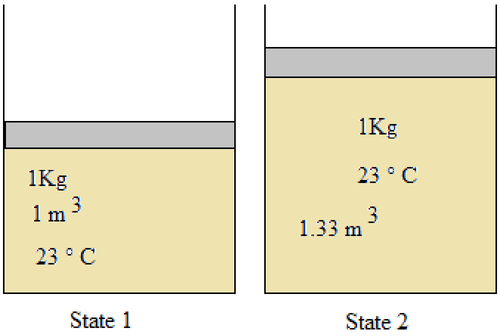


Figure I.6. A system in two distinct states

The equilibrium state of a system is a condition in which all state variables remain constant. In this state, there is no exchange of energy or matter with the surroundings. The system does not change over time, and its temperature remains constant. When an external influence is applied to the system to induce a change, the transition from one equilibrium state to another is referred to as a shift in equilibrium.

- **Thermodynamic equilibrium** is a fundamental concept in thermodynamics that describes a state in which a system is in complete balance, with no net flow of matter or energy within the system or between the system and its surroundings. In this state, all macroscopic properties of the system (such as temperature, pressure, and chemical composition) are uniform and do not change over time.
- **Types of thermodynamic equilibrium**

Thermal equilibrium: Achieved when the temperature is uniform throughout the system.

Mechanical equilibrium: Achieved when the pressure is uniform throughout the system, and there are no unbalanced forces.

Chemical equilibrium: Achieved when the chemical potentials of all components are equal, and there is no net chemical reaction.

Phase equilibrium: Achieved when multiple phases (e.g., solid, liquid, gas) coexist in a system without any net transfer of matter between them.

In non-equilibrium states, there are gradients in temperature, pressure, or chemical potential, leading to flows of heat, matter, or chemical reactions. These states are common in real-world processes, but they eventually tend toward equilibrium if isolated from external influences.

I.1.a.8) Reversible and irreversible transformations

A reversible process is an idealized thermodynamic process that occurs infinitely slowly and remains in thermodynamic equilibrium at every stage. It can be reversed without leaving any trace or change in the surroundings. This is an idealized case that can only be approximated in practice. It assumes an infinitely slow evolution, also called a quasi-static process, where the system passes through a continuous sequence of equilibrium states.

Examples:

- ✓ Isothermal expansion of an ideal gas in a perfectly controlled manner.
- ✓ Slow compression of a gas in a piston with negligible friction.
- ✓ Carnot cycle**,** an ideal thermodynamic cycle composed of reversible processes.

An **irreversible process** in thermodynamics is a process that cannot be reversed to restore both the system and its surroundings to their original states. In other words, once an irreversible process occurs, there is no way to completely undo the changes made to the system and the environment without leaving some net effect. In another words it is a spontaneous process that cannot be stopped or directly reversed. In fact, from a thermodynamic perspective, all real transformations are irreversible. It is worth noting that once such a transformation has occurred, it can still be reversed by altering the experimental conditions. However, the return to the initial state does not follow the same intermediate states as those encountered during the forward transformation.

Key characteristics of irreversible processes:

Energy dissipation: Irreversible processes often involve energy dissipation in the form of heat, friction, or other non-conservative forces, which cannot be fully recovered.

Entropy increase: The total entropy of the system and its surroundings increases during an irreversible process. This is a consequence of the second law of thermodynamics.

Non-equilibrium states: Irreversible processes typically occur when a system is far from thermodynamic equilibrium, and the process involves finite differences in temperature, pressure, or other driving forces.

Real-world processes: In thermodynamics, most processes occurring in nature are irreversible. This means they cannot spontaneously return to their initial state without external intervention. Several examples illustrate this principle:

- **Heat transfer**: Energy naturally flows from a hot object to a cold one, but the reverse does not occur spontaneously.
- **Diffusion**: Particles of a substance spread out to occupy available space, and they do not spontaneously regroup into their original region.
- **Gas expansion into a vacuum**: When a gas expands freely into an empty space, it cannot return to its original volume without external work.
- **Combustion reactions**: The burning of fuel in engines is an irreversible process, as the products of combustion cannot spontaneously revert to the original fuel and oxygen.
- **Mixing of substances**: When two different gases or liquids are mixed, they form a homogeneous mixture that cannot spontaneously separate into the original components.

I.1.b) Behavior of gases at low pressures

I.1.b.1) Clapeyron diagram

Process diagrams plotted by employing thermodynamic properties as coordinates are very useful in visualizing the processes. Some common properties that are used as coordinates are temperature T, pressure P, and volume V (or specific volume v). To represent multiple equilibrium states of a thermodynamic system, one of the most accessible graphical tools is the pressure-volume (P-V) diagram, where pressure (P) is plotted as a function of volume (V). This type of graph is commonly referred to as the Clapeyron diagram. A PV diagram is drawn for a thermodynamic process occurring in a closed system. Figure I.7 presents the P-V diagram depicting various processes that can occur in a gas. Note that the process path indicates a series of equilibrium states through which the system passes during a process and has significance for quasiequilibrium processes only. An isothermal process, for example, is a process during which the temperature T remains constant; an isobaric process is a process during which the pressure P remains constant; and an isochoric (or isometric) process is a process during which the specific volume v remains constant, an adiabatic process is a process during which no heat flows in and out of the system. A system is said to have undergone a cycle if it returns to its initial state at the end of the process. That is, for a cycle the initial and final states are identical.

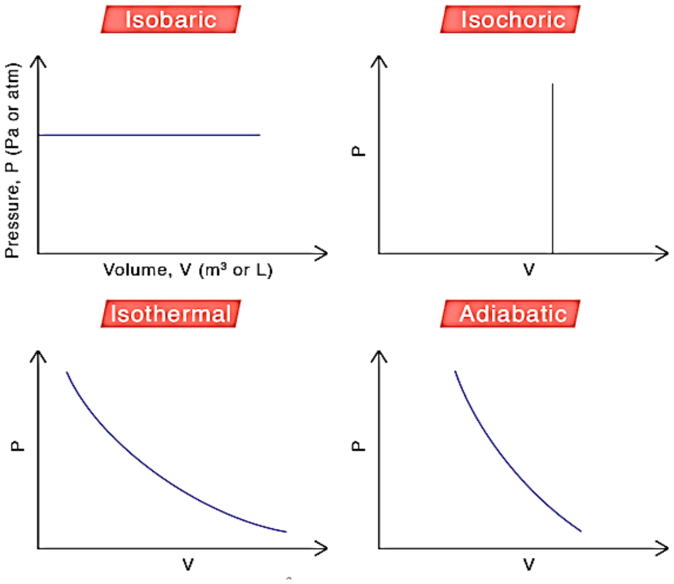


Figure I.7.P-V diagrams

Multiple thermodynamic processes can be integrated into a cycle (Figure I.8).

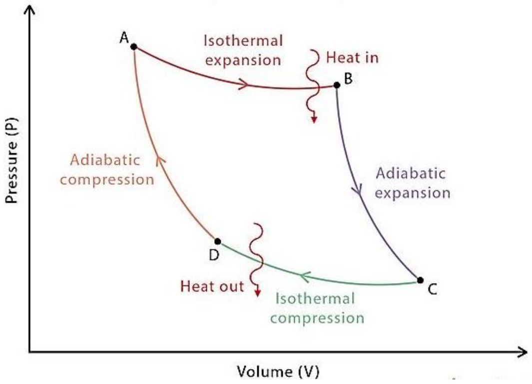


Figure I.8. Combination of multiple thermodynamic processes

I.1.b.2) Variation of Amagat's coordinates as a function of pressure

An ideal gas consists of tiny particles in random motion that undergo elastic collisions. While no gas is truly ideal, real gases can exhibit ideal behavior under specific conditions. An ideal gas follows the equation PV = nRT at all pressures and temperatures, assuming its molecules are point-like with no volume and no intermolecular forces. In contrast, real gases deviate from ideal behavior due to molecular interactions and finite volume. As pressure increases, volume decreases, but it never reaches zero because gas molecules occupy space that cannot be further compressed. All gases exhibit some degree of deviation from ideality, especially at high pressures and low temperatures. Certain gases, such as H_2, N_2,O_2 and CO_2, do not strictly obey the ideal gas law. In the 19th century, Amagat demonstrated that the product of pressure and volume (PV) is not entirely independent of pressure, even for gases like H_2, O_2, and N_2—contradicting Boyle's law. The extent of deviation is evident in a plot of PV versus P, known as Amagat's curves (Figure 9).

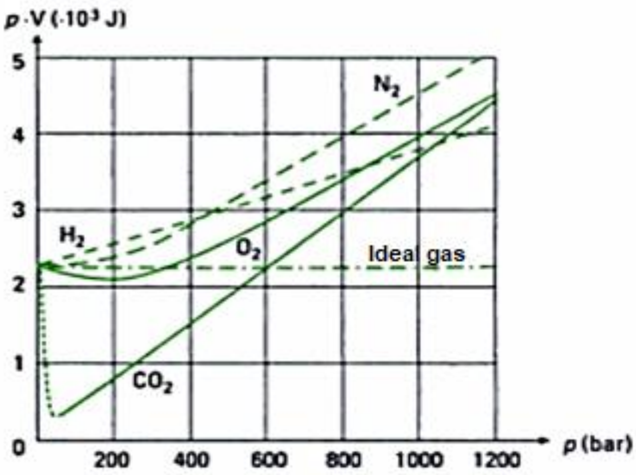


Figure I.9. Amagat's coordinates against P

If a gas perfectly followed Boyle's law, these curves would be horizontal, maintaining a constant ordinate equal to RT. The above figure shows the graph constructed for some gases at 273.15 K. Looking at the graph, it is seen that at constant temperature the pV vs p plot is not a straight line for real gases. There is a significant deviation from the ideal behaviour. As seen in Figure I.9, three types of result for real gases can clearly observed:

- ✓ If we raise the pressure, the value of PV decreases primarily and then the value starts rising for the gases like- carbone monoxide , oxygen, methane, ammoniac,etc.
- ✓ If we raise the pressure, the value of PV starts rising initially for gases like – hydrogen, helium, etc.

At low pressures, in Amagat coordinates, the isotherms are almost straight lines and can be extrapolated to P = 0. The product PV changes very little with pressure, and its limiting value as P → 0 is the same for all gases at a given temperature (Figure I.10). At sufficiently low pressures, real gases behave almost like ideal gases, because intermolecular forces and molecular volumes become negligible. At different temperature, the product PV changes greatly with pressure, and its limiting value as P → 0 is not the same for all gases (Figure I.11).

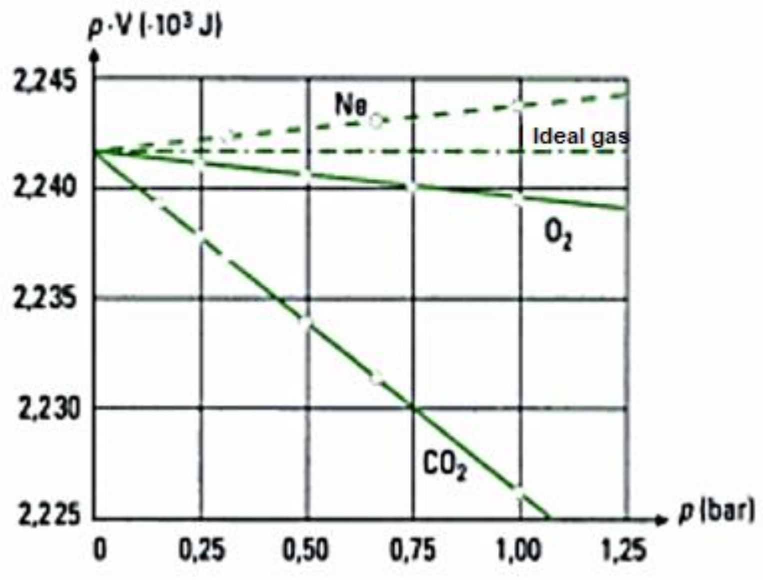


Figure I.10. Amagat's coordinates at low pressure

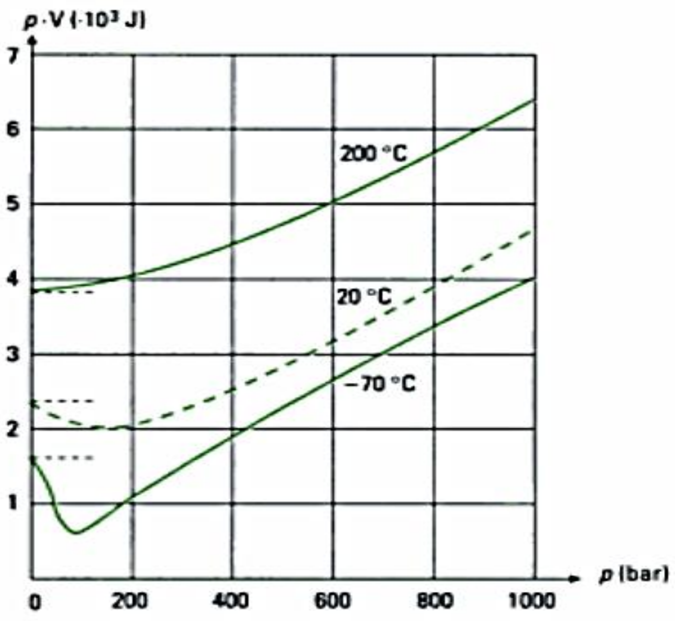


Figure I.11. Amagat's coordinates for P = 0 at different temperature for methane

I.1.b.3) Absolute temperature scale

The absolute temperature scale is a system of measuring temperature that starts at absolute zero, the point at which all thermal motion ceases. If we consider an ideal gas as one that, at a given temperature, has the same limiting behavior at P → 0 as a real gas—but for which PV = constant — then its isothermal curves in Amagat coordinates are parallel to the x-axis (Figure 9). The temperature scale of ideal gases is defined so that, for a gas at two different temperatures T_1 and T_2, the ratio of the limiting values of the product PV as P → 0 is equal to the ratio of the two temperatures.

$$\lim_{P\to 0}\left(\frac{P_1V_1}{P_2V_2}\right)=\frac{T_1}{T_2} \qquad (I.7)$$

The choice of a reference point and a unit completely defines the scale. The absolute temperature scale, denoted **T**, for an ideal gas is defined by:

- A unit — the **kelvin (K)**,
- A reference point — the triple point of water, whose temperature is fixed at 273.16 K,
- The triple point of water corresponds to the unique value of **T** (and **P**) at which the three physical states of water coexist simultaneously (Figure I.12).

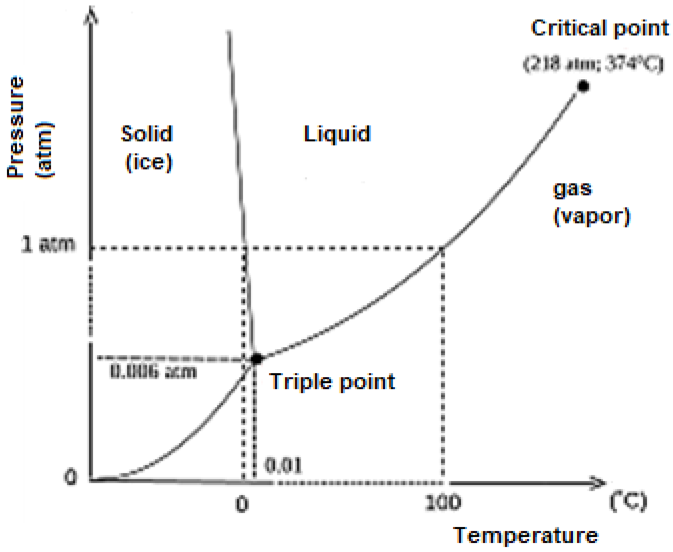


Figure I.12. Phase diagram of water. The triple point of water occurs at T = 273,16 K (or 0,01 °C) and P = 611 Pa

At 1 atm, ice melts at 273.15 K, and the correspondence between the **Kelvin**, **Celsius**, and **Fahrenheit** temperature scales is shown in the figure below. This relationship can be expressed mathematically by the following equations:

$$t(°C) = T(K) – 273.15 \qquad (I.8)$$

$$(t(°C) \times 9/5) + 32 = °F \qquad (I.9)$$

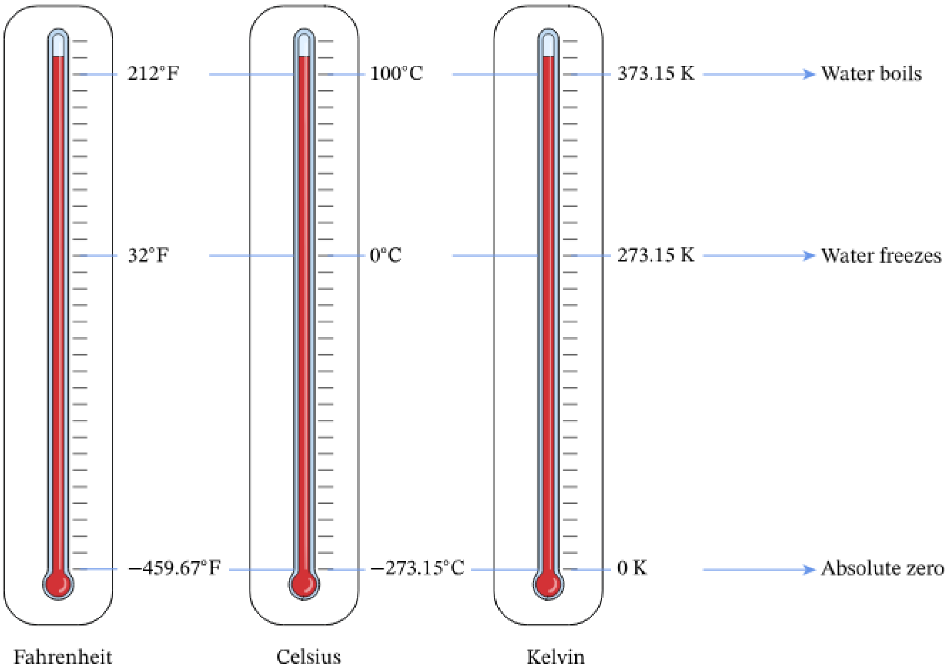


Figure I.13.Relationship between different temperature scales

I.1.c) Ideal gas model

The ideal gas model is a theoretical framework used to describe the behavior of gases under various conditions. It assumes that gases consist of point particles (molecules) that do not interact except during elastic collisions and occupy no volume. This model is particularly useful for understanding the relationships between pressure, volume, temperature, and the amount of gas. Below are the key components of the ideal gas model:

I.1.c.1) Ideal gas equation of state

The ideal gas equation of state combines the relationships described by Boyle-Mariotte's law, Charles' law, and Gay-Lussac's law into a single equation. It is expressed as:

$$PV = nRT \quad (I.10)$$

Where:

P : Pressure of the gas (in Pascals or atm),

V :Volume of the gas (in m^3 or liters),

n : Number of moles of the gas,

R : Universal gas constant (8.314 J/(mol.K) or 0.0821L.atm /(mol.K)),

T : Absolute temperature (in Kelvin).

This equation describes the state of an ideal gas and is valid for most gases under low pressure and high temperature conditions.

I.1.c.2) Boyle-Mariotte's Law

Boyle-Mariotte's law describes the relationship between the pressure and volume of a gas at constant temperature. It states:

$$P \propto 1/V \quad \text{or} \quad PV = \text{constant} \quad (I.11)$$

Graphically , this equation is represented as in the figure I. 14.

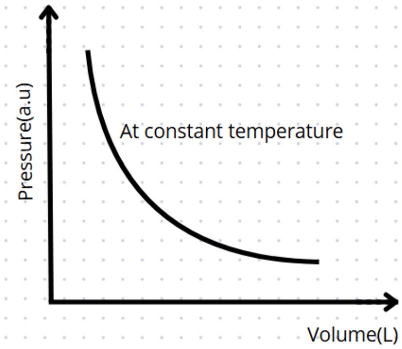


Figure I.14. The relationship between pressure (*P*) and volume (*V*)

If the temperature (*T*) and the amount of gas (n) are held constant, the pressure of the gas is inversely proportional to its volume. For example, if the volume of a gas is halved, its pressure will double.

In a mathematical form**:** $P_1V_1 = P_2V_2$, where P_1 and V_1 are the initial pressure and volume, and P_2 and V_2 are the final pressure and volume.

I.1.c.3) Charles' Law

Charles' law describes the relationship between the volume and temperature of a gas at constant pressure. It states:

$$V \propto T \quad \text{or} \quad V / T = \text{constant} \quad (I.12)$$

Explanation: If the pressure (P) and the amount of gas (n) are held constant, the volume of the gas is directly proportional to its absolute temperature (in Kelvin). For example, if the temperature of a gas is doubled, its volume will also double.

Mathematical Form: $V_1/T_1 = V_2 / T_2$, where V_1 and T_1 are the initial volume and temperature, and V_2 and T_2 are the final volume and temperature.

Graphically, the variation of gas volumes as a function of temperature (expressed in Kelvin (K)) gives straight lines, as shown in Figure 11. The extrapolation of these lines to lower temperatures, where the volume of each gas tends toward zero, intersects the temperature axis at a value of –273.15 °C.

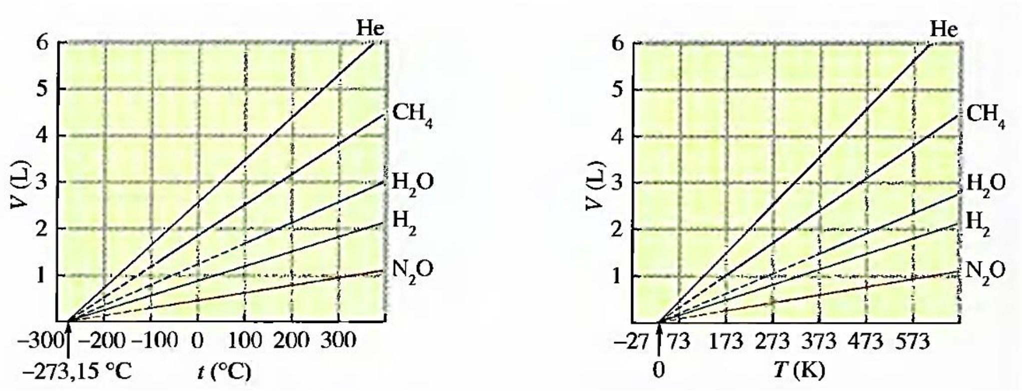


Figure I.15. Volume variation as function of temperature

I.1.c.4) Gay-Lussac's Law

Gay-Lussac's law describes the relationship between the pressure and temperature of a gas at constant volume. It states:

$$P \propto T \quad \text{or} \quad P / T = \text{constant} \quad (I.13)$$

Explanation: If the volume (V) and the amount of gas (n) are held constant, the pressure of the gas is directly proportional to its absolute temperature (in Kelvin). For example, if the temperature of a gas is doubled, its pressure will also double.

Mathematical Form: $P_1 / T_1 = P_2 / T_2$, where P_1 and T_1 are the initial pressure and temperature, and P_2 and T_2 are the final pressure and temperature.

So, the pressure divided by the absolute temperature of the gas is constant, provided we also keep the volume and the amount of gas constant.

This has some interesting implications. If the absolute temperature of the gas is decreased all the way to zero, the particles stop moving entirely. This means that there are no collisions taking place with the walls of the container, so the pressure of the gas must also be zero. However, as mentioned previously, it is physically impossible to cool a gas to absolute zero. Or, going in the other direction, if we increase the temperature of the container hugely, there will be many collisions taking place, each exerting a greater force on the wall, so the pressure of the gas will become very large. A possible graph of this relationship is shown in Figure I.16:

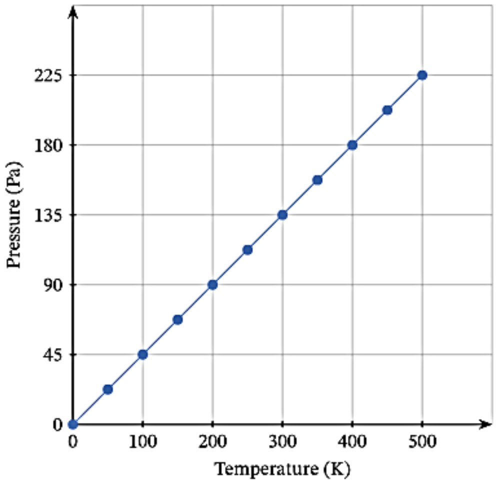


Figure I.16: Pressure vs temperature

Let us take a look at a series of temperature changes at constant volume. The following diagram shows a container of gas at three different temperatures (Figure I.17):

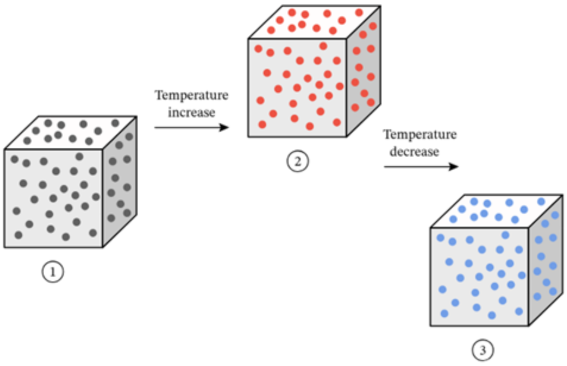


Figure I.17 : Effect of temperature on gas pressure at constant volume

1. *Initial state (Box 1, Gray)*

The gas molecules are distributed randomly throughout the container. Their average kinetic energy corresponds to the initial temperature. At this temperature, the pressure results from the frequency and force of collisions of molecules against the container walls.

2. Temperature increase (Box 2, Red)

When the temperature increases, the average kinetic energy of molecules rises. Molecules move faster and collide with the container walls more frequently and with greater force. Since the volume is fixed, the only way to accommodate the increased energy is for the pressure to rise. This illustrates the direct proportionality between pressure and temperature at constant volume.

3. Temperature decrease (Box 3, Blue)

Lowering the temperature decreases the kinetic energy of molecules. The molecules move slower, collisions are less frequent and weaker, leading to a drop in pressure. Again, volume is unchanged, so only pressure responds to temperature changes.

I.1.c.5) Gas mixtures

When different gases are combined in a container, they form a gas mixture where each gas retains its own properties while following the laws of ideal gases. The behavior of gas mixtures is governed by Dalton’s Law of Partial Pressures and the concept of mole fraction.

1. Number of moles in a gas mixture

The total number of moles in a gas mixture is the sum of the moles of each individual gas:

$$n_{total} = n_1 + n_2 + n_3 + \cdots + n_n \qquad (I.14)$$

where:

n_{Total}: number of moles in the mixture

$n_1, n_2, \ldots, n_n$: moles of individual gas components

The ideal gas law can be applied to the gas mixture as:

$P_{Total}\, V = n_{Total}\, RT$

where , P_{Total} : is the total pressure exerted by the gas mixture.

Dalton’s law of additive pressures: The pressure of a gas mixture is equal to the sum of the pressures each gas would exert if it existed alone at the mixture temperature and volume (Figure I.18).

Mathematically, the pressure of a mixture of ideal gases can be defined as the summation:

$$P_{Total} = \sum_{i=1}^{n} P_i = P_1 + P_2 + P_3 + \ldots. P_n \qquad (I.15)$$

Where

$p_1, p_2, ..., p_n$ represent the partial pressures of each component.

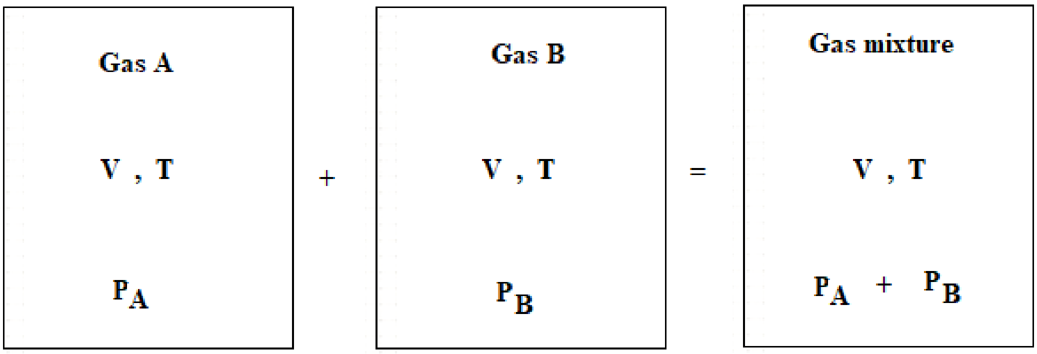


Figure I.18. Dalton’s law of additive pressures for a mixture of two ideal gases

2. *Mole Fraction* (x_i)

The mole fraction of a particular gas component in a mixture is the ratio of its number of moles to the total number of moles:

$$x_i = n_i / n_{Total} \qquad (I.16)$$

where:

x_i : mole fraction of gas i

n_i : moles of gas i

n_{total} : total moles in the mixture

The sum of all mole fractions in a mixture is always equal to 1:

$$x_1 + x_2 + x_3 + \cdots + x_n = 1 \qquad (I.17)$$

3. Partial Pressure (P_i)

The partial pressure of a gas in a mixture is the pressure that the gas would exert if it occupied the entire volume alone at the same temperature. It is given by Dalton’s Law of Partial Pressures**:**

$$P_i = x_i P_{Total} \qquad (I.18)$$

where:

P_i : partial pressure of gas i

x_i : mole fraction of gas i

P_{Total} : total pressure of the mixture

Application 2:

a) Suppose a gas mixture contains 2 moles of oxygen **(O_2)** and 3 moles of nitrogen **(N_2)** in a 10 L container at 300 K. The total pressure is 5 atm.

Total moles in the mixture

$n_{Total} = n_{O2} + n_{N2} = 2 + 3 = 5$ moles

Mole fractions

$X_{O2} = 2 / 5 = 0.4$, $X_{N2} = 3 / 5 = 0.6$

Partial pressures

$P_{O2} = 0.4 \times 5 = 2$ atm , $P_{N2} = 0.6 \times 5 = 3$ atm

b) The volumetric composition of a sample of gas exhaled by an individual is as follows: N_2, 74,1%; O_2, 15,0%; H_2O, 6,0%; Ar, 0,9%; CO_2, 4,0%. What is the partial pressure of each of the five gases, given that the sample temperature is 37 °C and its total pressure is 1 atm?

Answer:

P_{N2}= 0,741 atm ;PO_2 = 0,150 atm ; P_{H2O} = 0,060 atm ; P_{Ar} = 0,009 atm ; P_{CO2}= 0,040 atm.

c) At 23.5 °C, a 75.0 L sample of natural gas contains methane (CH_4) with a partial pressure of 67.3 kPa, ethane (C_2H_6) at 26.8 kPa, propane (C_3H_8) at 5.73 kPa, and 10.5 g of butane (C_4H_{10}). Calculate the mole fraction of each of the four components in the sample.

Answer:

CH_4 : 0,636 ; C_2H_6 : 0,253 ; C_2H8 : 0,0542 ; C_4H_{10} : 0,0561.

I.1.d) Real gases

Real gases are gases that do not perfectly follow the ideal gas laws due to the presence of intermolecular forces and the finite volume occupied by gas molecules or atoms. Unlike ideal gases, which are hypothetical and assume no interactions between molecules and zero molecular volume, real gases exhibit deviations from ideal behavior, especially under conditions of high pressure and low temperature.

Non-ideal behavior

Real gases deviate from the ideal gas equation of state (PV = nRT) under certain conditions. These deviations are more pronounced at:

High pressures: Molecules are forced closer together, making intermolecular forces and molecular volume significant.

Low temperatures: Molecules move slower, allowing intermolecular forces to have a greater effect.

I.1.d.1) Comparison: Real gases vs. ideal gases

Real gases deviate from ideal gas behavior, especially under conditions of high pressure and low temperature. Understanding these deviations is crucial for accurate predictions in various scientific and engineering applications. Below is a comparison between real gases and ideal gases, along with an explanation of the Van der Waals equation, which accounts for these deviations.

Table I.1: Comparison: Real gases vs. Ideal gases

Property	**Ideal Gas**	**Real Gas**
Volume of Gas Particles	Assumes gas particles have negligible volume (point masses).	Gas particles have finite volume, which becomes significant at high pressure.
Intermolecular Forces	Assumes no intermolecular forces (no attraction or repulsion between particles).	Intermolecular forces (attraction and repulsion) are present and significant.
Behavior	Follows the Ideal Gas Law (PV=nRT) under all conditions.	Deviates from the Ideal Gas Law, especially at high pressure and low temperature.
Compressibility	Always follows PV = nRT; compressibility factor Z = 1.	Compressibility factor $Z \neq 1$, *for* $Z < 1$ (attractive forces dominate) or $Z > 1$ (repulsive forces dominate).
Applicability	Accurate for low pressure and high temperature.	Accurate for high pressure and low temperature.

I.1.d.2) Van der Waals Equation

It will not take the reader long to recognize the limitations of the ideal gas equation, which suggests that a non-zero mass of an ideal gas would occupy zero volume at zero temperature. Strictly speaking, the ideal gas cannot exist and hence the mathematical model loses its meaning at very low temperatures since it does not take into account the actual volume of the molecules themselves. There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The van der Waals equation improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$\left(p+\frac{an^2}{V^2}\right)\left(V-nb\right)=nRT \qquad (I.19)$$

Key terms in the Van der Waals equation:

P : pressure of the gas
V : volume of the gas
n : number of moles of the gas
R : universal gas constant
T: temperature of the gas

The constant a corresponds to the strength of the attraction between molecules of a particular gas, and the constant b corresponds to the size of the molecules of a particular gas. The “correction” to the pressure term in the ideal gas law is:

$$\frac{an^2}{V^2}$$

The “correction” to the volume is nb. Note that when V is relatively large and n is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, PV = nRT. Such a condition corresponds to a gas in which a relatively low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in Table I.2. At low pressures, the correction for intermolecular attraction , a, is more important than the one for molecular volume, b. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by PV= nRT over a small range of pressures .This behavior is reflected by the “dips” in several of the compressibility curves shown in Figure 8.35.The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing P).At very high pressures, the gas becomes less compressible (Z increases with P), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume. Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligibleandthegasmoleculesthemselvesdonotoccupyanappreciablepartofthewholevolume.These criteria are satisfied under conditions of low pressure and high temperature. Under such conditions, the gas is said to be have ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Table I.2: van der Waals coefficients for selected gases

Gas	*Chemical formula*	*a (L^2 atm mol^{-2})*	*b (L mol^{-1})*
Xenon	Xe	4.137	0.032
Argon	Ar	1.34	0.0320
Carbon dioxide	CO_2	3.59	0.0427
Helium	He	0.0342	0.0237
Nitrogen	N_2	1.39	0.0391
Oxygen	O_2	1.36	0.0318
Water	H_2O	5.46	0.0305

***Application 3*:** A 4.25-L flask contains 3.46 mol CO_2 at 229 °C. Calculate the pressure of this sample of CO_2: (a) from the ideal gas law (b) from the van der Waals equation (c) Explain the reason(s) for the difference.

Given: a = 3.59 L^2 atm mol^2 and b = 0.0427 L mol^{-1} for CO_2 gas

(a) From the ideal gas law:

$$P = \frac{nRT}{V} = \frac{3.46 \times 0.082 \times 502}{4.25} = 33.5 atm$$

(b) From the van der Waals equation:

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

$$P = \frac{3.46 \times 0.082 \times 502}{4.25 - 3.46 \times 0.0427} - \frac{3.46^2 3.59}{4.25^2} = 32.4 atm$$

(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO_2 molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

I.2) Energy Exchanges

I.2.a.1) Heat and Energy

At the outset, it is important to make a major distinction between internal energy and heat, terms that are often incorrectly used interchangeably in popular language. Internal energy is all the energy of a system that is associated with its microscopic components (atoms and molecules). Heat is defined as a process of transferring energy across the boundary of a system because of a temperature difference between the system and its surroundings. It is also the amount of energy Q transferred by this process.

I.2.a.2) Concept of temperature

The first approach to the concept of temperature is the simple physical sensation of heat. Temperature plays a fundamental role in thermodynamics and can be defined in two ways:

Macroscopic: Based on the zeroth law of thermodynamics and measured using a thermometer or a thermocouple.

Microscopic: Temperature is a measure of the average kinetic energy of the particles in a system.

It determines the direction of heat flow: heat always flows from a region of higher temperature to a region of lower temperature. Temperature is measured using scales such as Celsius (°C), Fahrenheit (°F), and Kelvin (K). The Kelvin scale is the SI unit for thermodynamic temperature.

I.2.a.3) Thermal equilibrium

Thermal equilibrium occurs when two systems in contact with each other no longer exchange heat, meaning they have reached the same temperature. At thermal equilibrium, the net heat flow between the systems is zero.

I.2.a.4) Zeroth law of thermodynamics

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

This law establishes the basis for temperature measurement and the concept of thermal equilibrium. It allows for the use of thermometers to compare temperatures of different systems.

I.2.a.5) Different types of energy

Energy is the capacity to do work or produce heat. It exists in various forms, and it can be converted from one form to another. Below is a detailed explanation of the different forms of energy, their characteristics, and examples (Table I.3).

Table I.3: Forms of energy

Form of Energy	**Description**	**Examples**
Kinetic energy	Energy of motion.	Moving car, wind.
Potential energy	Stored energy due to position or configuration.	Book on a shelf, compressed spring.
Thermal energy	Energy from random particle motion.	Heat from the Sun.
Chemical energy	Energy stored in chemical bonds.	Food, gasoline.
Electrical energy	Energy from moving electric charges.	Electricity in wires.
Nuclear energy	Energy stored in atomic nuclei.	Nuclear power plants.
Radiant energy	Energy carried by electromagnetic waves.	Sunlight, X-rays.
Sound energy	Energy carried by sound waves.	Music, noise.
Mechanical energy	Sum of kinetic and potential energy.	Swinging pendulum.
Magnetic energy	Energy stored in magnetic fields.	Magnets, electromagnets.
Gravitational energy	Energy due to gravitational forces.	Planets orbiting the Sun.

Energy units in thermodynamics:

In thermodynamics, energy is a fundamental quantity, and it is measured in various units depending on the context. The **joule (J)** and the **calorie (cal)** are two commonly used units of energy.

1. Joule (J)

Definition: The **joule** is the SI (International System of Units) unit of energy.

$$1\ \text{J} = 1\ \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$$

2. Calorie (cal)

Definition: The **calorie** is a non-SI unit of energy, commonly used in chemistry and nutrition. 1 cal is defined as the amount of energy required to raise the temperature of 1 gram of water by 1°C (from 14.5°C to 15.5°C at standard atmospheric pressure).

The joule and calorie are related by a conversion factor:

$$1\ \text{cal} = 4.184\ \text{J}$$

I.2.a.6) Heat transfer with temperature change

When two bodies at different temperatures are brought into contact, their temperatures tend to equalize through a spontaneous transfer of energy. This form of energy is called heat. Heat, denoted Q, is a form of energy measured in joules. On the macroscopic scale, it corresponds to a transfer of energy in a disordered form.

When heat is added to or removed from a system, its temperature changes. The relationship between heat (Q), mass (m), specific heat capacity (c), and temperature change (ΔT) is given by:

$$Q = m\,c\,\Delta T \quad (I.20)$$

This equation applies when there is no phase change.

I.2.a.7) Heat transfer mechanisms

There are three primary mechanisms of heat transfer:

Conduction: Transfer of heat through a material without the movement of the material itself (e.g., heat flowing through a metal rod).

Convection: Transfer of heat by the physical movement of a fluid (e.g., hot air rising).

Radiation: Transfer of heat through electromagnetic waves (e.g., heat from the Sun).

I.2.a.8) Heat capacities

The natural question that arises is the following: if the system consists of a substance *i* (simple or compound), what amount of heat must be supplied (or removed) to produce a temperature change ΔT per unit mass or per mole?

This requires introducing a characteristic property of the substance: its specific heat capacity, denoted as *Cj*. It may be expressed as:

- *Specific heat capacity* (per unit mass): J/(kg·K), or
- *Molar heat capacity* (per mole): J/(mol·K).

Thus, if a substance *i* of mass *m* undergoes a temperature change ΔT, the corresponding heat exchange is given by equation (20).

Specific heat capacity (c): The amount of heat required to raise the temperature of 1 gram of a substance by 1°C (or 1 K).

$$c = Q / m\Delta T \qquad (I.21)$$

Molar heat capacity: The amount of heat required to raise the temperature of 1 mole of a substance by 1°C (or 1 K).

$$c = Q / n\Delta T \qquad (I.22)$$

where n is the number of moles

Heat capacity (C): The amount of heat required to raise the temperature of a system by 1°C (or 1 K).

$$C = Q / \Delta T \quad (I.23)$$

If the variation of specific heat with temperature must be taken into account, the previous expression (20) is replaced by an integral:

$$Q = m \int_{T_1}^{T_1+\Delta T} c(T)dT \qquad (I.24)$$

The table I.4 presents the specific heat capacities of aluminum, copper, ethanol, iron, and water. Specific heat capacity, expressed in J/(g·°C). Metals are characterized by relatively low specific heat values. Copper, with a specific heat of 0.384 J/(g·°C), heats up and cools down the fastest, as it requires the least energy for a temperature change. Iron has a slightly higher value of 0.449 J/(g·°C), while aluminum shows the highest value among the metals at 0.901 J/(g·°C). This means aluminum requires more energy to change its temperature compared to copper and iron, although still significantly less than liquids like water. Liquids generally exhibit higher specific heat capacities compared to metals. Ethanol, with a specific heat of 2.43 J/(g·°C), can store and transfer more heat than metals, making it slower to change temperature. Water, however, stands out with a remarkably high value of 4.18 J/(g·°C). This is nearly five times greater than aluminum and more than ten times greater than copper. Such a high specific heat capacity explains why water is an effective coolant and plays a crucial role in stabilizing climates and regulating temperature in natural and industrial processes.

Table I.4: Specific heats and molar heat capacities at 25°C.

Substance	Specific heat (J/(g.°C))
Aluminum, Al	0.901
Copper, Cu	0.384
Ethanol, C_2H_5OH	2.43
Iron, Fe	0.449
Water, H_2O	4.18

I.2.a.9) Heat transfer with phase change

During a phase change (e.g., melting, boiling), heat is absorbed or released without a change in temperature. The energy required for a phase change is called latent heat**.**

Examples:

- Melting: Solid to liquid (heat absorbed).
- Freezing: Liquid to solid (heat released).
- Vaporization: Liquid to gas (heat absorbed).
- Condensation: Gas to liquid (heat released).

I.2.a.9.1) Latent heat

When a pure substance is liquefied from the solid state or vaporized from the liquid or solid at constant pressure, no change in temperature occurs; however, these processes require the transfer of finite amounts of heat to the substance. These heat effects are called latent heats: of fusion, of vaporization, and of sublimation. Le changement de phase se fait à température et pression constantes, and is expressed by the thermodynamic equation:

$$Q = mL \quad (I.25)$$

Where:

Q: heat transferred,

m: mass of the substance,

L: latent heat (specific to the phase change).

Examples of latent heat:

Latent heat of fusion (L_f): For solid-liquid transitions.

Latent heat of vaporization (Lv): For liquid-gas transitions.

Latent heat arises from the work required to overcome the forces that hold together atoms or molecules in a material. The regular structure of a crystalline solid is maintained by forces of attraction among its individual atoms, which oscillate slightly about their average positions in the crystal lattice. As the temperature increases, these motions become increasingly violent until, at the melting point, the attractive forces are no longer sufficient to maintain the stability of the crystal lattice. However, additional heat (the latent heat of fusion) must be added (at constant temperature) in order to accomplish the transition to the even more-disordered liquid state, in which the individual particles are no longer held in fixed lattice positions but are free to move about through the liquid. A liquid differs from a gas in that the forces of attraction between the particles are still sufficient to maintain a long-range order that endows the liquid with a degree of cohesion. As the temperature further increases, a second transition point (the boiling point) is reached where the long-range order becomes unstable relative to the largely independent motions of the particles in the much larger volume occupied by a vapour or gas.

Once again, additional heat (the latent heat of vaporization) must be added to break the long-range order of the liquid and accomplish the transition to the largely disordered gaseous state.

I.2.a.10) Heat measurements

Heat measurement, or calorimetry, is a branch of thermodynamics that focuses on quantifying the amount of energy transferred as heat during physical or chemical processes. Heat is not a substance but a form of energy exchange that occurs when a system and its surroundings are at different temperatures. Measuring heat is essential for understanding energy balances, reaction enthalpies, phase changes, and thermal properties of materials.

In practice, heat is commonly measured using calorimeters, devices designed to minimize energy loss to the environment. By tracking changes in temperature, mass, and specific heat capacity of substances, calorimetry allows scientists to calculate heat flow accurately. Such measurements play a key role in chemistry, physics, biology, and engineering, where they help evaluate fuel efficiency, metabolic rates, reaction energetics, and material stability.

I.2.a.10.1.Calorimetry

Calorimetry is the experimental technique used to measure heat transfer during physical or chemical processes.

A **calorimeter** is a device used to measure the heat absorbed or released in a reaction.

Types of Calorimeters:

Constant-Volume calorimeter (Bomb calorimeter): Measures heat changes at constant volume. The Figure I.19 shows a sample of graphite being burned in oxygen within a vessel called the bomb. An electric current passing through the ignition coil starts the graphite burning. The temperature of the water surrounding the bomb rises as heat flows from the exothermic reaction of graphite and oxygen. This calorimeter is used generally for reactions involving gases.

Constant-Pressure calorimeter (Coffee-Cup calorimeter): This apparatus is used to measure the heat at constant pressure (Q_P). (Figure I.20). The heat of the reaction is calculated from the temperature change caused by the reaction, and since this is a constant-pressure process, the heat can be directly related to the enthalpy change, ΔH. Research versions of a constant-pressure calorimeter are available, and these are used when gases are not involved.

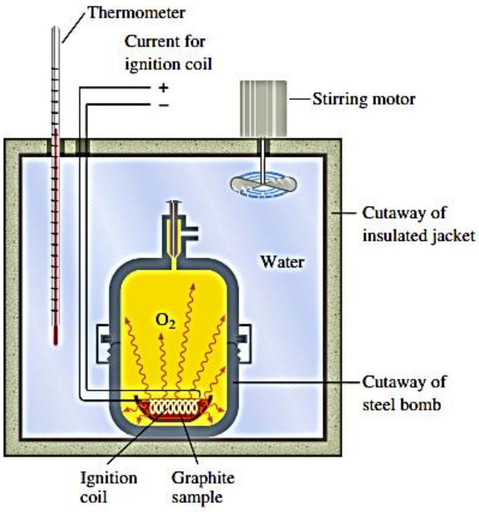


Figure I.19: A bomb calorimeter

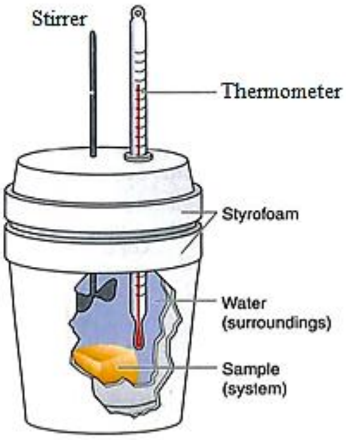


Figure I.20. Coffee-cup calorimeter

The heat transfer (Q) is calculated using:

$$Q = C\Delta T$$

where:

C : heat capacity of the calorimeter,

$\Delta T = T_f - T_i$: temperature change.

When a body at higher temperature is brought in contact with another body at lower temperature, the heat lost by the hot body is equal to the heat gained by the cold body. No heat is allowed to escape to the surroundings. It can be mathematically expressed as:

$$\sum_{i=1}^{n} Q_i = 0 \qquad \text{(I.26)}$$

For two systems: $Q_1 + Q_2 = 0$

Body 1 is the hotter one, so it transfers a quantity of energy to the colder body. The energy balance is expressed as:

$$m_1\, c_1\, (T_{eq} - T_1) + m_2\, c_2\, (T_{eq} - T_2) = 0$$

where:

- Q_1 is the heat released by the hot body,
- Q_2 is the heat absorbed by the cold body,
- m_1 and m_2 are the respective masses of bodies 1 and 2,
- c_1 and c_2 are their specific heat capacities.

Alternatively, the relation can be expressed using the number of moles n and the molar heat capacities (c_m) of the substances involved in the calorimeter. A dimensional analysis of each parameter makes it possible to group the different heat units, as summarized in Table I.5.

Table I.5: Units of the different quantities in the heat relation

Parameters	Symbole	SI Unit
Heat	Q	J
mass	m	Kg
Number of moles	n	mol
Temperature	T	K
Specific heat capacities	c	J/(K.Kg)
Molar heat capacities	c_m	J/(K.mol)
heat capacities	C	J/K

***Application 4*:**

A calorimeter, assumed to be perfectly insulated from the surroundings, initially contains a mass of water m_1=200 gm at an equilibrium temperature of T_1=24.9°C. A second mass of water, m_2=157 gm , at a higher temperature T_2=80°C, is then introduced into the calorimeter. After mixing, a new equilibrium temperature of T_{eq}=45.7°C is established. The objective is to determine the heat capacity of the calorimeter (C_{cal}).

Given: The specific heat capacity of water is c = 4184 J\ ($kg^{-1}K^{-1}$).

Solution:

The inner vessel of the calorimeter is initially at the same temperature as the cold water, T_1. Because the calorimeter is assumed to be perfectly insulated, there is no heat exchange with the external environment. Therefore, the principle of conservation of energy can be applied to the entire system (cold water + hot water + calorimeter).

Mathematically, the energy balance can be expressed as the algebraic sum of all heat exchanges being equal to zero:

$$\sum_{i=1}^{n} Qi$$

For the three subsystems (cold water, calorimeter, and hot water), this gives:

$$Q_1 + Q_2 + Q_3 = 0$$

Where:

$Q_1 = m_1c_e(T_{eq} - T_1)$: heat absorbed by the cold water (since its temperature rises from T_1 to T_{eq}

$Q_2 = C_{cal}\ (T_{eq} - T_1)$: heat absorbed by the calorimeter,

$Q_3 = m_2c_e\ (T_{eq} - T_2)$, heat released by the hot water (since its temperature decreased from T_2 to T_{eq})

Thus, the energy balance becomes:

$m_1c\ (T_{eq} - T_1) + C_{cal}\ (T_{eq} - T_1) + m_2c_e\ (T_{eq} - T_2) = 0$

Rearranging to isolate the calorimeter's heat capacity:

$C_{cal} = m_2c_e\ (T_2 - T_{eq})/(T_{eq} - T_1)\ - mc_e = 0.157 \times 4185\ (80 - 45.7)/(54.7 - 24.9)\ - 0.2 \times 4185$

$C_{cal} = 246.5 J/K.$

This means that for each degree Kelvin increase in its temperature, the calorimeter absorbs about 246 J of heat.

In this calorimetric experiment, the heat exchanges between the three components (cold water, hot water, and the calorimeter) are well balanced. The cold water, initially at 24.9 °C, absorbs about 17.4 kJ as it warms up to the equilibrium temperature of 45.7 °C. The calorimeter, which is also heated from 24.9 °C to 45.7 °C, absorbs an additional 5.1 kJ. Together, these two heat gains amount to 22.5 kJ, which corresponds exactly to the heat released by the hot water (initially at 80 °C), as it cools down to 45.7 °C. This shows that the first law of thermodynamics is fully satisfied: the energy lost by the hot water is entirely redistributed to the cold water and the calorimeter. It is also noteworthy that the calorimeter itself absorbs about 23% of the total heat released, which is significant. If its contribution were neglected, the predicted equilibrium temperature would be higher than the measured value. This highlights the importance of including the calorimeter's heat capacity when studying thermal balance in practical calorimetry.

Application 5 (Calculating ΔH from calorimetric data):

Suppose 0.562 g of graphite is placed in a calorimeter with an excess of oxygen at 25°C and 1 atm pressure. Excess O_2 ensures that all carbon burns to form CO_2. The graphite is ignited, and it burns according to the equation:

$$C(graphite) + O_2(g) \rightarrow CO_2(g)$$

On reaction, the calorimeter temperature rises from 25°C to 25.89 °C. The heat capacity of the calorimeter and its contents was determined in a separate experiment to be 20.7 kJ/C. What is the heat of reaction at 25°C and 1 atm pressure?

Solution:

The energy balance can be expressed as the algebraic sum of all heat exchanges being equal to zero:

$$Q_{reaction} + Q_{calorimeter} = 0$$

The heat from the graphite sample is: $Q_{reaction} = -Q_{calorimeter}$

This means that the heat released by reaction of the sample (a negative quantity) equals the heat absorbed by the calorimeter (a positive quantity).

$$Q_{reaction} = -\ C_{cal}\Delta T$$

$$Q_{reaction} = -20.7 \times (25.89\ -\ 25) = -18.4kJ$$

The negative sign indicates the reaction is exothermic, as expected for a combustion.

For one mol of carbon graphite © , the heat released is then:

$$Q_{reaction} = -392.88kJ/mol$$

When 1 mol of carbon burns, 392.88 kJ of heat is released.

I.2.b) Mechanical work performed by a pressure force

In thermodynamics, mechanical work performed by a pressure force is a key concept that describes the energy transfer associated with the expansion or compression of a system (e.g., a gas). This type of work is particularly important in processes involving gases, such as in engines, compressors, and thermodynamic cycles.

Work, W, is performed whenever a force acts through a distance. By its definition, the quantity of work is given by the equation:

$$dW = F\,dl \qquad (I.27)$$

where F is the component of force acting along the line of the displacement dl. The SI unit of work is the newton·meter or joule, symbol J. When integrated, Eq. (I.27) yields the work of a finite process. By convention, work is regarded as positive when the displacement is in the same direction as the applied force and negative when they are in opposite directions. Work is done when pressure acts on a surface and displaces a volume of fluid. An example is the movement of a piston in a cylinder so as to cause compression or expansion of a fluid contained in the cylinder. The force exerted by the piston on the fluid is equal to the product of the piston area and the pressure of the fluid. The displacement of the piston is equal to the total volume change of the fluid divided by the area of the piston. Equation (I.27) therefore becomes:

$$dW = -P_{ext}\,dV \qquad (I.28)$$

Integration yields: $$W = -\int_{V_1}^{V_2} P_{ext}\,dV \qquad (I.29)$$

- P_{ext}: external pressure exerted on the system.
- For reversible processes, $P_{ext} = P_{int} = P$
- For irreversible processes, $P_{ext} \neq P$, often constant (e.g., sudden expansion against 1 atm).

Note: A matter of convention

Heat flow is defined from the system to its surroundings as negative

Work is defined as by the system on its surroundings as negative

The minus signs in these equations are made necessary by the sign convention adopted for work. When the piston moves into the cylinder so as to compress the fluid, the applied force and its displacement are in the same direction; the work is therefore positive. The minus sign is required because the volume change is negative (Figure I.20).

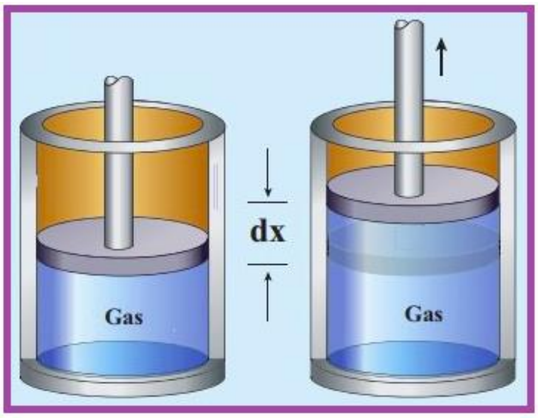


Figure I.20:Work done by the gas.

For an expansion process, the applied force and its displacement are in opposite directions. The volume change in this case is positive, and the minus sign is again required to make the work negative.

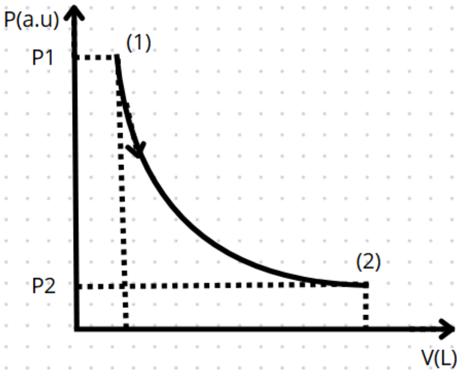


Figure I.21: Diagram showing a P vs. V path.

Equation (I.25) expresses the work done by a finite compression or expansion process. Figure 21 shows a path for expansion of a gas from point 1, initial volume V_1 at pressure P_1, to point 2, volume V_2 at pressure P_2. This path relates the pressure at any point of the process to the volume. The work required is given by Eq. (I.26) and is proportional to the area under the curve of Figure. I.21.

- ***For constant volume (Isochoric process dV = 0)***

- ***Reversible or Irreversible:***
- $W = -\int_{V_1}^{V_2} P_{ext}\, dV = 0$

No work is done because the system's volume does not change, it means that the isochoric processes involve no mechanical work, regardless of reversibility.

3. Constant Pressure (Isobaric process, P_{ext}= constant)

(a) Irreversible isobaric work

If the system expands/compresses against a fixed external pressure:

$$W_{irr} = -P_{ext}(V_f - V_i)$$

(b) Reversible isobaric work

For a reversible transformation at constant pressure, internal pressure $P_{int} = P_{ext} = P$ is equal throughout:

$$W_{rev} = -P(V_f - V_i)$$

Since P is constant, the expression looks identical to the irreversible case — but the key difference is the pressure balance condition:

- In reversible: $P_{ext} = P_{int}$ at each step.
- In irreversible: P_{ext} is imposed externally, often far from equilibrium.

➢ *Physical meaning:*

- **Isochoric:** No displacement of the piston → no work. Energy transfer occurs only as heat.
- **Isobaric reversible:** System stays infinitesimally close to equilibrium; work is maximized.
- **Isobaric irreversible:** Sudden, non-equilibrium change; work is smaller in magnitude than the reversible case for the same initial and final states.

➢ *Reversible isothermal work*

For an ideal gas at constant temperature (T= const):

$$W_{rev} = -\int_{V_1}^{V_2} P_{ext}\, dV$$

Since : $$P = \frac{nRT}{V}$$

$$W_{rev} = -\int_{V_i}^{V_f} \frac{nRT}{V}\, dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V} = -nRT\ln\frac{V_f}{V_i}$$

Work depends logarithmically on the ratio of final to initial volumes.

- Expansion ($V_f > V_i$) → work negative (system does work on surroundings).
- Compression ($V_f < V_i$) → work positive (surroundings do work on system).

➢ 3. Irreversible isothermal work

If the system expands or compresses against a constant external pressure P_{ext}:

$$W_{irr} = -P_{ext}(V_f - V_i)$$

Application 6:

A sample of an ideal gas with an initial volume of 2 L is maintained at 25 °C under a pressure of 5 atm (state 1). The gas undergoes an isothermal expansion until it occupies a final volume of 10 L (state 2).

1. ***Case (a):*** Calculate the work performed during a reversible expansion.
2. ***Case (b):*** Calculate the work performed during an irreversible expansion.

Next, at the same temperature (25 °C), the gas is brought back from state 2 to its original state 1 (compression).

3. ***Case (c):*** Determine the work for a reversible compression.
4. ***Case (d):*** Determine the work for an irreversible compression.

Here's a full, step-by-step solution.

Given (state 1): V_1= 1L ,P_1 = 2.5 atm, T= 25°C = 298.15K

Given (state 2): V_2= 5L ,P_2 = ? atm, for isothermal transformation T= 298.15K.

$P_2 = P_1V_1/V_2 = 2.5\times1/5 = 0.5$ atm.

Useful constants: R = 0.082057 L atm mol^{-1} K^{-1}, 1 L.atm = 101.325 J

(a) Reversible isothermal expansion (1 L → 5 L)

$$W_{rev} = -\int_{V_i}^{V_f} P_{ext}\, dV$$

Since the transformation is reversible, so $P_{ext} = P_{gas}$ at each moment.

$$W_{rev} = -\int_{V_i}^{V_f} P_{gas}\, dV = -\int_{V_i}^{V_f} \frac{nRT}{V}\, dV = -nRT\int_{V_i}^{V_f} \frac{dV}{V} = -nRT\ln\frac{V_f}{V_i}$$

Since nRT = P_1V_1= 2.5 L.atm = 253.3J

$$W_{rev} = -\mathrm{nRT}\ln\frac{V_f}{V_i} = -2.5\ln\frac{5}{1} = -4.0236\,L.atm = -407.7\,J$$

(b) ***Irreversible isothermal expansion against a constant external pressure***

For a single-step constant-pressure expansion that ends at V_2 at the same T, the external pressure must equal the final internal pressure: $P_{ext} = P_2 = 0.50$ atm.

Then:

$$W_{irr} = -P_2(V_f - V_i) = -0.50\,(5-1) = -2\ \mathrm{L.atm} = -202.65\mathrm{J}$$

Return path at the same temperature (25 °C): state 2 → state 1

(c) Reversible isothermal compression (5 L → 1 L)

$$W_{rev} = -\int_{V_i}^{V_f} P_{gas}\,dV = -\int_{V_i}^{V_f}\frac{nRT}{V}\,dV = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -nRT\ln\frac{V_f}{V_i} = 2.5\ln 5 = 407.7\,J$$

(d) Irreversible isothermal compression against a constant external pressure

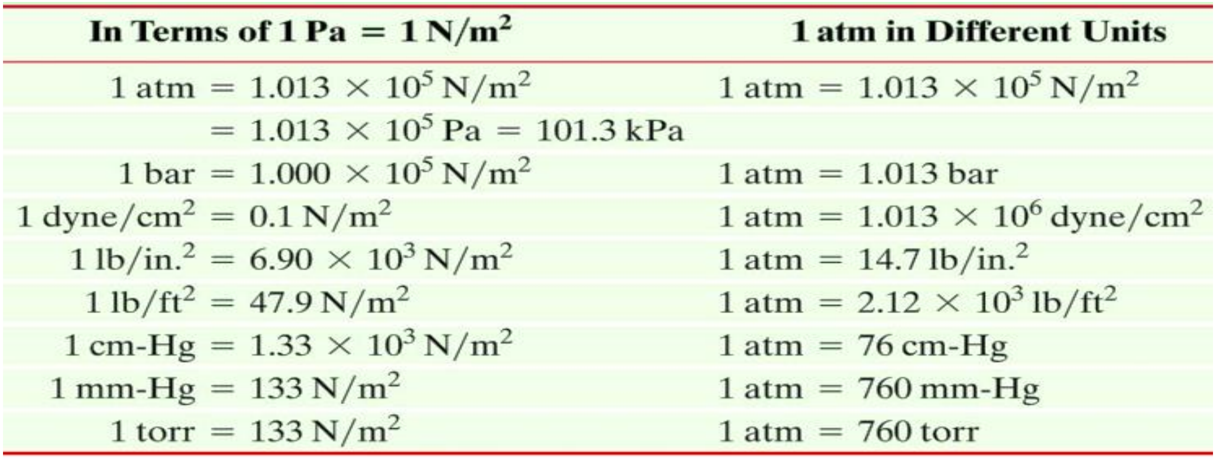
For a single-step constant-pressure compression that ends at V_1 at the same T,

take $P_{ext} = P_1 = 2.50$ atm.

Then:

$$W_{irr} = -P_1(V_f - V_i) = -2.5\,(1-5) = 10\ \mathrm{L.atm} = 1.013.25\mathrm{J}$$

4.Pressure unit conversions : Pressure is measured in a variety of different units. This table gives the conversion factors.



In Terms of 1 Pa = 1 N/m²	1 atm in Different Units
1 atm = 1.013×10^5 N/m²	1 atm = 1.013×10^5 N/m²
= 1.013×10^5 Pa = 101.3 kPa	
1 bar = 1.000×10^5 N/m²	1 atm = 1.013 bar
1 dyne/cm² = 0.1 N/m²	1 atm = 1.013×10^6 dyne/cm²
1 lb/in.² = 6.90×10^3 N/m²	1 atm = 14.7 lb/in.²
1 lb/ft² = 47.9 N/m²	1 atm = 2.12×10^3 lb/ft²
1 cm-Hg = 1.33×10^3 N/m²	1 atm = 76 cm-Hg
1 mm-Hg = 133 N/m²	1 atm = 760 mm-Hg
1 torr = 133 N/m²	1 atm = 760 torr

CHAPTER II

The First Law of Thermodynamics

II.1. Statement of the principle – Notion of internal energy

The internal energy of a system is a fundamental concept in thermodynamics. It represents the total energy contained within the system. The total energy of a system can be divided in two groups: macroscopic and microscopic. The macroscopic forms of energy are those a system possesses as a whole with respect to some outside reference frame, such as kinetic and potential energies. The microscopic forms of energy are those related to the molecular structure of a system and the degree of the molecular activity, and they are independent of outside reference frames. The sum of all the microscopic forms of energy is called the internal energy of a system and is denoted by U. The term later can be viewed as the sum of the kinetic and potential energies of the molecules.

$$\textit{Total}\ \text{energy} = E_T = U + KE + PE \qquad \text{(II.1)}$$

In thermodynamics, a system can evolve from one equilibrium state to another, each characterized by a set of state variables. These two equilibrium states differ in their total energy, which includes both mechanical energy and the energy associated with microscopic phenomena (known as *internal energy*). Thermodynamics studies the changes in a system's total energy between two equilibrium states and considers two modes of energy transfer: work and heat transfer. The internal energy U of a system represents the microscopic kinetic energy and the potential energy associated with internal forces.

The internal energy U, by definition, is always positive, but its variation ΔU is not necessarily positive.

II.1.a) Conservation of internal energy

The First law of thermodynamics states that energy cannot be created or destroyed, only transferred or converted from one form to another. For a closed system, the change in internal energy (ΔU) is equal to the heat added to the system (Q) plus the work done on the system (W):

$$\Delta U = Q + W \ \text{(II.2)}$$

This equation is a statement of the conservation of energy for thermodynamic systems.

If the system undergoes an infinitesimal transformation, the first law is written as:

$$dU = \delta w + \delta Q \qquad \text{(II.3)}$$

We can only access *changes* in internal energy. A finite change in internal energy, obtained by integrating dU, is denoted: ΔU

Work (W) and heat transfer (Q) are *not* state functions: their values depend on the *path* taken during the process. In mathematics, infinitesimal amounts of work and heat are written as δW and δQ, respectively. These are not exact differentials, even though their expressions may involve total differentials like dV and dT.

These equations do not provide a definition of internal energy. Indeed, they presume prior affirmation of the existence of internal energy, as expressed in the following axioms:

1-There exists a form of energy, known as internal energy U, which is an intrinsic property of a system, functionally related to the measurable coordinates that characterize the system. For a closed system, not in motion, changes in this property are given by Eqs. (1) and (2).

2- The total energy of any system and its surroundings is conserved.

If a system goes from an initial state 1 to a final state 2 by exchanging energy ΔU with the surroundings, energy conservation is expressed as:

$$\Delta U = U_2 - U_1 = Q + W$$

- If $\Delta U > 0$: the system has gained energy.
- If $\Delta U < 0$: the system has lost energy to the surroundings.

The sign convention for Q and W is the same as that used for ΔU.

II.1.b) Internal energy as a state function

Internal energy (U) is a state function, meaning it depends only on the current state of the system (e.g., temperature, pressure, volume) and not on the path taken to reach that state (Figure II.1).

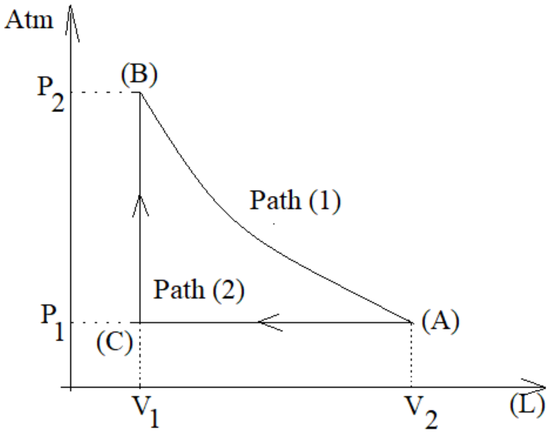


Figure II.1: PV diagram showing two paths

Mathematically, this means that the change in internal energy (ΔU) between two states is the same, regardless of the process (e.g., isothermal, adiabatic, isobaric, isochoric) (Figure).

II.1.c) Total exact differential

Since internal energy is a state function, it can be expressed as an exact differential:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \text{(II.4)}$$

For an exact differential, the mixed partial derivatives are equal:

$$\frac{\partial^2 U}{\partial T \partial V} = \frac{\partial^2 U}{\partial V \partial T} \qquad \text{(II.5)}$$

Application 1:

Let's take the example for exact differential: $dF(x,y)=(2xy)dx+(x^2)dy$

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

Since: $(2xy)\,dx+(x^2)\,dy$ satisfies the condition for equality of mixed partial derivatives, it represents an exact differential. Therefore, $F(x,y)$ is a well-defined state function.

Take a second example for an inexact differential: $\delta f = ydx - xdy$

$$\frac{\partial^2 f}{\partial x \partial y} = 1 \text{ and } \frac{\partial^2 f}{\partial y \partial x} = -1$$

When the differential of a quantity does not correspond to the total differential of a state function, it is said to be an inexact differential. This is like heat and work, they are not state functions.

II.1.d) Case of a cycle

A thermodynamic cycle is a series of processes that transfer energy as heat and work to return a system to its initial state**.** These cycles are fundamental in engines, refrigerators, power plants, and many industrial applications.

A thermodynamic cycle operates within a closed system, meaning no mass enters or leaves the system, but energy (heat and work) can be exchanged with the surroundings. After completing the cycle, the system returns to its initial thermodynamic state, meaning all state variables (pressure, volume, temperature, internal energy) are restored to their original values. During the cycle, heat (Q) is transferred into or out of the system, and work (W) is done by or on the system. Since internal energy is a state function, the change in internal energy over a complete cycle is zero (Figure 2):

$$\Delta U_{cycle} = Q_{cycle} + W_{cycle} = 0 \quad \text{(II.6)}$$

This equation implies that in a closed system undergoing a thermodynamic cycle**,** any work (W) performed by the system must be exactly balanced by an equivalent amount of heat (Q).

This indicates that if the system performs work on its surroundings, it must absorb an equivalent amount of heat to maintain energy conservation. Conversely, if the system requires work to operate, it will release the same amount of heat to the surroundings. Thermodynamic cycles are split into two primary classes – refrigeration cycles (also known as heat pump cycles) and power cycles such as the combustion engine cycle. Cycles which transfer heat from low temperature to high temperature are classified as heat pump cycles, whereas cycles that convert heat input into mechanical work are designated as power cycles. And so, not inappropriately, thermodynamic power cycles provide the foundation for the operation of a heat engine. Power cycles are then further divided into groups depending on the type of heat engine. For cycles modeling internal combustion engines the groups are the Otto, Diesel, and Brayton cycles and for external combustion engines, they are the Rankine, Organic Rankine, and Kalina cycles.

If we consider two successive processes:

$$A \rightarrow B$$

$$B \rightarrow A$$

represented by the two associated curves (Figure II.2), then for the complete cycle we have:

$$W_{cycle} = W_{1AB} + W_{2BA}$$

By comparing the areas:

$$|W_{1AB}| > |W_{2BA}|$$

From an algebraic perspective:

$$W_{1AB} < 0 \text{ and } W_{2BA} > 0.$$

Therefore, for the overall cycle: $W_{cycle} < 0.$

The work exchanged by a system over a cycle is:

- **Negative** when the cycle is traversed in the clockwise direction;
- **Positive** when the cycle is traversed counterclockwise.

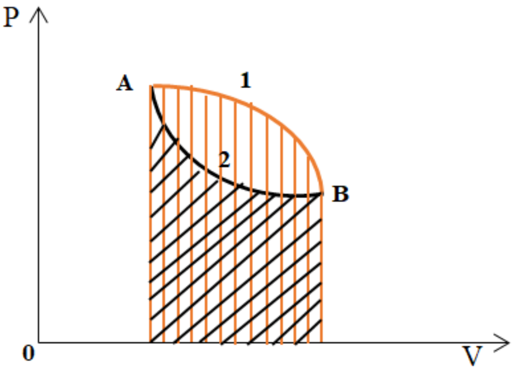


Figure II.2: Thermodynamic simple cycle

II.1.e) Case of an isolated system

In an isolated system, the internal energy remains constant because an isolated system does not exchange energy (heat or work) or matter with its surroundings. This is a direct consequence of the First Law of thermodynamics. This means that:

$$Q = 0 \text{ (no heat transfer)},$$

$$W = 0 \text{ (no work done)}.$$

Thus, the change in internal energy in an isolated system: $\Delta U = 0$

II.2. Notion of enthalpy

The notion of enthalpy is a fundamental concept in thermodynamics, particularly useful for analyzing processes occurring at constant pressure. Below, we'll discuss the expression and differential form of enthalpy, as well as the transformations at constant volume (Q_V) and constant pressure (Q_P).

Expression and differential form of H

Enthalpy is a thermodynamic property defined as the sum of the internal energy (U) of a system and the product of its pressure (P) and volume (V):

$$H = U + PV \quad \text{(II.7)}$$

Since the enthalpy is a state function, its differential form is total exact can be derived using the first law of thermodynamics. For a reversible process, the first law is:

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

Enthalpy is an extensive property and is proportional to the size of the system. For a doing only PV work: $\delta W = -PdV \quad \text{(II.8)}$

Substituting this into the first law:

$$dU = \delta Q - PdV \qquad (II.9)$$

Now take the differential of the enthalpy definition:

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

Substitute dU in the equation above:

$$dH = \delta Q - PdV + PdV + VdP = \delta Q + VdP \qquad (II.10)$$

II.3.Transformations at constant volume and constant pressure: Q_V and Q_P

II.3.a) Transformations at constant pressure (Q_P)

For a process at constant pressure ($dP = 0$): $dH = \delta Q_p$

This shows that the change in enthalpy (dH) is equal to the heat exchanged between the system and the surrounding at constant pressure (δQ_p).

Integration yields: $\Delta H = Q_p$ (II.11)

II.3.b) Transformations at constant volume (Q_V)

At **constant volume** ($dV=0$), no PV-work is done ($\delta W=0$).

From the first law: $dU = \delta Q_V$ (II.12)

Here, δQ_V is the heat exchanged with the surrounding at constant volume.

Integration yields: $\Delta U = U_f - U_i = Q_V$

II.4. Application of the first law to an ideal gas

The application of the first law of thermodynamics to an ideal gas involves analyzing how energy (in the form of heat and work) is exchanged and how the internal energy of the gas changes.

II.4.1) Joule’s Law

Joule’s Law is a specific result derived from analysis above, which describes the behavior of the internal energy of an ideal gas. Joule’s experiment is a classic experiment conducted by James Prescott Joule in the 19th century to study the relationship between heat, work, and the internal energy of gases (Figure II.3). This experiment played a crucial role in establishing the first law of thermodynamics and provided experimental evidence for Joule’s Law, which states that the internal energy of an ideal gas depends only on its temperature.

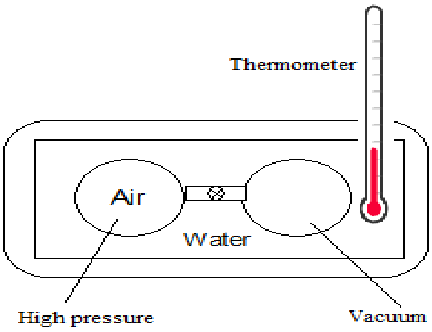


Figure II.3: Joule's experiment

In his classical experiment, Joule submerged two tanks connected with a pipe and a valve in a water bath, as shown in Fig. Initially, one tank contained air at a high pressure and the other tank was evacuated. When thermal equilibrium was attained, he opened the valve to let air pass from one tank to the other until the pressures equalized. Joule observed no change in the temperature of the water bath and assumed that no heat was transferred to or from the air. Since there was also no work done, he concluded that the internal energy of the air did not change even though the volume and the pressure changed. Therefore, he reasoned, the internal energy is a function of temperature only and not a function of pressure or specific volume. (Joule later showed that for gases that deviate significantly from ideal-gas behavior, the internal energy is not a function of temperature alone.)

Mathematically this can be expressed by following equations:

The air is considered as a given amount of ideal gas obeying the ideal gas law, $PV = nRT$. The first law of thermodynamics: $\Delta U = U_f - U_i = W + Q = 0$ (no heat exchanged and no work is done). The internal energy , $U = F(P,V,T)$ is the same before and after the expansion : $U_f = U_i$, this means that $P_1V_1 = P_2V_2 =$ Constant , then $U = F(PV,T) = U(T)$.

The same conclusion applies to enthalpy, which is defined as: $H=U+PV$

- For an ideal gas, the equation of state gives $PV=nRT$. Substituting this into the enthalpy definition: $H = U + nRT$
- Since the internal energy U of an ideal gas depends only on temperature T, and nRT is also solely a function of T, it follows that: $H = H(T)$
- Therefore, for an ideal gas, enthalpy is a function of temperature only.

II.4.2) Specific heats

The specific heat capacity at constant volume, Cv, and the specific heat capacity at constant pressure, Cp, play an important role in chemical thermodynamics.The specific heat is defined as the energy required raising the temperature of a unit mass of a substance by one degree. In thermodynamics, there are two kinds of specific heats: specific heat at constant volume c_v and specific heat at constant pressure c_p. The specific heat at constant volume can be viewed as the energy required raising the temperature of the unit mass of a substance by one degree as the volume is maintained constant.

$$c_v = \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{(II.13)}$$

This implies the change in internal energy with temperature at constant volume.

$$dU = c_v(T)dT \Rightarrow U_f - U_i = \Delta U = \int_i^f c_v(T)dT \qquad \text{(II.14)}$$

The specific heat at constant pressure can be viewed as the energy required raising the temperature of the unit mass of a substance by one degree as the pressure is maintained constant.

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p \Rightarrow dH = c_p(T)dT \Rightarrow H_f - H_i = \Delta H = \int_i^f c_P(T)dT \qquad \text{(II.15)}$$

II.4.3) Mayer's relation

Mayer's relation connects the heat capacities C_P and C_V for an ideal gas. It is derived as follows:

- For an ideal gas, the enthalpy is: $H = U + PV$
- Using the ideal gas equation ($PV = nRT$): $H = U + nRT$ (II.16)
- Differentiating with respect to temperature (T):

$$dH = dU + nRdT \Rightarrow \frac{dH}{dT} = \frac{dU}{dT} + nR \qquad \text{(II.17)}$$

- From the definitions of heat capacities C_P and C_V: $C_p = C_v + nR$ (II.18)
- For molar specific heats, this becomes: $C_{P.m} - C_{V.m} = R$ (II.19)

Where:

- $C_{P.m}$: Molar specific heat at constant pressure,
- $C_{V.m}$: Molar specific heat at constant volume,

- R: Universal gas constant.

This is **Mayer's relation**, which shows that C_{Pm} is always greater than C_{Vm} by R for an ideal gas.

For a monatomic ideal gas: at any temperature:

$$Cv = \frac{3}{2}R \quad \text{and} \quad C_p = \frac{5}{2}R$$

For a polyatomic ideal gas: at sufficiently high temperatures

For linear molecules: $C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$

For nonlinear molecules: $C_v = 3R$ and $C_p = 4R$

***Ratio of specific heats (γ)*:**

The ratio of specific heats, γ, is an important parameter in thermodynamics and is defined as:

$$\gamma = \frac{C_P}{C_V} = \frac{C_{P.m}}{C_{V.m}} = \frac{C_{V.m} + R}{C_{V.m}} = 1 + \frac{R}{C_{V.m}}$$

$$C_{P.m} = \frac{\gamma R}{\gamma - 1} \ (18) \quad \text{and} \quad C_{V.m} = \frac{R}{\gamma - 1} \quad (II.20)$$

The specific ratio also varies with temperature, but this variation is very mild. For monatomic gases, its value is essentially constant at 5/3. Many diatomic gases, including air, have a specific heat ratio of about 7/5 at room temperature.

- ***Heat capacities of solids and liquids***

It can be mathematically shown (Table II.12) that the constant-volume and constant-pressure specific heats are identical for incompressible substances. Therefore, for solids and liquids, the subscripts on C_p and C_v can be dropped, and both specific heats can be represented by a single symbol c. That is, $C_p = C_v = C$.

By denoting C as the common value of the two heat capacities, it is therefore possible to write the relation for both states of matter : dH = dU = C.dT

Table II.12: Specific heat capacities of some substances in J/(K.Kg)

Glace	2100
Lead	129.5
Silver	236
Ethanol	2424
Water	4185
Ethanoic acid	2058

At low pressures, all real gases approach ideal-gas behavior, and therefore their specific heats depend on temperature only.

II.4.3) Different types of transformations

A transformation refers to the evolution of a system caused by a change in at least one state variable. The system moves from an initial state to a final state. Different types of transformations are identified depending on how the state variables (temperature, pressure, and volume) evolve, as well as on the nature of heat exchange.

The main types of thermodynamic transformations are:

- ***Isothermal transformation***: occurs at constant temperature ($\Delta T = 0$).
- ***Isobaric transformation***: occurs at constant pressure ($\Delta P = 0$).
- ***Isochoric (or isovolumetric) transformation***: occurs at constant volume ($\Delta V = 0$).
- ***Adiabatic transformation***: occurs without heat exchange with the surroundings ($Q = 0$).

➢ **For reversible transformations**

Process calculations provide work and heat quantities. The work of a mechanically reversible closed-system process is given by Eq. (II.21), here written:

$$dW = -P_{gas}\,dV \quad \text{(II.21)}$$

With, $P_{sys} = P_{gas} = P_{ext}$

For the ideal-gas state in any closed-system process, the first law of thermodynamic can be written as: $\delta Q + \delta W = C_V\,dT = n\,C_{V.m}\,dT$

Substitution for dW by Eq. (II.21) and solution for dQ yields an equation valid for the ideal-gas state in any mechanically reversible closed-system process:

$$dQ = C_V\,dT + PdV \quad \text{(II.22)}$$

A)For an isothermal transformation:

$$\Delta U = \Delta H = 0$$

$\delta Q = -\delta W = P_{gas}\,dV$, with $P = nRT / V$, $W = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$

$$Q = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

B)For isobaric transformations:

The process takes place at a constant pressure (P = constant).

During this transformation, the volume changes, and the expression for the work is written as:

$\delta W = -P_{ext}\, dV \Rightarrow W = P(V_i - V_f)$, with V_i the initial volume and V_f the final volume.

$$dH = \delta Q = C_p\, dT \Rightarrow \Delta H = Q_p = \int_{T_i}^{T_f} C_p dT$$

The amount of heat can be recalculated from the equation: $Q_p = \Delta U - W$

With $\Delta U = \int_{T_i}^{T_f} c_v(T) dT$

C)For isochoric transformations:

The process takes place at a constant volume (V = constant).

$\delta W = 0 \Rightarrow W = 0$ and $\delta Q_v = dU = C_v\, dT \Rightarrow \Delta U = Q_v = C_v\, \Delta T$

$$dU = c_v(T)dT \Rightarrow U_f - U_i = \Delta U = \int_{Ti}^{Tf} c_v(T)dT$$

And the enthalpy change: $\Delta H = \int_{T_i}^{T_f} C_p dT$

D) For adiabatic transformations:

For adiabatic transformation the process occurs without heat transfer with the surrounding (Q = 0).

For an ideal gas undergoing a thermodynamic process, we start with the First Law of Thermodynamics:

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

Here:

- dU is the change in internal energy,
- δQ is the heat exchanged with surrounding,
- δW is the work done by the system.

The internal energy U depends only on temperature (T), and the heat added at constant pressure can be expressed as:

$$\delta Q = nC_{V.m}dT + PdV$$

Using the ideal gas law, PV= nRT, we can express the volume *V* and its differential dV as:

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

$$dV = \frac{nR}{P}\left(dT - \frac{TdP}{P} \right)$$

Substituting dV into the expression for δQ:

$$\delta Q = nC_{V.m}dT + P\left(\frac{nR}{P}\left(dT - \frac{TdP}{P} \right) \right)$$

Simplifying this and using the relationship between the molar heat capacities at constant pressure ($C_{P.m}$) and constant volume ($C_{V.m}$) for an ideal gas:

$$C_{P.m} - C_{V.m} = R$$

We can rewrite δQ as: $\delta Q = nC_{p.m}dT - \frac{nRTdP}{P}$

In a reversible adiabatic transformation**,** Laplace relations describe how an ideal gas exchanges energy internally during reversible adiabatic transformations, where temperature variations result solely from the conversion between internal energy and mechanical work. These relations apply when:

- the gas is ideal,
- the transformation is reversible,
- no heat is exchanged: δQ = 0

They establish relationships between:pressure P, volume V and temperature T.

For a process where δQ = 0, we have: $C_{p.m}dT = \frac{RTdP}{P}$

Dividing both sides by T and $C_{P.m}$: $\frac{dT}{T} = \frac{RdP}{C_{p.m}P}$

Integration with C_{pm} constant gives:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{R}{C_{P.m}}} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} = \left(\frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} \qquad \text{II.23}$$

Where C_{pm} and C_{vm} are molar heat capacities at constant pressure and constant volume , respectively.

For T and V relationship:

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

$\delta Q = nC_{V.m}\ dT + P\ dV$

Using the ideal gas law, PV=nRT, we can express the volume V as:

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

Substituting V into the expression for δQ

$$\delta Q = nC_{V.m}\ dT + \frac{nRT}{V}\ dV$$

For a process where δQ=0 (adiabatic process), we have: $\frac{dT}{T} = -\frac{R}{C_{V.m}}\frac{dV}{V}$

Integration with C_{Vm} constant gives:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V.m}}} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \text{II.24}$$

The last Laplace equation is given by the mathematical analysis:

$nC_{V.m}\ dT = -P\ dV \Rightarrow dT = -\frac{PdV}{n \times C_{V.m}}$

For ideal gas: $PV=nRT \Rightarrow P\ dV+VdP = nRdT$

Then: $PdV+VdP = -R\frac{PdV}{C_{V.m}}$

$With: R = C_{P.m} - C_{V.m}, so \quad PdV+VdP = -(C_{P.m} - C_{V.m})\frac{PdV}{C_{V.m}}$

$PdV+VdP = -(\gamma - 1)\ PdV \Rightarrow -\gamma PdV = VdP \Rightarrow \frac{dP}{P} = -\gamma\frac{dV}{V}$

$\Rightarrow PV^{\gamma} = Constant$ II.25

The two equations (II.23) and (II.24) may also be expressed as:

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

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

All these equations apply for the ideal-gas state with constant heat capacities and are restricted to mechanically reversible adiabatic expansion or compression.

We thus obtain three simple relationships for an ideal gas undergoing a reversible adiabatic process. It is important to note once again that, although by definition no heat is exchanged, the temperature still changes systematically, as shown by the relations (II.23) and (II.24).

The first law for an adiabatic process in a closed system ($\delta Q = 0$) becomes :

$\delta W = dU = nC_{V.m}\ dT$

For constant $C_{V.m}$, $W = \Delta U = nC_{V.m}\Delta T = \frac{nR}{\gamma - 1}\Delta T = \frac{nR}{\gamma - 1}(T_2 - T_1) = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$ Eq. (II.26)

This equation is general for adiabatic compression and expansion processes in a closed system, whether reversible or not, because P, V, and T are state functions, independent of path. However, T_2 and V_2 are usually unknown. Elimination of V_2 from Eq. (II.26) by using the Equation: $P\,V^{\gamma} = \text{const}$, valid only for mechanically reversible processes, leads to the expression:

$$W = \frac{PV}{\gamma - 1}\left[\left(\frac{P}{P}\right)^{\frac{\gamma - 1}{\gamma}} - 1\right] \qquad \text{(II.27)}$$

This equation is valid only for the ideal-gas state, for constant heat capacities, and for adiabatic, mechanically reversible, closed-system processes.

- **For irreversible transformations:**

A) Isothermal irreversible process (Constant temperature, irreversible expansion / compression):

Unlike reversible expansion, where pressure changes infinitesimally, an irreversible expansion occurs against a fixed external pressure ($P_{ext} = P_{final}$).

Work done is given by: $\delta W = -P_{ext}dV \Rightarrow W = -P_{ext}\ (V_f - V_i)$

Since the process is isothermal for an ideal gas: $\Delta U = 0$

Using the first law: $Q = -W = P_{Final}\ (V_f - V_i)$

B) Irreversible isobaric transformation

An irreversible isobaric transformation is a thermodynamic process that takes place at constant pressure: P=constant

while the system evolves under non-equilibrium conditions, such as finite temperature gradients, frictional effects, or rapid evolution of the system.

At constant pressure, the heat exchanged by the system is equal to the enthalpy variation:

$$Q_p = \Delta H$$

The mechanical work associated with the transformation is: $W = -P(V_2 - V_1)$

where:

- V_1 and V_2 are the initial and final volumes.

C) Irreversible Isochoric Transformation

An irreversible isochoric transformation is a process occurring at constant volume:

$$V=\text{constant}$$

Since the volume remains unchanged: $dV = 0$

The mechanical work is zero: $W=0$

Applying the first law of thermodynamics: $\Delta U = Q_v$

D) Adiabatic Irreversible : Expansion against constant external pressure **(**$P_{ext} = P_{final}$)

The process happens so quickly that heat exchange does not occur, but external work is done.

Work done: $W = -P_{ext}(V_f - V_i)$

First law of thermodynamics: $\Delta U = Q + W$

Since $Q = 0$, we get: $\Delta U = W$ and using: $dU = n\, C_{v.m}\, dT$ and $\Delta U = n \int_{Ti}^{Tf} \mathrm{Cv.m}\, dT$

Then : $n \int_{Ti}^{Tf} \mathrm{Cv.m}\, dT = -P_{Final}(V_f - V_i)$

And $\Delta H = n \int_{Ti}^{Tf} \mathrm{Cp.m}\, dT$

E) Comparison between the adiabatic and isothermal curves in Clapeyron coordinates

The slope of a curve representing an isothermal process in Clapeyron coordinates (P-V) is:

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

For an adiabatic process, the slope can be written as:

$$\left(\frac{\partial P}{\partial V}\right) = -\gamma\frac{P}{V}$$

Both curves therefore have negative slopes in Clapeyron coordinates, meaning pressure decreases as volume increases. Since the adiabatic coefficient γ is greater than 1, the slope of the adiabatic curve is steeper (larger in absolute value**)** than that of the isothermal curve at the same point in the Clapeyron diagram.

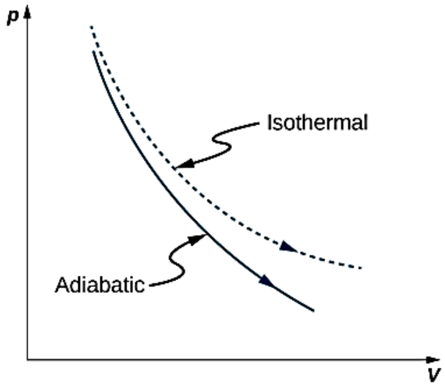


Figure II.4: Quasi-static adiabatic and isothermal expansions of an ideal gas.

Application 2 (Problem statement for multiple processes):

One mole of an ideal gas is contained in a variable-volume vessel that is not thermally insulated from the surroundings. Initially, the gas is at state A, under a pressure P_A= 2 bar and a temperature of 298 K, with a volume V_A.

1. *Experiment 1*: The gas is taken, at constant temperature, to a state B where its pressure is 1 bar and its volume V_B.
2. *Experiment 2*: Starting again from the same initial state A, the gas is cooled at constant volume until its pressure reaches 1 bar (state C). It is then heated at constant pressure until the temperature returns to 298 K.
3. *Experiment 3*: From state A, the gas is heated at constant pressure until it reaches a state D where its volume is equal to that of state B. Then, it is cooled at constant volume until its temperature returns to 298 K.

Tasks:

a) For each experiment, calculate the work W, the heat exchange Q between the system and its surroundings, and the change in internal energy ΔU of the gas.
b) Determine the temperatures of the gas in states C and D.

Solution: It is essential to determine V_A and V_B, which can be easily calculated using the ideal gas law:

$$V_A = 12{,}2\text{ L},\ V_B = 24{,}4\text{ L}$$

All the data obtained from the problem statement and the analysis of the situations are summarized in the graph below (Figure II.4).

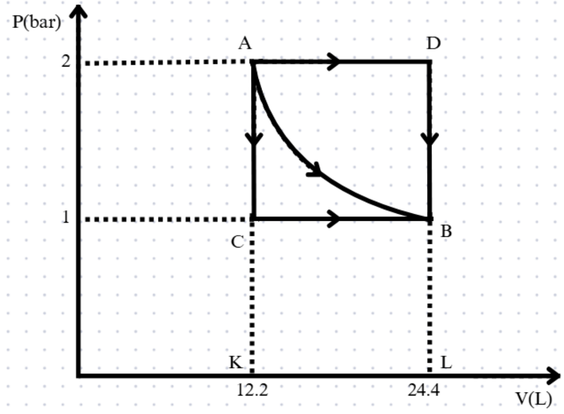


Figure II.4: PV diagram with different paths

Experiment 1 (A → B): An isothermal expansion is carried out, represented in the graph by the curve corresponding to the relation PV=constant. Work is performed by the system since the volume increases against the external pressure while the gas temperature remains constant.

Calculation of the work produced:

$$\delta W = -PdV \Rightarrow W_{AB} = -\int_{V_A}^{V_B} PdV = -\int_{V_A}^{V_B} \frac{RT}{V} dV = -RT\ln\left(\frac{V_B}{V_A}\right) = -8.314\times 298\times\ln 2 = -1.72kJ$$

This work corresponds to the area KABL on the diagram.

Internal energy: $\Delta U_{AB} = Q_{AB} + W_{AB} = 0 \Rightarrow$ heat : $Q_{AB} = -W_{AB} = 1.72kJ$

Experiment 2 (***A*** − ***C*** − ***B***): We carry out two different transformations.

A → C (isochoric) then C → B (isobaric at 1 bar)

From A to C, no work is produced since the volume does not change.

$\Delta U_{AC} = Q_{AC} = C_V\Delta T = -149C_V$ kJ

From C to B, work is done by the system against the constant external pressure of 1 bar. The work is given by: $W_{CB} = -P\,(V_B - V_C) = -10^5\times 12.2\times 10^{-3} = -1.22$ kJ

This work corresponds to the area KCBL on the diagram. The temperature at point C, using the ideal gas law, is $T_C = 149K$.

$\Delta U_{CB} = Q_{CB} + W_{CB} = C_V\Delta T = 149C_V$ kJ $\Rightarrow Q_{CB} = 149C_V - W_{CB}$

$Q_{CB} = (149C_V - 1.22)$kJ

$Q_{Total} = -149C_V + 149C_V - W_{CB} = 1.22$ kJ et $W_{Total} = -1.22$ kJ $\Rightarrow \Delta U_{Total} = 0$

Experiment 3 (***A*** − ***D*** − ***B***): All the work is performed between states A and D. It is given by:

$W_{AD} = -P\,(V_D - V_A) = -2\times 10^5\times 12{,}2.10^{-3} = -2.44kJ$.

This work corresponds to the area KADL on the diagram.

The temperature of the gas in state D is 596 K.

$\Delta U_{AD} = Q_{AD} + W_{AD} = C_V (T_D - T_A) = 298\ C_V \Rightarrow Q_{AD} = \Delta U_{AD} - W_{AD} = 298\ C_V + 2.44$

$W_{DB} = 0$

$\Delta U_{DB} = Q_{DB} + W_{AD} = C_V (T_B - T_D) = -298\ C_V \Rightarrow Q_{DB} = \Delta U_{DB} - W_{DB} = -298\ C_V$

$Q_{Total} = 298 C_V + 2.44 - 298\ C_V = 2.44$ kJ and $W_{Total} = -2.44$ kJ $\Rightarrow \Delta U_{Total} = 0$

Application 3 (Problem statement for adiabatic process):

For air, the measured values are:

c_p (air) = 1005J.kg^{-1} .K^{-1} , c_v (air) = 718 J.kg^{-1} .K^{-}, Rair = 287 J.kg^{-1} .K^{-}, et air = 1,4.

A 200-L compressed-air tank contains air at 40 bar and 50°C. The surrounding atmosphere is at 1 bar.

Task: What is the maximum amount of work that can be extracted from the compressed air without supplying heat?

Solution:

The maximum work will be obtained if the expansion is reversible. Since no heat can be supplied, the best option here is to perform a reversible adiabatic expansion from 40 bar down to 1 bar. We need to calculate the final temperature, because it determines the change in internal energy, and therefore the work lost by the gas. Among the three somewhat intimidating relations, it is the second one that is of interest to us:

$$T\,P^{\frac{1-\gamma}{\gamma}} = \text{const} \quad \text{(II.23)}$$

Thus:
$$\frac{T_B}{T_A} = \left(\frac{P_A}{P_B}\right)^{\frac{1-\gamma}{\gamma}}$$

$$T_B = T_A\left(\frac{P_A}{P_B}\right)^{-\left(\frac{\gamma-1}{\gamma}\right)} = (50+273.15)\left(\frac{40}{1}\right)^{-\left(\frac{1.4-1}{1.4}\right)} = 112.6K = -160.7°C$$

The work performed by the closed system consisting of the gas is therefore:

$W_{AB} = \Delta U_{AB} - Q_{AB} = c_v\Delta T = 718\times(-160.7 - 50) = -151.1$ kJ/Kg

By calculating the mass: $m_A = \dfrac{P_A V_A}{R T_A} = \dfrac{40\times10^5\times0.2}{287\times323.15} = 8.626 Kg$

For a mass m_A , we therefore have:

$$W_{AB} = (-151.1)\times8.626 = -1303388.6\ \text{J} \approx -1.3\text{MJ}.$$

Application 4(Problem for an adiabatic and isothermal expansions):

We consider a diatomic ideal gas with $\gamma = 1.4$. Starting from the same initial state A (P_A=10 bar, V_A=1 L) , the gas undergoes two quasi-static expansions: one isothermal, and the other adiabatic, until it reaches a final volume of V_B=10 L.

Task: Compare the pressures and temperatures obtained in the final state for each case.

Let’s solve it step by step:

Isothermal condition: PV= constant, so:

$$P_B = \frac{P_A V_A}{V_B} = \frac{10 \times 1}{10} = 1 bar$$

For an adiabatic reversible process:

$$\mathrm{P_A}\ \mathrm{V_A^{\gamma}} = \mathrm{P_B}\ \mathrm{V_B^{\gamma}} \Rightarrow \mathrm{P_B} = \frac{\mathrm{P_A}\ \mathrm{V_A^{\gamma}}}{\mathrm{V_B^{\gamma}}} = 10 \times \left(\frac{1}{10}\right)^{1.4} = 0.4 bar$$

Final temperatures:

Isothermal: $T_B = T_A$ (temperature unchanged).

Adiabatic: $TV^{\gamma-1}$ = const, so:

$$\frac{T_B}{T_A} = \left(\frac{V_A}{V_B}\right)^{\gamma-1} = \left(\frac{1}{10}\right)^{1.4-1} = 0.4$$

The final pressure is lower after the adiabatic expansion, which is consistent with the relative positions of the two curves on the Clapeyron diagram. This occurs because, in an adiabatic process, the gas does not exchange heat with its surroundings. As a result, the internal energy decreases during expansion, causing the temperature, and thus the pressure, to drop more sharply than in the isothermal case.

CHAPTER III

The Second Law of Thermodynamics

III.1.Introduction

The **second law of thermodynamics** is a fundamental principle that governs the direction of natural processes. Unlike the **first law**, which deals with energy conservation, the **second law** introduces the concept of irreversibility and entropy. It explains why certain processes, such as heat transfer from a hot body to a cold one, occur spontaneously, while their reverse processes do not happen naturally without external intervention. This law plays a crucial role in defining the efficiency of heat engines, refrigerators, and other thermodynamic systems. It establishes limitations on energy conversion, showing that while energy remains conserved, the **quality** of energy degrades over time due to increased disorder.

III.2.Statement of the principle – Notion of entropy

Entropy (denoted as **S**) is a fundamental thermodynamic property that measures the degree of disorder or randomness within a system. It provides the mathematical foundation for the second law of thermodynamics**.**

Entropy is a state function, meaning it depends only on the current state of the system—not on the path taken to reach that state. It is also an extensive property, so its value depends on the size or quantity of the system.

There are several formulations of the second law of thermodynamics. One general statement is:

- *The entropy of an isolated system never decreases over time.*

A more specific and historically significant formulation comes from *Rudolf Clausius*, a pioneer of thermodynamics:

- *Heat cannot, by itself, flow from a colder body to a hotter one.*

More precisely, this state function can be defined by the principle that:

During any spontaneous transformation, the entropy of the universe (i.e., the system plus its surroundings) increases. The entropy change is zero for a reversible process and positive for an irreversible process.

This can be generalized mathematically as:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur}$$

where:

- ΔS_{univ} is the change in entropy of the universe,
- ΔS_{sys} is the change in entropy of the system,

- ΔS_{sur} is the change in entropy of the surroundings (environment).

This relation expresses the total entropy change of the universe as the sum of the entropy variations of the system and its surroundings.

- For a reversible process: $\Delta S_{univ} = 0$
- For an irreversible process: $\Delta S_{univ} > 0$

The irreversible transformations produce a net increase in the entropy of the universe.

In the International System of Units (SI)**:**

- Entropy is measured in joules per kelvin (J/K**)**.
- Molar entropy (entropy per mole of substance) is expressed in joules per kelvin per mole (J/(K·mol**)**).

III.3.Reversible and irreversible transformations

It is useful to clearly define reversible and irreversible processes in thermodynamics:

- **Reversible process**: A process in which both the system and its surroundings can be returned to their original states without any net change in the universe. It is an idealized transformation that occurs infinitely slowly, allowing the system to remain in thermodynamic equilibrium at every stage. Entropy plays a central role during such processes.
- **Irreversible process**: A process in which it is impossible to restore both the system and the surroundings to their initial states. It leaves a permanent change in the universe, often accompanied by an increase in entropy.

III.3.a.Reversible transformations and entropy concepts

Entropy of a system (ΔS_{system})

Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place.This new property was expressed as the ratio of the reversible heat (Q_{rev}) and the kelvin temperature (T).The term reversible process refers to a process that takes place at such as low rate that it is always at equilibrium and its direction can be changed (it can be “reversed”)by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as irreversible.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$dS = \frac{\delta Q}{T}$$

where

- dS: small change in entropy;
- δQ is the infinitesimal heat exchange in a reversible process, and T is the absolute temperature.

For a finite change, entropy change is:

$$\Delta S = \int_1^2 \frac{\delta Q}{T}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

$$\Delta S_{sys}(rev) = \Delta S_{sys}(irrev)$$

The entropy change of any system and its surroundings, considered together, and resulting from any real process, is positive, approaching zero when the process approaches reversibility.
Mathematically:

$$\Delta S_{total} = \Delta S_{global} = \Delta S_{univers} = \Delta S_{system} + \Delta S_{external} \geq 0$$

The second law affirms that every process proceeds in such a direction that the total entropy change associated with it is positive, the limiting value of zero being attained only by a reversible process. This is because the system and surroundings are in perfect equilibrium, and the entropy gained by one is exactly balanced by the entropy lost by the other.

External medium entropy

- It accounts for the entropy variation in the surroundings due to heat exchange with the system.
- For a reversible process, entropy change of the external medium is equal and opposite to that of the system:

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

$$\Delta S_{system} = -\Delta S_{external}$$

$$\Delta S_{universe} = \Delta S_{total} = 0$$

Example: Reversible isothermal expansion of an Ideal Gas

During a reversible transformation, the entropy of the universe (system + surroundings) remains constant. This is because a reversible process is idealized as occurring infinitely slowly, with the system always in equilibrium with its surroundings. Let's explore this concept using the following example:

- An ideal gas undergoes a reversible isothermal expansion at a constant temperature T.
- The gas expands from an initial volume V_1 to a final volume V_2.
- The process is carried out slowly to maintain equilibrium with the surroundings.
- The gas absorbs heat Q from the surroundings to maintain constant temperature.
- The work done by the gas is:

$$W = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

- Since internal energy (U) of an ideal gas depends only on temperature and temperature is constant ($\Delta U=0$), then:

$$Q = -W$$

- The heat absorbed by the gas is equal to the absolute value of the work done by the gas during expansion.

$$Q = -W = nRT\ln\left(\frac{V_2}{V_1}\right)$$

The entropy change of the system due to heat absorption is:

$$\Delta S_{sys} = \Delta S_{gas} = \frac{Q_{rev}}{T} = nR\ln\left(\frac{V_2}{V_1}\right)$$

where:

- n : number of moles of gas,
- R : universal gas constant,
- V_2 : final volume,
- V_1 :initial volume.

Since $V_2 > V_1$, $\Delta S_{system} > 0$. This means the entropy of the gas increases as it expands.

- The heat absorbed by the system is given up by the surroundings. Since the process is reversible, the surroundings lose the exact same amount of heat:

$$Q_{\text{gas}} = -\ Q_{\text{suroundings}}$$

The entropy change of the surroundings is:

$$\Delta S_{\text{suroundings}} = -\frac{Q}{T} = -\,nR\ln\left(\frac{V_2}{V_1}\right)$$

This is negative because the surroundings lose heat.

The total entropy change of the universe is the sum of the entropy changes of the system and the surroundings:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Substituting the expressions of the change in both system and the suroundings:

$$\Delta S_{\text{universe}} = nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_2}{V_1}\right) = 0$$

In a reversible transformation, the entropy of the universe remains constant because any increase in the entropy of the system is exactly balanced by a decrease in the entropy of the surroundings.

III.3.b.Irreversible transformations and entropy concepts

In irreversible transformation and according to the second law of thermodynamics, in any spontaneous (irreversible) process, the total entropy of the universe (system + surroundings) always increases. Let’s explore this concept using the example of the irreversible isothermal compression of an ideal gas.

Let’s revisit the isothermal expansion of an ideal gas, but this time consider it done in an irreversible way. We’ll compare it to the reversible process and analyze the entropy changes for the system, surroundings, and the universe.

- An ideal gas undergoes an irreversible isothermal expansion at a constant temperature T.
- The gas expands against a constant external pressure P_{ext} (which is less than the pressure of the gas) from an initial volume V_1 to a final volume V_2.
- The process is rapid and not in equilibrium, leading to energy dissipation (e.g., heat loss).

Since the entropy is a state function, meaning it depends only on the initial and final states of the system, not on the path taken to get from one state to the other. This property allows us to equate the change in entropy for a reversible process to the change in entropy for an irreversible process, as long as the initial and final states are the same.

$$\Delta S_{sys}(rev) = \Delta S_{gas}(rev)=\Delta S_{gas}(irrev)= \frac{Q_{rev}}{T} = nR\ln\left(\frac{V_2}{V_1}\right)$$

In an irreversible process:

- The gas does work against the external pressure P_{ext} ($P_{gas} > P_{ext}$), and heat Q is absorbed from the surroundings to maintain constant temperature.
- The work done by the gas is:

$$W_{irr} = -P_{ext}(V_2-V_1) = -P_{final}(V_2-V_1)$$

- The heat absorbed by the gas is equal to the work done (since $\Delta U=0$ for an isothermal process):

$$Q_{irr} = -W_{irr} = P_{ext}(V_2-V_1) = P_{final}(V_2-V_1)$$

- The surroundings lose this same amount of heat Q to the gas.

  The entropy change of the surroundings is:

$$\Delta S_{suroundings} = -\frac{Q_{irr}}{T} = -P_{ext}\ (V_2-V_1)$$

Since $V_2 > V_1$, $\Delta S_{surroundings} < 0$.

The change in entropy of the surroundings differs from that in reversible process because heat exchange occurs differently in reversible and irreversible processes.

The total entropy change of the universe is the sum of the entropy changes of the system and the surroundings:

$$\Delta S_{universe} = \frac{nRT\ln\left(\frac{V_2}{V_1}\right)}{T} - \frac{P_{ext}\ (V_2-V_1)}{T}$$

Since $\Delta S_{system} > 0$ and $\Delta S_{surroundings} < 0$, the total entropy change of the universe depends on the magnitudes of these terms. Since $P_{ext} < P_{gas}$ ($P_{ext} = P_{final}$), $Q_{irrev} < Q_{rev}$. Then, for an irreversible process, the increase in the entropy of the system always outweighs the decrease in the entropy of the surroundings, so: $\Delta S_{universe} > 0$. The total entropy of the universe increases in an irreversible process .The tendency for the total entropy change of the universe **(ΔS_{total})** to increase is a general rule for all irreversible transformations**.** This is a direct consequence of the second law of thermodynamics. This requirement is taken into account by writing the entropy balance for both the system and its surroundings, considered together, and by including an entropy-generation term to account for the irreversibilities of the process. The increase of entropy principle does not imply that the entropy of a system cannot decrease. The entropy change of a system can be negative during a process (Fig. 7–8), but entropy generation (or creation) cannot. The increase of entropy principle can be summarized as follows:

- $\Delta S_{created} > 0$:for irreversible process
- $\Delta S_{created} = 0$:for reversible process
- $\Delta S_{created} < 0$:for impossible process

The entropy created in an irreversible process is often described as being inherent or produced within the system. This is formalized in non-equilibrium thermodynamics:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

$$\Delta S_{system} = \Delta S_{exchanged} + \Delta S_{created}$$

$$\Delta S_{universe} = \Delta S_{exchanged} + \Delta S_{created} + \Delta S_{surroundings}$$

$$\text{Knowing that, } \Delta S_{exchanged} = -\Delta S_{surroundings}$$

$$\text{Hence, } \Delta S_{universe} = \Delta S_{created}$$

In a **reversible process**:

$$\Delta S_{universe} = \Delta S_{created} = 0$$

In an **irreversible process**:

$$\Delta S_{universe} = \Delta S_{created} > 0$$

$$\Delta S_{system} = Q_{sys\ (irre)} / T + \Delta S_{created} \quad \text{with} \quad \Delta S_{created} > 0$$

The entropy variation of the system is therefore greater than the exchanged entropy

$$\Delta S_{system} > Q_{sys\ (irre)} / T$$

This increase in entropy reflects intrinsic internal irreversibilities like:

- Friction
- Viscosity
- Finite temperature gradients
- Unrestrained expansion
- Electrical resistance
- Chemical reaction kinetics

➢ Real-World Examples

Irreversible Process	What Happens	Why Entropy Increases
Heat flows from hot to cold	Energy spreads out	Greater disorder in cold reservoir
Mixing two gases	Molecules distribute randomly	More microstates available
Combustion	Chemical energy → heat and work	Energy disperses in surroundings
Stretching a rubber band quickly	Generates heat	Energy partially wasted, disordered motion

Why is entropy creation inherent***?***

Because entropy is a state function, its change doesn't depend on the path, *but* the entropy produced during a process *does depend* on how the process occurs.

- **Reversible path**: Entropy created = 0
- **Irreversible path**: Entropy created > 0

This "created" entropy cannot be eliminated — it's a natural consequence of how real systems operate. It's a manifestation of the Second Law, which states:

"*The entropy of the universe tends to increase*"

Some remarks about entropy

In light of the preceding discussions, we draw the following conclusions:

1. Processes can occur in a certain direction only, not in any direction. A process must proceed in the direction that complies with the increase of entropy principle, that is, $\Delta S_{created} \geq 0$. A process that violates this principle is impossible. This principle often forces chemical reactions to come to a halt before reaching completion.

2. Entropy is a non-conserved property, and there is no such thing as the conservation of entropy principle. Entropy is conserved during the idealized reversible processes only and increases during all actual processes.

3. The performance of engineering systems is degraded by the presence of irreversibilities, and entropy generation is a measure of the magnitudes of the irreversibilities present during that process. The greater the extent of irreversibilities, the greater the entropy generation. Therefore, entropy generation can be used as a quantitative measure of irreversibilities associated with a process. It is also used to establish criteria for the performance of engineering devices.

Application 1:

A heat source at 800 K loses 2000 kJ of heat to a sink at :

(a) 500 K

(b) 750 K.

Determine which heat transfer process is more irreversible.

Response:

Heat is transferred from a heat source to two heat sinks at different temperatures. The heat transfer process that is more irreversible is to be determined. The entropy change for each reservoir can be determined from Eq. 7–6 since each reservoir undergoes an internally reversible, isothermal process. (a) For the heat transfer process to a sink at 500 K:

$\Delta S_{source} = Q_{source} / T_{source} = -2000 / 800 = -2.5$ kJ/K

$\Delta S_{sink} = Q_{sink} / T_{sink} = -2000 / 500 = 4$ kJ/K

and

$\Delta S_{Total} = \Delta S_{created} = \Delta S_{source} + \Delta S_{sink} = -2.5 + 4 = 1.5$ kJ/K

(b) Repeating the calculations in part (a) for a sink temperature of 750 K, we obtain

$\Delta S_{source} = -2.5$ kJ / K

$\Delta S_{sink} = 2.7$ kJ / K

and $\Delta S_{created} = \Delta S_{Total} = (-2.5 + 2.7) = 0.2$ kJ / K

The total entropy change for the process in part (b) is smaller, and therefore it is less irreversible. This is expected since the process in (b) involves a smaller temperature difference and thus a smaller irreversibility.

➢ Application of the second law to isolated systems

A system is said to be *isolated* when it exchanges neither matter nor energy with its surroundings. In such a case:

$$Q_{exchanged} = 0 \quad \text{which means} \quad \Delta S_{exchanged} = 0$$

Therefore, the change in entropy of the system is entirely due to entropy *created within* the system:

$$\Delta S_{system} = \Delta S_{created} \geq 0$$

- Reversible process: $\Delta S_{created} = 0$
- Irreversible process: $\Delta S_{created} > 0$

In conclusion, for isolated systems, entropy either increases or remains constant. It can never decrease. This reflects the natural tendency of isolated systems to evolve toward thermodynamic equilibrium, which is accompanied by an increase in disorder or randomness (entropy).

III.4. Calculation of entropy variations in the case of ideal gases

For the four known transformations:

For an ideal gas undergoing reversible transformations, the entropy change can be calculated for the following four classical processes:

1. Isothermal Transformation (T = constant): $\Delta S = nR\ln(V_2/V_1) = nR\ln(P_1/P_2)$
2. Adiabatic Transformation (Q = 0): $\Delta S = 0$
3. Isochoric Transformation (V = constant): $\Delta S = n\,C_v \ln(T_2/T_1)$
4. Isobaric Transformation (P = constant): $\Delta S = n\,C_p \ln(T_2/T_1)$

Where:

- n: number of moles
- R: ideal gas constant
- C_v: molar heat capacity at constant volume
- C_p: molar heat capacity at constant pressure
- T_1,T_2: initial and final temperatures
- V_1,V_2: initial and final volumes
- P_1,P_2: initial and final pressures

III.5.Study of the Carnot cycle

The Carnot cycle is an idealized, fully reversible thermodynamic process. This cycle is described by dithermal machine in conjunction with two thermostats.It consists of four internally reversible steps: two isothermal processes and two adiabatic processes, arranged in an alternating sequence. Figure III.2 shows the P–V diagram of a Carnot power cycle in which the system is a gas in a piston–cylinder assembly. The piston and cylinder walls are non-conducting. The heat transfers are in the directions of the arrows. Also note that there are two reservoirs at temperatures T_H (hot heat source) and T_C (cold heat source), respectively, and an insulating stand. Initially, the piston–cylinder assembly is on the insulating stand and the system is at state 1, where the temperature is T_C. The four processes of the engine cycle are:

Process 1–2: The assembly is placed in contact with the reservoir at T_H. The gas expands isothermally while receiving energy Q_H from the hot reservoir by heat transfer.

Process 2–3: The assembly is again placed on the insulating stand and the gas is allowed to continue to expand adiabatically until the temperature drops to T_C.

Process 3–4: The assembly is placed in contact with the reservoir at T_C. The gas is com pressed isothermally to state 4 while it discharges energy Q_C to the cold reservoir by heat transfer.

Process 4–1: The gas is compressed adiabatically to state 1, where the temperature is T_H.

At the end of the fourth stage, the gas has returned to its original state and the cycle can be repeated as many times as needed.

Note: A heat engine cycle is represented in the *clockwise* direction on both the Clapeyron (P–V) diagram and the entropy (T–S) diagram. Therefore, it is a cycle for which the work done by the system is negative ($W < 0$), meaning the system delivers work to the surroundings. The **inverse** (counterclockwise) direction on the Clapeyron (P–V) or entropy (T–S) diagram represents a reversed cycle, such as that of a refrigerator or heat pump.

III.5.1.Operating principle of a two-temperature heat engine (Carnot power cycle principle) (Figure III.1):

This type of engine is a thermal machine that:

- Effectively produces work ($W_{cycle} < 0$),
- Receives heat from a hot reservoir ($Q_H > 0$) ,
- Releases heat to a cold reservoir ($Q_C < 0$).

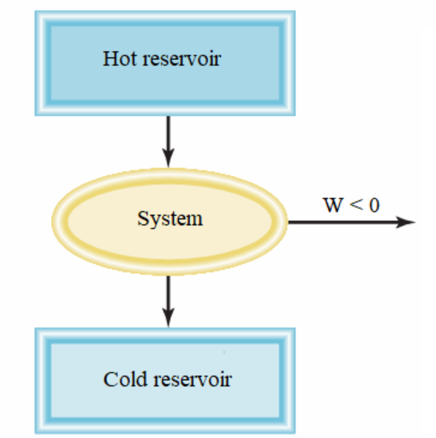


Figure III.1: Carnot power cycle schematic principle

For each of the four internally reversible processes of the Carnot cycle, the work can be represented as an area on Figure III.2.

- In (AB), the process is reversible isothermal gas expansion. In this process, the amount of heat absorbed by the ideal gas is Q_H from the heat source at a temperature of T_H. The gas expands and does work on the surroundings.
- In (BC), the process is reversible adiabatic gas expansion. Here, the system is thermally insulated, and the gas continues to expand and work is done on the surroundings. Now the temperature is lower, T_C.
- In (CD), the process is a reversible isothermal gas compression process. Here, the heat loss Q_C occurs when the surroundings do the work at temperature T_C.
- In (DA), the process is reversible adiabatic gas compression. Again the system is thermally insulated. The temperature again rises back to T_H as the surroundings continue to do their work on the gas.

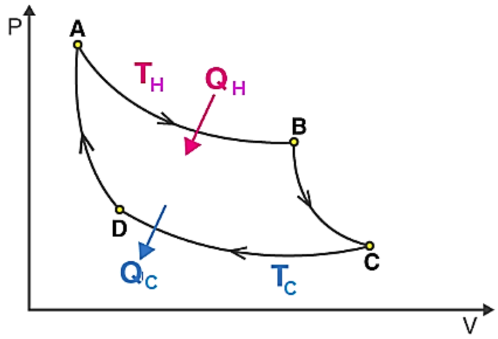


Figure III.2 : P–V diagram of a Carnot power cycle

Figure III.3 provides details of how the cycle is executed.

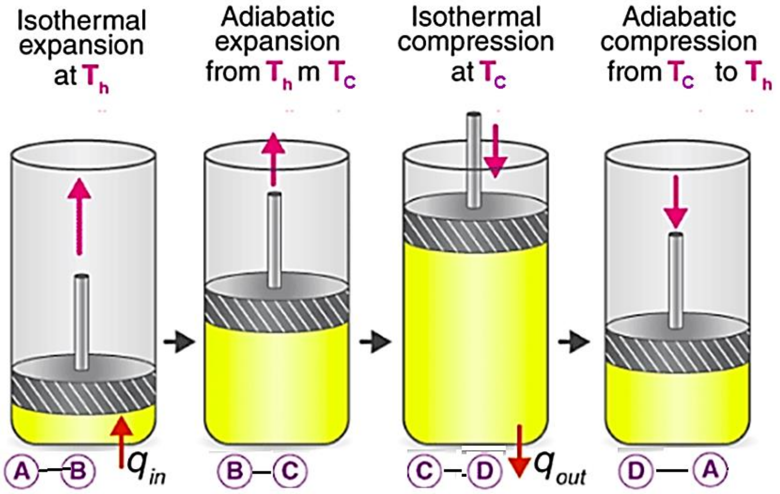


Figure III.3: Carnot power cycle executed by a gas in a piston–cylinder assembly.

III.5.2.Cycle efficiency for Carnot reversible power cycle (diathermal power cycle)

As shown in the P-V diagram of the Carnot power cycle (Figure III.2), in isothermal processes, $\Delta U = \Delta H = 0$ because $\Delta T=0$. In adiabatic processes, $Q = 0$. Work, heat, ΔU, and ΔH of each process in the Carnot cycle are determined as follows:

In the two isothermal processes (AB and CD) we have:

For process AB:

$$Q_{AB} = -W_{AB} = nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

For process CD:

$$Q_{CD} = -W_{CD} = nRT_C \ln\left(\frac{V_D}{V_C}\right)$$

In the two adiabatic processes (BCand DA) we have:

For process BC:

$$\Delta U_{BC} = W_{BC} = nC_v(T_C - T_H)$$

$$\Delta H_{BC} = nC_p(T_C - T_H)$$

For process DA:

$$\Delta U_{DA} = W_{DA} = nC_v(T_H - T_C)$$

$$\Delta H_{DA} = nC_p(T_H - T_C)$$

Full cycle: $Q_{cycle} = -W_{cycle} = nRT_H \ln\left(\frac{V_B}{V_A}\right) + nRT_C \ln\left(\frac{V_D}{V_C}\right)$

III.5.3. The temperature - entropy (T-S) diagram

The T-S diagram of the Carnot cycle is shown in Figure III.4. In the isothermal processes $\Delta T=0$. In the adiabatic processes, $\Delta S= 0$ because $Q = 0$. ΔS of each process in the Carnot engine cycle is determined as follows:

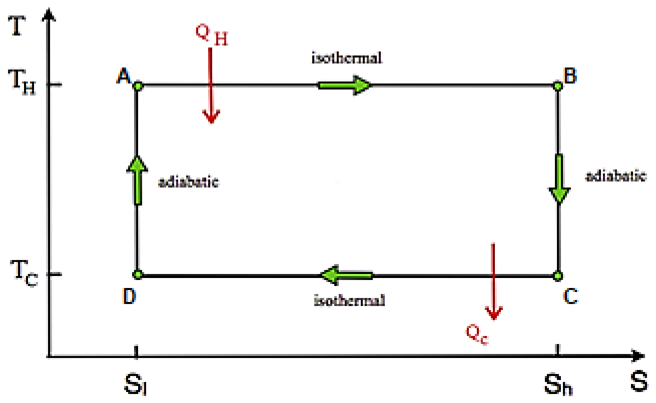


Figure III.4:T-S diagram

- In isothermal expansion (AB): the gas absorbs heat Q_H from a hot reservoir at temperature T_H
- Therefore, the increase in entropy is:

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

- In isothermal compression (CD): the gas transfers heat Q_C to a cold reservoir at temperature T_C.
- Therefore, the decrease in entropy is:

$$\Delta S_{CD} = \frac{Q_C}{T_C}$$

We know that the overall entropy of the system does not change in a cyclic process, therefore:

$$\Delta S_{\text{cycle}} = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA} = 0$$

$$\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0 \Rightarrow \frac{Q_C}{Q_H} = -\frac{T_C}{T_H}$$

The efficiency of a heat engine is given by: $\eta = \frac{useful\ work}{input\ \text{energy}} = \frac{-W_{cycle}}{Q_H}$

Where useful work is $W_{\text{cycle}} = -(Q_H + Q_C)$ $\Rightarrow \eta = \frac{Q_H + Q_C}{Q_H} = 1 + \frac{Q_C}{Q_H}$

Combining with the expression derived above gives: $\eta = 1 - \frac{T_C}{T_H}$

Here are some clear and insightful remarks about the Carnot engine cycle:

- The Carnot cycle represents the maximum possible efficiency that any heat engine operating between two temperature reservoirs can achieve.

- Its efficiency depends only on the temperatures of the hot (T_H) and cold (T_C) reservoirs:
- All processes in the Carnot cycle are internally reversible, meaning no entropy is produced within the system.
- This is an idealization; in reality, no engine can operate in a perfectly reversible manner.
- If a Carnot power cycle is operated in the opposite direction, the magnitudes of all energy transfers remain the same but the energy transfers are oppositely directed. Such a cycle may be regarded as a reversible refrigeration or heat pump cycle.

III.5.4. Refrigerators and heat pumps

We all know from experience that heat is transferred in the direction of decreasing temperature, that is, from high-temperature mediums to low temperature ones. This heat transfer process occurs in nature without requiring any devices. The reverse process, however, cannot occur by itself. The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called refrigerators and heat pumps. Refrigerators and heat pumps operate on the same cycle but differ in their objectives. The objective of a refrigerator is to maintain the refrigerated space at a low temperature by removing heat from it. The objective of a heat pump, however, is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low- temperature source, such as well water or cold outside air in winter, and supplying this heat to the high-temperature medium such as a house.

III.5.4.1. Operating principle of both devices (Heat pumps and Refrigerators): As depected in Figure III.5 both thermal machines:

- Receive work ($W_{cycle} > 0$),
- Deliver heat to a hot reservoir ($Q_H < 0$),
- Absorb heat from a cold reservoir ($Q_C > 0$).

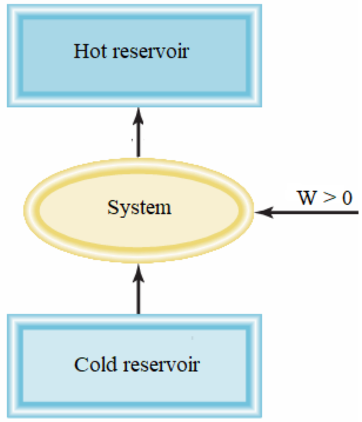


Figure III.5: Work principle for heat pumps and refrigerators

In the case of a refrigerator, the useful energy is the heat transfer Q_C received from the cold source. The efficiency, or the coefficient of performance (COP) of the refrigerator, is given by the following relation:

$$\eta_R = \frac{Q_C}{W_{cycle}} = \frac{T_C}{T_H - T_C}$$

For a heat pump, the useful energy is the heat transfer delivered to the hot source. The coefficient of performance (COP) for the heat pump is given by:

$$\eta_{HP} = -\frac{Q_H}{W_{cycle}} = \frac{T_H}{T_H - T_C}$$

III.6.Mixing entropy

Entropy of mixing refers to the increase in entropy (disorder) when two or more different substances are combined without chemical reaction, especially in ideal systems. It is a direct consequence of the Second Law of Thermodynamics, which favors increased disorder in spontaneous processes. When two different substances are mixed, the number of ways the particles can be arranged (microstates) increases. Since entropy (S) measures the number of accessible microstates, the entropy of the system increases upon mixing.

III.6.1.Cases of gases of the same nature or the different nature

Let’s consider two different ideal gases, Gas A and Gas B, in separate compartments of a rigid, insulated container:

- Each gas has:
  - Number of moles: $n_A = n_B = n$
  - Volume: $V_A = V_B = V$
  - Temperature: T
  - Pressure: $P_A = P_B = P$

They are allowed to mix by removing a partition (no energy exchange with the environment). First Law of Thermodynamics: $\Delta U = W + Q = 0$ (T constant).

Entropy S is a state function, so only the initial and final states matter—not the path.

- Before mixing: each gas is confined to its own volume
- After mixing: each gas expands to occupy the total volume, $V_T = V_A + V_B = 2V$

➡ The change in entropy is the sum of the entropy changes for each gas as they expand irreversibly into the larger volume.

To calculate entropy change for irreversible mixing, we use a reversible path for evaluation:

For a reversible isothermal expansion of an ideal gas:

$$\Delta S_A = \text{nRln}\left(\frac{2\text{V}}{\text{V}}\right) = \text{nRln } 2 > 0$$

$$\Delta S_B = \text{nRln}\left(\frac{2\text{V}}{\text{V}}\right) = \text{nRln } 2 > 0$$

The total system is isolated, so:

$$\Delta S_{\text{created}} = \Delta S_{\text{total}} = \Delta S_{\text{mixture}} = \Delta S_A + \Delta S_B > 0$$

This value is positive, indicating increased disorder.

Remarks

- No heat or work is exchanged, yet entropy increases ⇒ this shows that entropy is not tied to energy exchange alone.
- The increase in entropy arises from the increase in microstates available after mixing.
- Entropy is a state function, so its change is independent of the irreversible nature of the actual process.
- The system reaches a new equilibrium with greater disorder.

III.7.Entropy variations during phase changes

Let us consider the example of the freezing of a liquid, an exothermic process occurring at the transition temperature T_{tr} (a constant temperature), where the system releases heat $Q = \Delta H < 0$. As a result, there is a negative entropy change:

$$\Delta \text{S}_{\text{tr}} = \frac{\Delta H_{tr}}{T_{tr}} < 0$$

This decrease in entropy is associated with an increase in the degree of order, which is exactly what happens when a liquid becomes a solid—the number of accessible microscopic configurations is reduced.

In the case of melting, the process is endothermic, the system absorbs heat $Q = \Delta H > 0$, and

$$\Delta \mathrm{S}_{\mathrm{tr}} = \frac{\Delta H_{tr}}{T_{tr}} > 0$$

Here, entropy increases, and the degree of order decreases**,** since the liquid state has a greater number of accessible configurations than the solid state**.**

III.8.Statistical considerations of entropy

Entropy is a fundamental concept in thermodynamics and statistical mechanics that measures the degree of disorder or randomness in a system. From a statistical perspective, entropy quantifies the number of possible microscopic configurations (microstates) that correspond to a given macroscopic state (microstate). Macroscopic state variables describe the bulk properties of a system, which are measurable and observable (T,P,V….).Microscopic state variables describe the properties of individual particles (atoms, molecules, etc.) in a system (Position, Momentum, Energy ,Velocity, Spin……..).

III.8.1.Notion of disorder

Entropy, a measure of molecular disorder or randomness, can be observed in real-world phenomena such as the melting of ice and the evaporation of water. In these processes, the system's randomness increases, reflecting a rise in entropy.

In the solid phase, such as ice, molecules are arranged in a highly organized crystal structure, allowing little movement. The molecules oscillate around their fixed positions, and their locations can be predicted with relative certainty. As a result, entropy is lowest in the solid phase. When ice melts into water, the molecules become less organized and can move more freely, increasing the system's randomness. This trend continues as water evaporates into vapor, where molecules move even more freely and unpredictably. In the gas phase, molecules move randomly, collide, and change direction, making it extremely difficult to predict their positions.

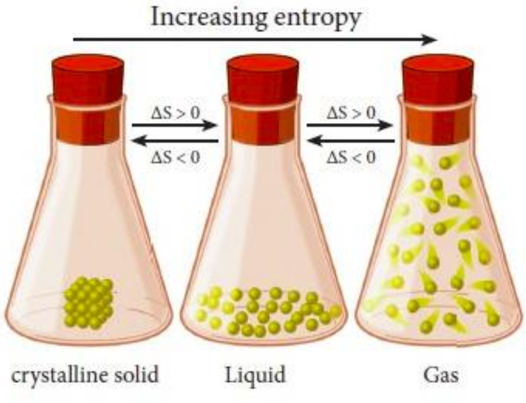


Figure III.6: Increase of disorder in different state of matter

Consequently, entropy is highest in the gas phase. These phase changes (melting and evaporation) are spontaneous processes that result in an increase in molecular disorder and entropy. This relationship is illustrated in Figure III.6, which shows how entropy increases as a substance transitions from solid to liquid to gas.

III.8.2.Boltzmann's relation

Boltzmann's relation, formulated by Ludwig Boltzmann, provides a fundamental connection between entropy (S) and the microscopic states of a system. It is expressed as:

$$S = k_B \ln \Omega$$

where:

- S is the entropy of the system,
- k_B is the Boltzmann constant (1.38×10^{-23} J/K),
- Ω (Omega) is the number of microscopic configurations (or microstates) that correspond to the system's macroscopic state.

At the microscopic level, "disorder" refers to the number of ways (Ω) the particles (atoms, molecules, etc.) of a system can be arranged while maintaining the same macroscopic properties (e.g., temperature, pressure, volume). A system with more possible microscopic configurations (higher Ω) is considered more disordered and has higher entropy.

III.8.3.Nernst's principle and the third law of thermodynamics

Walter Nernst formulated the *Third law of thermodynamics*, which states:

"***The entropy of a perfect crystal approaches zero as the temperature approaches absolute zero.***"

$$\lim_{T\to 0} S = 0$$

This implies that at absolute zero **(**0 K**)**, a perfectly ordered crystalline substance has only one possible microstate (Ω = 1), leading to zero entropy (S = 0).

However, real substances may have residual entropy due to disorder in their atomic or molecular structures.

III.8.4.Absolute entropy

The third law of thermodynamics provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is called absolute entropy, and it is extremely useful in the thermodynamic analysis of chemical reactions. Notice that the entropy of a substance that is not pure crystalline (such as a solid solution) is not zero at absolute zero temperature. This is because more than one molecular configuration exists for such substances, which introduces some uncertainty about the microscopic state of the substance. The entropy change (per mole) associated with heating a pure substance A from the initial temperature of 0 K to a final temperature T at a pressure of 1 bar (standard conditions, at constant pressure) is, according to the third law of thermodynamics, equal to the absolute entropy of the pure substance A at temperature T.

$$\underset{T = 0K}{A(\text{Initial state})} \xrightarrow{\Delta S^0_{0\to T}} \underset{T}{A(\text{Final state})}$$

Taking into account that $\delta Q = C°_p\ dT$ for a reaction at constant pressure, we obtain for this state function (per mole):

$$\Delta S^0_{0\to T} = S^0_{final} - S^0_{Initial} = S^0_T(A) - S^0_0(A) = S^0_T(A) = \int_0^T \frac{C^0_P}{T} dT$$

The same reasoning applies between two non-zero temperatures. Thus, if the entropy of a system is known at a temperature T_1, and it receives a quantity of heat δQ_{rev} to reach a temperature T_2 through a reversible process with no work other than pressure–volume work, we have:

$$S^0_{T_2} = S^0_{T_1} + \int_T^{T_2} \frac{\delta Q_{rev}}{T}$$

And, at constant pressure, with $\delta Q_{rev} = C°_p\, dT$:

$$S^0_{T_2} = S^0_{T_1} + \int_{T_1}^{T_2} \frac{C^0_P dT}{T}$$

If, over the temperature range, $C°_p$ can be considered constant, it follows:

$$S^0_{T_2} = S^0_{T_1} + C^0_P \int_{T_1}^{T_2} \frac{dT}{T} = S^0_{T_1} + C^0_P \ln \frac{T_2}{T_1}$$

If phase changes occur within the temperature range, the heat exchanged during these changes must be taken into account.

Application 2:

Let us calculate the increase in entropy of one mole of CO gas whose temperature rises, at constant pressure, from 100 K to 200 K, given that the molar heat capacity at constant pressure is $Cp°$ (CO)=29.3 J/(mol.K) (assumed constant over the temperature range). We simply write:

$$S^0_{T_2}(CO) = S^0_{T_1}(CO) + C^0_P \int_{T_1}^{T_2} \frac{dT}{T} = S^0_{T_1}(CO) + C^0_P \ln\frac{T_2}{T_1}$$

This results in an entropy increase of: $C_p°\ln 2 = 29.3 \times 0.693 = 20.31$ J/(mol.K).

CHAPTER IV

Application of the first and second laws to chemical reactions – Thermochemistry

IV.1.Introduction

Thermochemistry is a branch of chemistry that studies the heat energy changes associated with chemical reactions and physical transformations. It is based on the principles of thermodynamics. By measuring heat exchanged during reactions, thermochemistry helps us understand whether a process is exothermic (releases heat) or endothermic (absorbs heat), and provides essential data for predicting reaction behavior, designing energy-efficient processes, and studying reaction spontaneity.

IV.2.Thermochemistry related to the first law

IV.2.a) Reaction heats

Reaction heats refer to the amount of heat released or absorbed during a chemical reaction. Depending on the conditions, this heat corresponds to different thermodynamic quantities. At constant volume, the reaction heat equals the change in internal energy, while at constant pressure, it equals the change in enthalpy. This could be essential for understanding energy changes in chemical processes.

IV.2.a.i) Reaction heat at constant pressure and constant volume

➤ **First law of thermodynamics:** $\Delta U = Q + W$

For PV work only ($W = -P\Delta V$):

- At **constant volume (V)**: $W = 0 \Rightarrow Q_V = \Delta U$ soit $\Delta U = U_2 - U_1 = Q_v$

Meaning that at constant volume (Isochoric process) the heat change equals the internal energy change**.**

➢ From the enthalpy relation: $H = U + PV$

We take the total differential of both sides: $dH = dU + d(PV)$

Assuming that P and V are independent variables, the differential of the product is:

$$d(PV) = P\,dV + V\,dP$$

So:

$$dH = dU + PdV + V\,dP$$

Recall the first law of thermodynamics: $dU = \delta Q + \delta W$

$dH = \delta W + \delta Q + PdV + VdP$

For a system where the only work is expansion work, $\delta W = - PdV$, we obtain :

$$dH = \delta Q + VdP$$

For a process at constant pressure, $dP = 0$, and therefore, denoting the heat exchanged at constant pressure as Q_p , we obtain:

$$dH = \delta Q \text{ soit } \Delta H = H_2 - H_1 = Q_p$$

Meaning: At constant pressure**,** the change in enthalpy equals the heat absorbed or released**.**

- **Relation Between ΔH and ΔU:**

The enthalpy **(H)** of a system is defined as: $H = U + PV$

where:

- U : Internal energy
- P : Pressure
- V : Volume

For a change in state (e.g., a chemical reaction), the enthalpy change (ΔH) is:

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

Case 1: Constant Pressure (Isobaric Process)

If pressure is constant (P = constant), then: $\Delta(PV) = P\Delta V$

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

Case 2: Ideal Gases

For ideal gases, $PV = nRT$, so: $\Delta(PV) = \Delta(nRT) = RT\Delta n_g$(if T is constant)

where $\Delta n_g = n(\text{products})\ (\text{gas}) - n(\text{reactants})\ (\text{gas})$

Thus: $\Delta H = \Delta U + \Delta n_g RT$

➢ If Δn_g **= 0** (no change in moles of gas), then: $\Delta H = \Delta U$

Example: $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ ($\Delta n_g=0$)

- If Δng **> 0** (gas moles increase, e.g., decomposition): $\Delta H > \Delta U$

  Example: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ ($\Delta ng = +1$)
- If Δng < 0 (gas moles decrease, e.g., combination): $\Delta H < \Delta U$

Example: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ ($\Delta ng = -2$)

Special case:

For reactions involving only condensed matter (liquids or solids)**,** the change in volume (ΔV) is usually very small, almost negligible, because liquids and solids are nearly incompressible.
Since the relation between enthalpy and internal energy is: $\Delta H = \Delta U + \Delta(PV)$
and at constant pressure: $\Delta(PV) \approx P\Delta V$
Then for condensed phases, $\boldsymbol{\Delta V \approx 0 \Rightarrow}$ $\Delta H \approx \Delta U$**.**

This implies that in solid–state and liquid–phase reactions, the difference between enthalpy change and internal energy change is negligible, so the two can be treated as essentially the same.

- Reaction enthalpy is an extensive state function whose change (ΔH) represents the heat exchanged during a process at constant pressure. Two types of enthalpy are distinguished: exothermic enthalpy and endothermic enthalpy. The table below shows the difference between them with examples.
- ***Exothermic reaction**:* An exothermic reaction is a chemical reaction that releases energy, usually in the form of heat, to its surroundings. As a result, the temperature of the surroundings increases. The enthalpy change (ΔH) is negative because energy is given off.
- ***Endothermic reaction:*** An endothermic reaction is a chemical reaction that absorbs energy from its surroundings, typically in the form of heat. This causes the temperature of the surroundings to decrease. The enthalpy change (ΔH) is positive because energy is taken in.

Reaction type	Sign of ΔH	Examples
Exothermic	$\Delta H < 0$	Combustion, neutralization
Endothermic	$\Delta H > 0$	Photosynthesis, melting ice

Note: The change in enthalpy is very close to the change in internal energy in chemical reactions. The difference between these two quantities becomes significant only at high temperatures.

IV.2.a.ii) Standard state

A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, we will use a subscripted "298" to designate this temperature. Thus, the symbol ($\Delta H°_{298}$) is used to indicate an enthalpy change for a process occurring under these conditions. The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.

For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar; the standard state of solid iron at 500 K is pure iron at 500 K and 1 bar. The standard enthalpy change for a reaction or a physical process is the difference between the products in their standard states and the reactants in their standard states, all at the same specified temperature.

Remarks:

- In reality, each temperature corresponds to a specific standard state. The concept of the standard state of a substance at temperature T does not necessarily mean that the physical state of the substance is the most stable one at that temperature.
- The standard state of a gaseous substance, whether pure or in a mixture, at temperature T is defined as the state of the gas at the same temperature and at a pressure of 1 bar.
- The reference standard state of an element, at temperature T, is the standard state of the simple substance in its most stable physical form at the given temperature.

- For a crystalline solid, this corresponds to the stable allotropic form at the chosen temperature. Example: under normal conditions, graphite is the standard state of carbon, whereas diamond is metastable.

IV.2.a.iii) Standard enthalpy of formation

The fact that standard reaction enthalpies can be derived from other reaction enthalpies provides a very efficient way to tabulate standard enthalpies and calculate values for unknown reactions. Any reaction can be conceptually broken down into two hypothetical steps: first, the decomposition of the reactants into their constituent elements, and second, the formation of the products from these elements. The first step is simply the reverse of forming the reactants from their elements. Therefore, any reaction enthalpy can be expressed in terms of the enthalpies of formation of the substances from their elements. These formation enthalpies are fundamental quantities in thermochemistry.

The enthalpy of formation of a compound is defined as the enthalpy change associated with its synthesis from its constituent elements in their simple, natural forms under atmospheric pressure. At the experimental temperature and atmospheric pressure, the compound formed and the simple elements from which it is derived are considered to be in their so-called standardized or **standard state**. More precisely, this is referred to as the standard enthalpy of formation, denoted at a given temperature $\Delta_f H°_T$.

In thermodynamic tables, standard enthalpies of formation are usually listed at 298 K (Table IV.1). By convention, since enthalpies are defined only up to an arbitrary reference point, the standard enthalpy of formation of any pure element in its standard state is assigned a value of zero. The standard enthalpy of formation of a certain compound, $\Delta_f H^o_T$, is defined as the enthalpy change for the formation of one mole of that compound from its elements in the most stable form under standard conditions (25 °C and 1 bar).

Table IV.1: Example of standard enthalpy of formation at 298 K

Compound	$-\ \Delta_f H^{\circ}_{298K}$ (KJ/mol)
H_2O(gas)	241.8
H_2O(liquid)	285.2
HCl(gas)	1206.9
$CaCO_3$(s)	288.4

C_2H_2(gas)	− 226.7
CH_3OH(liquid)	238.7
FeO(s)	266.1
CO_2(gas)	393.5

For example, the standard enthalpy of formation of CO_2(g) is − 393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$C_s + O_{2(gas)} \rightarrow \mathbf{CO_2}(gas)$$

starting with the reactants at a pressure of 1 bar and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, NO_2(g), $\Delta_f H°$ is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\tfrac{1}{2} N_{2(g)} + O_{2(g)} \rightarrow NO_2(g)$$

A reaction equation with ½ mole of N_2 and 1 mole of O_2 is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, NO_2(g).

Standard enthalpies of formation have the advantage of being combinable to determine the standard enthalpy change of any reaction.

IV.2.b) Determination of reaction enthalpies

Determination of reaction enthalpies involves measuring or calculating the heat change that occurs during a chemical reaction. This can be done experimentally, using calorimetry, or indirectly through thermodynamic principles like Hess's law. Accurate determination of reaction enthalpies is essential for understanding energy flow, assessing reaction feasibility, and designing efficient chemical processes.

IV.2.b.i) Measurement of reaction enthalpies by calorimetry

In direct methods, the heat exchanged during a reaction is measured experimentally using a calorimeter.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature. The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

When measuring heat in chemical processes, the conditions under which the experiment is conducted are crucial. At constant pressure, the heat absorbed or released by the system corresponds directly to the enthalpy change (ΔH). This is the basis of a coffee-cup calorimeter, where reactions are carried out at atmospheric pressure. In contrast, at constant volume, no expansion work is done, so the heat measured is equal to the change in internal energy (ΔU). This principle is applied in a bomb calorimeter, which is commonly used for combustion reactions. Before we practice calorimetry problems involving chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium. If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$Q_M + Q_W = 0$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$Q_M = - Q_W$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that Q_M and Q_W are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, Q_M is a negative value and Q_W is positive, since heat is transferred from M to W.

IV.2.b.ii) Indirect determination of reaction enthalpies (Hess's law)

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes.

Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment. This type of calculation usually involves the use of Hess's law, which states: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish.

Application 1:

For example, we can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The direct process is written by:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta_r H°_{298} = -\,394 kJ/mol$$

In the two-step process, first carbon monoxide is formed:

$$C(s) + ½O_2(g) \longrightarrow CO(g) \qquad \Delta_r H°_{298} = -111 kJ/mol$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO(g) + ½O_2(g) \longrightarrow CO(g) \qquad \Delta_r H°_{298} = -283 kJ/mol$$

The equation describing the overall reaction is the sum of these two chemical changes:

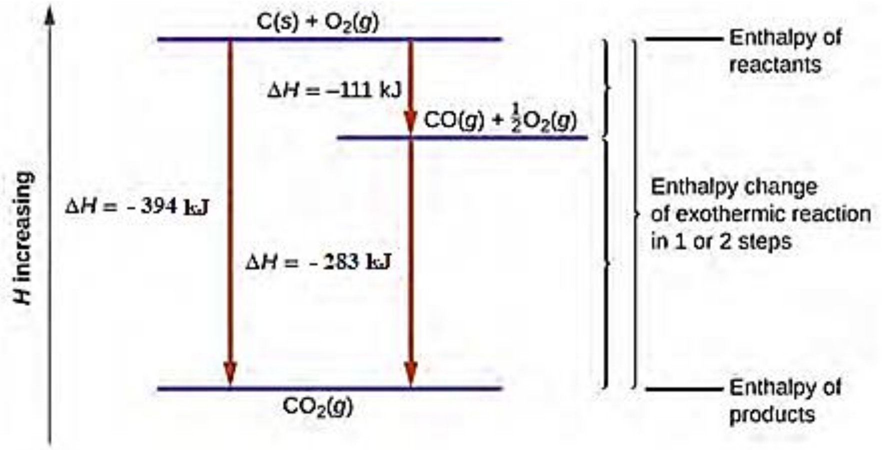
Step 1: $C(s) + ½O_2(g) \longrightarrow CO(g)$
Step 2: $CO(g) + ½O_2(g) \longrightarrow CO_2(g)$
Sum: $C(s) + ½O_2(g) + CO(g) + ½O_2(g) \longrightarrow CO(g)+CO_2(g)$
Because the CO produced in Step 1 is consumed in Step 2, the net change is:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

According to Hess's law, the enthalpy change of the overall reaction will equal the sum of the enthalpy changes of the two steps:

$$\Delta_r H°_{298} = -111 - 283 = -\,394 KJ/mol$$

We can schematized these process by the following diagram (Scheme IV.1):



Scheme IV.1: Enthalpy change in the formation of $CO_2(g)$

The following are two important rules for manipulating thermochemical equations:

1-When a thermochemical equation is multiplied by any factor, the value of ΔH for the new equation is obtained by multiplying the value of ΔH in the original equation by that same factor.

2-When a chemical equation is reversed, the value of ΔH is reversed in sign.

Consider the thermochemical equation for the synthesis of ammonia.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g);\ \Delta H \approx -92\ kJ$$

Suppose you want the thermochemical equation to show what happens when twice as many moles of nitrogen and hydrogen react to produce ammonia. Because double the amounts of substances are present, the enthalpy of reaction is doubled (enthalpy is an extensive quantity). Doubling the previous equation, you obtain :

$$2N_2(g) + 6H_2(g) \rightarrow 4NH_3(g);\ \Delta H \approx -184\ kJ$$

Suppose you reverse the first equation we wrote for the synthesis of ammonia. Then the reaction is the dissociation of 2 mol of ammonia into its elements. The thermochemical equation is :

$$2NH_3 \rightarrow N_2(g) + 3H_2(g)\ ;\ \Delta H \approx 92kJ$$

If you want to express this in terms of 1 mol of ammonia, you simply multiply this equation by a factor of 1/ 2.

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available:

$$\Delta_r H = \sum \upsilon_j \Delta_f H°_j(\text{produits}) - \sum \upsilon_i \Delta_f H°_i(\text{réactifs})$$

υ : Coefficients stœchiométriques ; $\Delta_f H°$: Enthalpie de formation

Application 2:

For example we want to calculate the standard enthalpy change for the reaction:

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

Given data: standard enthalpies of formation (KJ/mol):

$NO_2(g)$: 33.2 , $NO(g)$: +90.2 , $HNO_3(aq)$: − 207.4 , $H_2O(l)$: −285.8

$\Delta_r H° = 2(-207.4 kJ)+1(+90.2\ kJ)-3(+33.2\ kJ)-1(-285.8 kJ) = -138.4\ kJ$

$\Delta_r H° < 0$, this means that heat is released which correspond to exothermic reaction**.**

IV.2.b.iii) Influence of temperature on reaction enthalpy

IV.2.b.iii.1) Kirchhoff's relation

Kirchhoff's Law describes how the enthalpy change (ΔH) of a chemical reaction varies with temperature. It accounts for the heat capacities of reactants and products.

The temperature dependence of ΔH is given by:

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T1}^{T2} \Delta Cp dT$$

where:

- $\Delta H(T_1)$: Enthalpy change at reference temperature (T_1) (usually 298 K).
- $\Delta H(T_2)$: Enthalpy change at new temperature T_2.
- ΔCp: Difference in heat capacities between products and reactants:

$$\Delta Cp = \sum Cp(\text{products}) - \sum Cp(\text{reactants})$$

➢ ***Simplified cases***

(a) If ΔCp is constant (independent of T):

$$\Delta H(T_2) = \Delta H(T_1)+\Delta Cp(T_2-T_1)$$

(b) If ΔCp varies with T (empirical form $Cp = a + bT + c/T^2$):

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T1}^{T2} (a + bT + c/T2)\, dT$$

a, b, and c are empirical parameters independent of temperature

Application 3:

Reaction: $N_2(g)+3H_2(g) \rightarrow 2NH_3(g)$

Given data:

- $\Delta rH°_{298} = -92.2$ kJ / mol
- Cp values (J/mol·K):

  ○ $N_2(g) = 29.1$, $H_2(g) = 28.8$, $NH_3(g) = 35.1$

Step 1: Calculate ΔCp

$\Delta Cp = 2(35.1) - [29.1 + 3(28.8)] = -45.3$ J/mol·K

Step 2: Find $\Delta_r H$ at 400 K (assuming ΔCp constant)

$\Delta_r H°_{400} = -92.2 + (-45.3\times10^{-3})(400-298) = -96.8$ kJ/mol

IV.2.b.iii.2) Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the standard enthalpy of transition and is denoted $\Delta_{tr}H°$. The standard enthalpy of vaporization, $\Delta_{vap}H°$, is one example. Another is the standard enthalpy of fusion, $\Delta_{fus}H°$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta_{fus}H° = 6.01 \text{ Kj/mol}$$

As in this case, it is sometimes convenient to know the standard enthalpy change at the transition temperature as well as at the conventional temperature. Because enthalpy is a state function, a change in enthalpy is independent of the path between the two states.

For example, we can picture the con- version of a solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour), or as occurring in two steps,

$$H_2O(s) \rightarrow H_2O(g) \quad \Delta_{sub}H° = ?$$

first fusion (melting) and then vaporization of the resulting liquid:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta_{fus}H°$$

$$H_2O(l) \rightarrow H_2O(g) \quad \Delta_{vap}H°$$

$$\text{Overall:} \quad H_2O(s) \rightarrow H_2O(g) \quad \Delta_{sub}H° = \Delta_{fus}H° + \Delta_{vap}H°$$

Because the overall result of the indirect path is the same as that of the direct path, the overall enthalpy change is the same in each case (1), and we can conclude that (for processes occurring at the same temperature).

Another consequence of H being a state function is that the standard enthalpy changes of a forward process and its reverse differ in sign (2):

$$\Delta H° (A\rightarrow B) = -\Delta H° (B\rightarrow A)$$

For instance, because the enthalpy of vaporization of water is + 44 kJ mol^{-1} at 298 K, its enthalpy of condensation at that temperature is − 44 kJ mol^{-1}.

IV.2.b.iii.3) Hess's cycle with phase change

Hess's cycle is based on Hess's law. Since enthalpy is a state function that depends only on the initial and final states of a reaction not on the path taken, the cycle provides an alternative pathway that leads to the same final state from the same initial state.

Application 4:

The molar enthalpy of combustion of methane at 25 °C and under 1 atmosphere is equal to – 212.8 kcal. Knowing the enthalpies of the following reactions:

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g)\ (1)\quad \Delta rH°_{298} = -94,05\ kcal$$

$$H_2\ (g) + ½\ O_2\ (g) \rightarrow H_2O\ (l)\qquad (2)\quad \Delta rH°_{298} = -68.3\ kcal$$

a) Calculate the standard molar enthalpy of formation of gaseous methane, $\Delta_f H°298\ (CH_4,g)$.
   Let us apply Hess's law to determine the standard molar enthalpy of formation of methane gas:

$$\Delta_r H° = \sum \upsilon_j \Delta_f H°_j(produits) – \sum \upsilon_i \Delta_f H°_i(réactifs$$

We note that:

$\Delta_f H°_{298}\ (CO_2, g) = \Delta H°_1$ and $\Delta_f H°_{298}\ (H_2O, l) = \Delta H°_2$

Since the standard molar enthalpies of formation of simple substances are defined as zero.

$\Delta rH°_{298} = \Delta_f H°_{298}\ (CO_2, g) + 2\ \Delta_f H°_{298}\ (H_2O,l) – \Delta_f H°_{298}\ (CH_4, g) – 2\Delta_f H°_{298}\ (O_2,g)$

$\Delta_f H°_{298}\ (CH_4, g) = \Delta_f H°_{298}\ (CO_2, g) + 2\ \Delta_f H°_{298}\ (H_2O,l) – \Delta rH°_{298}$

$\Delta_f H°_{298}\ (CH_4, g) = – 94,05 +2(– 68,3) – (–212,8) = –17,85\ kcal.mol^{-1}$

$\Delta_f H°_{298}\ (CH_4, g) = –17,85\ kcal.mol^{-1}$

b) Calculate the molar enthalpy of combustion of methane at 1 atmosphere and 1273 K using the cycle method and Kirchhoff's law.

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

Given the standard molar enthalpy of combustion at 1 atmosphere and 298 K, we can determine the molar enthalpy of combustion at 1 atmosphere and 1273 K. At this higher temperature, all products are in the gaseous state, meaning that water undergoes a phase change between 298 K and 1273 K.

The molar heat capacities (assumed constant between 298 K and 1273 K) of the following substances are given:

Cp (CH_4, g) = 13.2 cal mol^{-1} K^{-1}

Cp (O_2, g) = 7.6 cal mol^{-1} K^{-1}

Cp (CO_2, g) = 11.2 cal mol^{-1} K^{-1}

Cp (H_2O,g) = 9.2 cal mol^{-1} K^{-1}

Cp (H_2O, l) = 18.0 cal mol^{-1} K^{-1}

The enthalpy of vaporization of water is: $\Delta_{vap}H°_{373}(H_2O, l) = 9.7$ cal mol^{-1} K^{-1}

The cycle method:

$\sum \Delta Hi$ (cycle) = 0

$\Delta H°_1 + \Delta H°_2 + \Delta_r H°_{1273} - \Delta H°_3 - \Delta H°_4 - \Delta H°_5 - \Delta H°_6 - \Delta_r H°_{298} = 0$

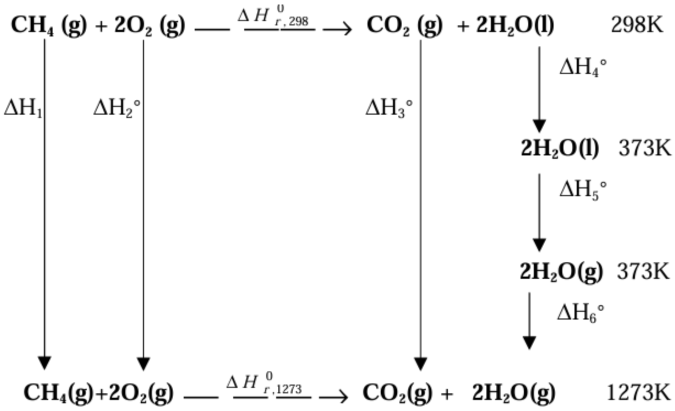
$\Delta H_1° + \Delta H°_2 = \int_{298}^{1273} [Cp(CH4, g) + 2Cp(O2, g)]dT$ = 27.69 kcal.

$\Delta H°_3 = \int_{298}^{1273} [Cp(CO2, g)]dT$ = 10,92 kcal.

$\Delta H°_4 = \int_{298}^{373} [2Cp(H2O, l)]dT$ = 2,70 kcal.

$\Delta H°_5 = 2\Delta_{vap}H° \, (H2O, l)$ = 19.4 kcal

$\Delta H°_6 = \int_{373}^{1273} [2Cp(H2O, g)]dT$ =16.56 kcal.



We then obtain : $\Delta_r H°_{1273} = -$ 190,91kcal.

We can obtain the same result by applying Kirchhoff's method with a phase change:

$\Delta_r H°_{1273} = \Delta_r H°_{298} + \int_{298}^{373} \Delta Cp dT + 2\Delta_{vap} H°_{373} + \int_{373}^{1273} \Delta C'p dT$

$\Delta Cp = Cp\ (CO_2\ (g) + 2\ Cp\ H_2O\ (l)) - Cp\ (CH_4\ (g) - 2\ Cp\ (O_2\ (g))$

$\Delta C'p = Cp\ (CO_2\ (g) + 2\ Cp\ H_2O\ (g)) - Cp\ (CH_4\ (g) - 2\ Cp\ O_2\ (g))$

The final result:

$\Delta_r H°_{1273} = -\ 190{,}91$kcal.

IV.2.c) Bond enthalpies (or bond energy)

If two atoms can form a bond and thus create a molecule, it is because the energy of the molecule is lower than the sum of the energies of the free atoms. The molecular state is therefore more stable, and the formation of the molecule releases energy. The bond energy corresponds to the energy released when a covalent bond forms in a gaseous product from two gaseous atoms at a pressure of one atmosphere.

$$X(g) + Y(g) \rightarrow X\text{-}Y\ (g)$$

The bond energy between two atoms, which is always negative, represents an average value, and calculations based on these data are often approximate. In fact, bond energy varies with the chemical environment of compounds containing more than two atoms. It therefore depends on the molecular geometry as well as on electron delocalization.

For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 413 kJ of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. A C–C bond has an approximate bond energy of 83 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. Some bond energies are given in table IV.2 in kJ / mol or kcal/mol.

Table IV.2 : Bond energy (kJ / mol)

H−H	**− 436**
Cl−Cl	− 242
C− C	− 346
C−H	− 413
C=C	− 606

When a bond is strong, there is a higher bond energy because it takes more energy to break a strong bond. This correlates with bond order and bond length. When the Bond order is higher, bond length is shorter, and the shorter the bond length means a greater the Bond Energy because of increased electric attraction. In general, the shorter the bond length, the greater the bond energy**.**

IV.2.c.1) Bond formation enthalpy or energy

The bond formation enthalpy is the amount of energy **released** when a bond is formed between two atoms in the gas phase, forming one mole of a compound. It is always negative (exothermic), as energy is released when stable bonds are formed. The energy is expressed in kJ/mol.

IV.2.c.2) Bond dissociation energy

Definition:

The bond dissociation energy (also called bond energy) is the amount of energy required to break one mole of a specific covalent bond in a molecule in the gas phase, producing free atoms or radicals.

- It is always **positive**, because breaking a chemical bond **requires energy** (endothermic process).
- Units: kJ/mol

  Example: $H_2(g) \rightarrow 2H(g) \qquad \Delta H = +436\ kJ/mol$

- This means it takes 436 kJ to break 1 mole of H–H bonds in hydrogen gas.

Bond formation energy = − (Bond dissociation energy)

Example:

- Breaking H–Cl: $HCl(g) \rightarrow H(g) + Cl(g) \qquad \Delta H = +431\ kJ/mol$
- Forming H–Cl: $H(g) + Cl(g) \rightarrow HCl(g) \qquad \Delta H = -431\ kJ/mol$

IV.2.c.3) Reaction enthalpy based on bond energies

When experimental values of reaction enthalpies aren’t available, we can estimate them using average bond enthalpies from known molecules:

Formula:

$$\Delta_r H° = \sum \upsilon_j \Delta_f H°_j(\text{formed bons}) - \sum \upsilon_i \Delta_f H°_i(\text{broken bonds})$$

Or

$$\Delta_r H° = \sum \upsilon_j \Delta_{dis} H°_j(\text{broken bonds}) - \sum \upsilon_i \Delta_{dis} H°_i(\text{formed bons})$$

Where:

- $\Delta_{dis}H°_j$: bond dissociation energy (positive values)
- Bonds **broken** (reactants): energy is absorbed → **positive**
- Bonds **formed** (products): energy is released → **negative**

Application 5: Combustion of methane

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Bonds broken:

- 4 × C–H → 4 × 412 = 1648 kJ
- 2 × O=O → 2 × 498 = 996 kJ

  Total = 2644 kJ

Bonds formed:

- 2 × C=O → 2 × 805 = 1610 kJ
- 4 × O–H → 4 × 463 = 1852 kJ

  Total = 3462 kJ

- $\Delta_r H \approx 2644 - 3462 = -818 \text{kJ/mol}$

  This estimate matches closely with the experimental enthalpy of combustion of methane.

Note:

- Average bond enthalpies are used because real molecules may have slightly different environments.
- Therefore, this method provides an approximation, not exact values.

We can calculate the enthalpy of the reaction:

$$2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (g)$$

From the bond dissociation energies:

$H_2\,(g) \rightarrow 2H(g) \qquad \Delta_{diss}H°_{298K}\,(H_2) = 436$ Kj/mol

$O_2\,(g) \rightarrow 2O(g) \qquad \Delta_{diss}H°_{298K}\,(O_2) = 498$ Kj/mol

$H_2O(g) \rightarrow 2H(g) + O(g) \qquad \Delta_{diss}H°_{298K}\,(H_2O) = 463$ Kj/mol

By constructing a cycle, we obtain:

$$\begin{tikzcd}
2H_2\,(g) + O_2\,(g) \arrow[r, "\Delta_rH°_{298K}"] \arrow[d, shift right=3, "2\Delta_{diss}H°(H_2)"'] \arrow[d, shift left=3, "\Delta_{diss}H°(O_2)"] & 2H_2O\,(g) \\
4H(g) + 2O(g) \arrow[ur, "-4\,\Delta_{diss}H°(OH)"'] &
\end{tikzcd}$$

$\Delta_rH°_{298K} = 2\,\Delta_{diss}H°_{298K}\,(H_2) + \Delta_{diss}H°_{298K}\,(O_2) - 4\Delta_{diss}H°_{298K}\,(OH) = -482$ Kj/mol.

Note that this reaction is actually a formation reaction, and therefore, the reaction enthalpy is equal to twice the formation enthalpy of the water molecule (g) under standard conditions, that is:

$$\Delta_rH°_{298K} = -2\Delta_fH°_{298K}\,(H_2O) = -2\,(241.8) = -483.6 \text{ Kj/mol}$$

IV.3. Reaction entropy

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants. As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation. When a chemical reaction or physical process occurs at a temperature different from the reference temperature (usually 298 K), we can calculate the change in entropy at the new temperature using Kirchhoff's relation for entropy.

IV.3.1.Application of Hess's and Kirchhoff's laws

a) Hess's law for entropy

Hess's Law states that: The total change in entropy for a reaction is the same, regardless of the path taken from reactants to products.

Just like enthalpy, entropy (**ΔS**) is a state function, so it depends only on the initial and final states (not on the specific reaction pathway).

Mathematical expression:

$$\Delta_r S° = \sum \nu i S°_{\text{products}} - \sum \nu j S°_{\text{reactants}}$$

where:

- $\Delta_r S°$: standard entropy change of the reaction
- $S°$: Absolute standard molar entropy (usually in $J \cdot mol^{-1} \cdot K^{-1}$)
- υ (nu): stoichiometric coefficient in the balanced chemical equation

Application 6:

For the reaction: $C_{(graphite)} + O_2(g) \rightarrow CO_2(g)$

Given (standard entropy in J/(mol.K): $S°_{C(graphite)} = 5.7$, $S°_{O2(g)} = 205$ and $S°_{CO2(g)} = 213.7$

Then: $\Delta_r S° = 213.7 - (5.7 + 205.0) = 213.7 - 210.7 = +3.0$ J\ (mol.K)

So, the entropy change is slightly positive.

b) **Kirchhoff's relation for entropy**

The equation that relates the change in entropy to Kirchhoff's law can be expressed as: $\Delta_r S°(T_2) = \Delta_r S°(T_1) + \int_{T1}^{T2} \Delta Cp \, dT/T$

Where:

- $\Delta_r S°(T_2)$: entropy change at temperature T_2
- $\Delta_r S°(T_1)$: known entropy change at reference temperature T_1
- $\Delta Cp = \sum Cp$ products $- \sum Cp$ reactants (change in heat capacity at constant pressure)
- T: absolute temperature (in Kelvin)

Integrated form

If ΔCp is assumed constant over the temperature range, the integral simplifies to:

$$\Delta_r S°(T_2) = \Delta_r S°(T_1) + \Delta Cp \ln(T_1/T_2)$$

Application 7:

At 25 °C, the enthalpy of the reaction between hydrogen and nitrogen to produce ammonia is – 22.8 kcal.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Calculate the enthalpy of the reaction as a function of temperature, given that the molar heat capacities are:

$Cp\ (N_2, g) = 6,85 + 0,28.\ 10^{-3}\ T$

$Cp\ (NH_3, g) = 5,72 + 8,96.\ 10^{-3}\ T$

$Cp\ (H_2, g) = 6,65 + 0,52.\ 10^{-3}\ T$

We assume that no phase change occurs within this temperature range.

Solution :

We apply Kirchhoff's law, since there is no phase change within this temperature range.

$$\Delta_r S°(T_2) = \Delta_r S°(T_1) + \int_{T1}^{T2} \Delta Cp\ dT/T$$

We find $\Delta Cp = -\ 15,36 + 16,08.\ 10^{-3}\ T$

$$\int_{T0}^{T} \Delta Cp\ dT = \int_{T1}^{T2} (-15,36\ + 16,08.10^{-3})dT$$

$$\int_{T0}^{T} \Delta Cp\ dT = -\ 15,36(T_2 - T_1) + 8,04.\ 10^{-3}\ (T_2{}^2 - T^2{}_1)$$

$$\Delta H_T = -\ 18,22 - 15,36\ .10^{-3}\ T_2 + 8,04.10^{-6}\ T_2^2\ (kcal/mol)$$

$\Delta H_{500K} = -\ 23.89$ Kcal/mol.

At T= 500K , it would appear that the process results in a ***decrease*** in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules.

CHAPTER V

Free Enthalpy – Free Energy

V.1.Introduction

We have just seen that the criterion for the evolution of a system is the increase in its entropy. One of the difficulties in using the second law to determine whether a reaction is spontaneous lies in the fact that, to evaluate the total change in entropy, it is necessary to calculate and add two quantities: the entropy change of the system and that of the surroundings. This process can be simplified by introducing a new state function (the Gibbs free energy (or free enthalpy)) which is the most widely used quantity in chemical thermodynamics.

V.2.Definition of Free enthalpy

The total entropy change, ΔS_{tot}, is the sum of the entropy change of the system, ΔS_{sys}, nd that of the surroundings,, ΔS_{sur}:

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{sur}$$

For a process occurring at constant pressure and temperature, the entropy change of the surroundings is given by the following expression:

$$\Delta S_{sur} = \Delta H_{sur} / T = - \Delta H_{sys} / T$$

Therefore, $\Delta S_{tot} = \Delta S_{sys} - \Delta H_{sys} / T$ (at constant T and P)

This equation allows the total entropy change to be calculated using information about the system alone.

V.2.a) Gibbs function

For a process that occurs at constant temperature and pressure, a new function called the Gibbs free energy can be defined to rearrange the second law of thermodynamics:

$$\text{Gibbs free energy: } G = H - TS$$

This quantity, commonly called *free enthalpy* and more formally known as *Gibbs free energy*, is defined entirely in terms of state functions; therefore, G is a state function. For a process occurring at constant temperature, the variation in Gibbs free energy is given by:

$$\Delta G = \Delta H - T\Delta S$$

By comparing this expression rewritten as follows:

$$\Delta G / T = \Delta H / T - \Delta S$$

From the equation: $\Delta S_{tot} = \Delta S_{sys} - \Delta H_{sys} / T$, we can see that $\Delta G / T = - \Delta S_{tot}$ and therefore $\Delta G = = - T\Delta S_{tot}$

The negative sign in this equation means that, under constant temperature and pressure, an increase in total entropy corresponds to a decrease in free enthalpy (Gibbs free energy). When using Gibbs free energy to determine the spontaneity of a process, we are only concerned with the change in G. This change represents the difference between G_{final}, the Gibbs free energy of the products, and $G_{initial}$, the Gibbs free energy of the reactants.

$$\Delta G = G_{final} - G_{initial}$$

For a process occurring at constant temperature and pressure, this relationship can be rewritten in terms of the system's enthalpy and entropy changes:

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

This relationship is often written without the subscripts indicating that the quantities refer to the thermodynamic properties of the system (and not those of the surroundings or the universe). However, it is clear that the values of ΔH and ΔS pertain to the system under study. This relation is powerful because it allows us to determine the change in Gibbs free energy from the system's enthalpy and entropy changes.

V.2.b) Spontaneity condition

From the sign of ΔG alone, we can predict whether the reaction will proceed in the forward direction, in the reverse direction, or if it is at equilibrium.

- When $\Delta G < 0$, the process is spontaneous and will proceed in the forward direction, producing more products.
- When $\Delta G > 0$, the process is non-spontaneous in the forward direction. Instead, it will be spontaneous in the reverse direction, forming more reactants.
- When $\Delta G = 0$, the system is at equilibrium, and the concentrations of reactants and products remain constant.

Thus, from the values of ΔH, ΔS, and T, one can determine the value of ΔG. Table xx summarizes the different cases of spontaneity.

According to Table V.1, if the process is exothermic ($\Delta H < 0$) and the entropy of the system increases ($\Delta S > 0$), the sign of ΔG is negative, regardless of the temperature. The process will always be spontaneous. Conversely, if the process is endothermic ($\Delta H > 0$) and the entropy of the system decreases ($\Delta S < 0$), the sign of ΔG is positive, regardless of the temperature. The process is never spontaneous.

Table V.1 : Spontaneity factors

ΔH	ΔS	**Observation**
−	+	$\Delta G < 0$
−	−	$\Delta G < 0$ si $\lvert T\Delta S\rvert < \Delta H$
+	+	$\Delta G <$) si $\lvert T\Delta S\rvert > \Delta H$
+	−	$\Delta G > 0$

For other combinations of ΔH and ΔS values, the spontaneity of the process depends on temperature. Exothermic reactions ($\Delta H < 0$) that decrease the system's entropy ($\Delta S < 0$) are spontaneous only at sufficiently low temperatures. Endothermic reactions ($\Delta H > 0$) that increase the system's entropy ($\Delta S > 0$) are spontaneous only at sufficiently high temperatures.

For a non-spontaneous process with $\Delta S < 0$, can it become spontaneous by increasing the temperature (assuming ΔH and ΔS are both independent of temperature)? No, a non-spontaneous process with $\Delta S < 0$ cannot become spontaneous by increasing the temperature. Since $\Delta S < 0$, then $-T\Delta S > 0$, meaning this term increases ΔG as temperature rises. Therefore, when $\Delta S < 0$, increasing the temperature makes ΔG more positive, making the process even less spontaneous.

Application 1:

The enthalpy of fusion of water and its entropy of fusion are respectively:

$\Delta H_f = 6.01$ Kj/mol **,** $\Delta S_f = 22$ J / (mol.K)

What is the value of ΔG for the melting of ice at 20°C?

The melting process of ice is the phase change from the solid state to the liquid state.

$$H_2O(s) \rightarrow H_2O(l)$$

By substituting the values of ΔH, T, and ΔS into the Gibbs free energy equation, we obtain:

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -0.44 \text{ KJ/mol}$$

Since ΔG is negative, we can conclude that ice melts spontaneously at 20°C.

Concept check: What would ΔG be for the melting of ice at –10°C? After calculation, we find: $\Delta G = +0.22$ KJ/mol

It is observed that at –10°C, the Gibbs free energy change (ΔG) for the melting of ice is positive. We can therefore conclude that this process is not spontaneous at –10°C.

V.3 Free energy

Let us consider a closed, non-isolated system (able to exchange heat but not matter with its surroundings) undergoing a reversible isothermal transformation between two states, 1 and 2, at constant temperature T and constant volume V.

We seek to determine the maximum work, W_{max} ,that this system can deliver. According to the first law of thermodynamics**:**

$$\Delta U = Q + W$$

For a reversible isothermal transformation**,** the heat exchanged is related to the entropy by**:**

$$Q_{rev} = T\Delta S$$

Thus, the maximum work that can be obtained is:

$$W_{max} = \Delta U - Q_{rev} = \Delta U - T\Delta S$$

We then define the Helmholtz free energy, A (or sometimes F), as:

$$F = U - TS$$

where

- *A* is the Helmholtz free energy[2] (sometimes also called *F*, particularly in the field of physics) (SI: joules, CGS: ergs),
- *U* is the internal energy of the system (SI: joules, CGS: ergs),
- *T* is the absolute temperature (kelvins) of the surroundings, modelled as a heat bath,
- *S* is the entropy of the system (SI: joules per kelvin, CGS: ergs per kelvin).

And its variation is given by: $\Delta F = \Delta U - T\Delta S$

Which leads to : $\Delta F = W_{max}$

According to the second law of thermodynamics, for a non-isolated system:

$\Delta F < 0 \Rightarrow$ spontaneous process possible (state 1 → state 2)

$\Delta F = 0 \Rightarrow$ thermodynamic equilibrium

$\Delta F > 0 \Rightarrow$ process impossible (in that direction)

The function F is a state function (since it is a combination of state functions). At constant temperature and volume, the spontaneous evolution of a system is governed by $\Delta F < \mathbf{0}$, which is the necessary condition for change if a pathway exists. At equilibrium, $\Delta F = \mathbf{0}$. Spontaneous evolution requires a decrease in U and an increase in entropy. In fact, the relevant criterion is the increase of the total entropy**.**

The decrease in the system's internal energy dU results in a transfer of heat to the surroundings. If the entropy balance involves dS, the increase in the system's entropy, then the system has released energy dU **(< 0)** as heat to the surroundings, leading to an increase in the surroundings' entropy.

➢ Relationship Between Gibbs Free Energy (G) and Helmholtz Free Energy (A)

- **Helmholtz Free Energy (A)**:

$$A = U - TS$$

Used when temperature **(T)** and volume **(V)** are constant.

- **Gibbs Free Energy (G)**:

$$G = H - TS$$

Used when temperature **(T)** and pressure **(P)** are constant.

But since enthalpy H = U + PV, we can rewrite Gibbs energy:

$$G = U + PV - TS$$

Now, substitute the expression of Helmholtz energy A = U − TS into this:

$$G = A + PV \text{ or } A = G - PV$$

- The difference between G and A lies in the PV work.
- A is the available energy at constant volume (excluding PV work).
- G is the available energy at constant pressure (including PV work).
- The term PV represents the expansion work done by the system under pressure.

V.4. Calculation of free enthalpy variation during chemical reactions

The change in Gibbs energy accompanying the progress of a reaction is called the Gibbs energy of reaction. However, it is important to distinguish between the Gibbs energy of reaction under standard conditions and its value under non-standard conditions. Let us first consider the value under standard conditions.

The standard Gibbs energy of reaction **($\Delta_r G°$)** is defined as the difference between the standard molar Gibbs energies of the products and those of the reactants, each multiplied by their respective stoichiometric coefficients in the chemical equation:

$$\Delta_r G^\circ = \sum_{products} nG_m^0(products) - \sum_{reac\tan ts} nG_m^0(reac\tan ts)$$

The standard Gibbs energy of the reaction:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(1)}$$

$\Delta_rG°$ is the change in Gibbs energy when pure hydrogen gas at 1 bar reacts with pure oxygen gas at 1 bar to produce pure liquid water at 1 bar.

It is not possible to calculate the standard Gibbs energy of reaction directly from the standard molar Gibbs energies themselves, since these values are not known.

One way to perform this calculation is by using the standard enthalpies and entropies of reaction, expressed as:

$$\Delta_rG° = \Delta_rH° - T\Delta_rS^\circ$$

The standard enthalpy of reaction is calculated using tables of standard enthalpies of formation, and the standard entropy of reaction is obtained from tables of standard molar entropies. The standard Gibbs energy of reaction is expressed in the same units as the standard enthalpy of reaction (kJ/mol). It is worth recalling that the study of standard enthalpies of reaction was simplified by using lists of standard enthalpies of formation.

A similar approach can be applied to standard Gibbs energies of reaction by providing the standard Gibbs energy of formation for each species involved in the reaction.

As a result, the standard Gibbs energies of formation, $\Delta_fG^\circ(X)$, are zero for pure chemical elements and nonzero for compounds. The following table gives a few examples (Table V.2).

Table V.2 : Standard Gibbs free energy of formation, $\Delta_rG°$ à 298K (kJ/mol).

$H_2O(l)$	− 237.1	$CH_4(g)$	− 50.7
$H_2O(g)$	− 228.6	$C_2H_4(g)$	68.2
HCl(g)	− 95.3	$C_2H_6(l)$	124.3
NaCl(s)	− 384.1	CH_3OH (l)	− 162
$NO_2(g)$	51.31	C2H5OH (l)	−74.8
$CO_2(g)$	− 394.4	CH3COOH (l)	− 390

The standard Gibbs free energy of formation, $\Delta_fG°$, of a substance is the standard Gibbs free energy change (per mole of substance) for its formation from the constituent elements in their reference states.

When the standard Gibbs free energies of formation are known, they can be easily combined to calculate the standard Gibbs free energy change for any reaction. This can be done using the expression:

$$\Delta_r G^\circ = \sum_{products} n\Delta_f G^0(products) - \sum_{reac\tan ts} n\Delta_f G^0(reac\tan ts)$$

Based on the available data, this calculation can be performed either using the standard Gibbs free energies of formation of the compounds or using their standard enthalpies and entropies of formation.

Application 2:

For example, to determine the standard Gibbs free energy of the following reaction:

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

We perform the following calculation:

$\Delta_r G° = 2\Delta_f G°\ (CO_2;g) - \{2\Delta_f G°\ (CO,g) + \Delta_f G°\ (O_2,g)\} = 2 \times (-394) - \{2 \times (-137) + 0\}$

$\Delta_r G° = -\ 514$ kJ/mol

Consider the reaction for the formation of water:

$$H_{2\ (g)} + 1/2\ O_{2\ (g)} \rightarrow H_2O_{\ (l)}$$

and the thermodynamic data for the reactants and the product:

$$\Delta_f H^0_{298K}\ (H_2, g) = 0 \qquad S^0_{298K}\ (H_2, g) = 130{,}7\ J \cdot K^{-1} \cdot mol^{-1}$$
$$\Delta_f H^0_{298K}\ (O_2, g) = 0 \qquad S^0_{298K}\ (O_2, g) = 205{,}1\ J \cdot K^{-1} \cdot mol^{-1}$$
$$\Delta_f H^0_{298K}\ (H_2O, l) = -\ 285{,}8\ kJ \cdot mol^{-1} \qquad S^0_{298K}\ (H_2O, l) = 69{,}9\ J \cdot K^{-1} \cdot mol^{-1}$$

The entropy of the reaction is given by:

$$\Delta_r S^0_{298K} = S^0_{298K}\ (H_2O, l) - S^0_{298K}\ (H_2, g) - 1/2\ S^0_{298K}\ (O_2, g)$$
$$= -\ 163{,}35\ J \cdot K^{-1} \cdot mol^{-1}$$

and there is a decrease in entropy, meaning an increase in order, which is expected for a chemical reaction involving 1.5 moles of gaseous reactants and 1 mole of liquid product. The Gibbs free energy of reaction at 298K , $\Delta_r G°_{298K} = \Delta_r H°_{298K} - T\Delta_r S°_{298K}$ requires the calculation of $\Delta_r H°_{298K}$.

$$\Delta_r H^0_{298K} = \Delta_f H^0_{298K}\ (H_2O, l) - \Delta_f H^0_{298K}\ (H_2, g) - 1/2\ \Delta_f H^0_{298K}\ (O_2, g)$$

Since H_2 and O_2 are simple substances, their enthalpy of formation is zero. Thus, we have:

$$\Delta_r H^0_{298K} = \Delta_f H^0_{298K}(H_2O, l) = -285{,}8\ kJ \cdot mol^{-1}$$
$$\Delta_r G^0_{298K} = -285{,}8 - 298 \times (-163{,}35\ 10^{-3}) = -237{,}1\ kJ \cdot mol^{-1}$$

The result is negative, confirming the spontaneous nature of the reaction. Conversely, the reverse reaction — the decomposition of water — is associated with a positive Gibbs free energy of reaction (as a property of state functions, its value is the opposite of that calculated). Therefore, this reaction is non-spontaneous and does not occur naturally (the electrolysis of water, which carries out this transformation, requires the use of electrical energy to proceed). Another approach is to use the standard Gibbs free energy of formation values for the reactants and products:

$$\Delta_r G^0_{298K} = \Delta_f G^0_{298K}(H_2O, l) - \Delta_f G^0_{298K}(H_2, g) - 1/2\ \Delta_f G^0_{298K}(O_2, g)$$

Since H_2 and O_2 are simple substances, their Gibbs free energy of formation is zero. Thus, we have $\Delta_f G°_{298}K$ (H_2O, l) = − 237.1 kJ·mol^{-1}, and therefore, we obtain the same Gibbs free energy of reaction:

$$\Delta_r G^0_{298K} = \Delta_f G^0_{298K}(H_2O, l) = -237{,}1\ kJ \cdot mol^{-1}$$

V.5.Molar free enthalpy

The molar free enthalpy is defined as the Gibbs free energy per mole of a substance**.**

V.5.1.Case of a pure ideal gas

The expression for the chemical potential in the simple case of a pure ideal gas is important, as it serves as a model for defining the chemical potential in condensed phases. In this case, at constant temperature, dG can be written as:

$$dG = VdP$$

Now, since $V = nRT/P$, it follows that $dG = nRT\ (dP/P)$

By integrating between the standard pressure P∘=1bar and the pressure P of the ideal gas:

$$G(T,P) = G°(T) + RT\ln(P/P°)$$

Where:

- G(T,P): molar Gibbs energy as function of T and P
- G°(T): molar Gibbs energy at standard pressure P°=1 bar
- R: gas constant (8.314 J/mol·K)
- T: absolute temperature
- P: pressure of the gas

V.5.2.Case of a gas mixture

For a gas mixture, the total molar free enthalpy of the mixture is the sum of the molar free enthalpies of each component (i) in the mixture. Each component's molar free enthalpy is calculated using its partial pressure:

$$\mathrm{G(T,P)_{tot}} = \sum_{\mathrm{i}} \mathrm{n_i G^{\circ}(T,P)_i}$$

$$\mathrm{G(T,P)_i = G^{\circ}(T)_i + RTln(P_i)}$$

V.5.3.The chemical potential

The differential of the Gibbs free energy, dG, is expressed in terms of the chemical potential:

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

$$dG = VdP - SdT + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq n_i} dn_i$$

The chemical potential: $\mu_i = \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq n_i}$

This latter definition of the chemical potential is most often used because reaction conditions are frequently isothermal and isobaric. The expression of G as a function of the chemical potential is:

$$G = \sum_i n_i \left(\frac{\partial G}{\partial n_i} \right) = \sum_i n_i \mu_i$$

At constant Tand P,where dT= 0 and dP = 0, the expression of dG is :

$$dG = \sum_i \mu_i dn_i$$

At equilibrium, it has been shown that dG=0. Therefore, for equilibrium at constant P and T:

$$dG = \sum_i \mu_i dn_i = 0$$

For a reaction to be spontaneous, the free enthalpy (Gibbs energy) of the system must decrease, that is, dG<0. Therefore, a reaction is spontaneous if:

$$\sum_i \mu_i dn_i < 0$$

By differentiating the expression: $\mathrm{G(T,P) = G^{\circ}(T) + RTln(P/P^{\circ})}$

With respect to the number of moles n, we obtain the expression for the chemical potential of a pure ideal gas:

$$\mu(T,P) = \mu^\circ(T) + RT\ln(P/P^\circ)$$

where $\mu^\circ(T)$ is the standard chemical potential of the gas at the standard pressure P° and temperature T.

V.5.4.Case of a mixture of ideal gases

When an ideal gas is part of a mixture, the pressure P in the previous expression is replaced by the partial pressure of gas i, P_i.Thus, the chemical potential of each ideal gas i in the mixture is:

$$\mu_i\,(T,P) = \mu_i^\circ\,(T) + RT\ln(P_i\,/P^\circ) = \mu_i^\circ(T) + RT\ln(x_i)$$

Where xi = P_i / P° , and $\mu_i^\circ(T)$ is the standard chemical potential of the pure gas i at the standard pressure P° and temperature T.

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