جامعة أبو بكر بلقايد
UNIVERSITY OF TLEMCEN

Ministry of Higher Education and Scientific Research
Abou Bekr Belkaid University – Tlemcen –
Faculty of Technology
Department of Industrial Engineering

Thermodynamics:
Principles with Problem Solutions

Presented by:

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Academic Year: 2024/2025

Syllabus

Semester: 2

Teaching Unit: UEF 1.2

Subject 3: Thermodynamics

Total Hours (VHS): 67h30 (Lectures: 3h00, Tutorials: 1h30)

Credits: 6

Coefficient: 3

Course Objectives

- To provide the necessary foundations of classical thermodynamics for applications in combustion and thermal machines.
- To standardize students' knowledge.

Targeted competencies:

- Acquisition of a scientific foundation in classical thermodynamics;
- Application of thermodynamics to various systems;
- Stating, explaining, and understanding the fundamental principles of thermodynamics.

Recommended Prerequisites:

Basic concepts in mathematics and general chemistry.

Course Content

Chapter 1: Generalities on Thermodynamics (3 weeks)

1. Fundamental properties of state functions;
2. Definitions of thermodynamic systems and surroundings;
3. Description of a thermodynamic system;
4. Evolution and thermodynamic equilibrium states of a system;
5. Possible exchanges between the system and its surroundings;
6. State transformations of a system (operation, evolution);
7. Review of the ideal gas laws.

Chapter 2: The First Law of Thermodynamics (3 weeks)

1. Work, heat, internal energy, concept of energy conservation;
2. The first law of thermodynamics: statement, concept of internal energy of a system, application to ideal gases, enthalpy function, heat capacity, reversible transformations (isochoric, isobaric, isothermal, adiabatic).

Chapter 3: Applications of the First Law of Thermodynamics to Thermochemistry (3 weeks)

Reaction heats, standard state, standard enthalpy of formation, enthalpy of dissociation, enthalpy of phase changes, enthalpy of a chemical reaction, Hess's law, Kirchhoff's law.

Chapter 4: The Second Law of Thermodynamics (3 weeks)

1. The second law for a closed system;
2. Statement of the second law: Entropy of an isolated closed system;
3. Calculation of entropy variation: reversible isothermal transformation, reversible isochoric transformation, reversible isobaric transformation, adiabatic transformation, during a phase change, during a chemical reaction.

Chapter 5: The Third Law and Absolute Entropy (1 week)

Chapter 6: Free Energy and Enthalpy – System Evolution Criteria (2 weeks)

1. Introduction;
2. Free energy and enthalpy;
3. Chemical equilibria.

Assessment Method:

Continuous assessment: 40%

Final exam: 60%

Foreword

This course handout for **Thermodynamics (UEF 1.2 – Subject 3)** is designed for first-year students in the scientific common core, including programs in Science and Technology, Materials Science, and Industrial Engineering. Its primary aim is to guide students in approaching classical thermodynamics with clarity, confidence, and intellectual curiosity.

Rather than providing either a superficial overview or an overly dense theoretical exposition, this document offers a structured, step-by-step exploration of the fundamental principles governing energy, heat, and work in physical systems. The content is organized in a logical sequence, starting with essential definitions and progressively advancing toward more complex laws, analytical methods, and real-world applications.

- **Chapter 1** establishes the foundation by introducing essential terminology and concepts, including thermodynamic systems, states, equilibrium, and state functions.
- **Chapter 2** presents the **First Law of Thermodynamics**, emphasizing internal energy, enthalpy, and the roles of work and heat, with particular attention to ideal gases and standard transformations such as isothermal and adiabatic processes.
- **Chapter 3** applies these principles to chemical reactions and phase transitions within the framework of **thermochemistry**, discussing enthalpy changes, Hess's Law, and Kirchhoff's Law in practical contexts.
- **Chapter 4** introduces the **Second Law of Thermodynamics**, developing the concepts of entropy and irreversibility key to understanding the directionality of natural processes and the limitations of energy conversion.
- **Chapter 5** explores the **Third Law of Thermodynamics** and the concept of absolute entropy, with a focus on behavior at very low temperatures.
- **Chapter 6** examines free energy functions (Gibbs and Helmholtz), providing tools to assess spontaneity and equilibrium from an energy-based perspective.

To reinforce key concepts, each chapter is supplemented with carefully selected, fully worked examples. These are not mere exercises; they are designed to cultivate scientific reasoning and analytical skills, bridging the gap between abstract theoretical principles and practical applications.

This handout goes beyond a simple summary of the laws of thermodynamics—it is intended as a training tool for scientific thinking. Students are encouraged not to rely on rote memorization, but to strive for deep understanding; not merely to apply procedures, but to question the underlying ‘why’ and ‘how’.

While thermodynamics may initially appear abstract, it is a cornerstone of modern science and engineering. With sustained effort and active engagement, it becomes a powerful framework for interpreting and predicting the behavior of physical systems.

List of Figures

Table of contents

Table of contents

Chapter I: Generalities on Thermodynamics

Chapter II: First principle of Thermodynamics

Chapter III: Applications of the first law of thermodynamics to thermochemistry

Chapter IV: Second Law of Thermodynamics

Chapter V: Third Law of Thermodynamics

Chapter VI: Free Energy and Enthalpy - Criteria for System Evolution

Chapter I:
Generalities on Thermodynamics

Learning Objectives:

At the end of this chapter, the student should be able to:

- Define thermodynamics and its main branches;
- Describe the concept of a system, its boundaries, and classifications;
- Differentiate between intensive and extensive properties, and identify state functions;
- Explain energy exchange in the form of work and heat, using the correct sign conventions;
- Recognize the conditions for thermodynamic equilibrium and the main types of transformations;
- Apply the ideal gas law and related gas laws (Boyle, Charles, Gay-Lussac, Avogadro, Dalton);
- Interpret thermodynamic diagrams such as Clapeyron and Amagat plots;
- Distinguish between ideal and real gases and use the Van der Waals equation when appropriate.

I.1 Introduction

The word thermodynamics has Greek origins. It is composed of two parts: "thermo," which means heat, and "dynamics," which means work or movement. The compound word implies movement produced from heat. Thermodynamics emerged as a science in the 18th century with the discovery of the steam engine. It aims to explore various types of energy and how they can be transformed from one form to another.

Thermodynamics has several branches:

- Classical Thermodynamics: Studies systems on a macroscopic scale using measurable quantities such as pressure (P), temperature (T), and volume (V).
- Chemical Thermodynamics: Examines the heat of reactions and the thermodynamic properties of chemical equilibria.
- Statistical Thermodynamics: Considers systems on a microscopic scale and relies on statistical mechanics.
- Technical Thermodynamics: Applies to thermal machines, refrigeration systems, heat pumps, etc.

I.2 The concept of system

I.2.1 State of matter

Matter exists in three states-solid, liquid, and gas-and transitions can occur between these states.

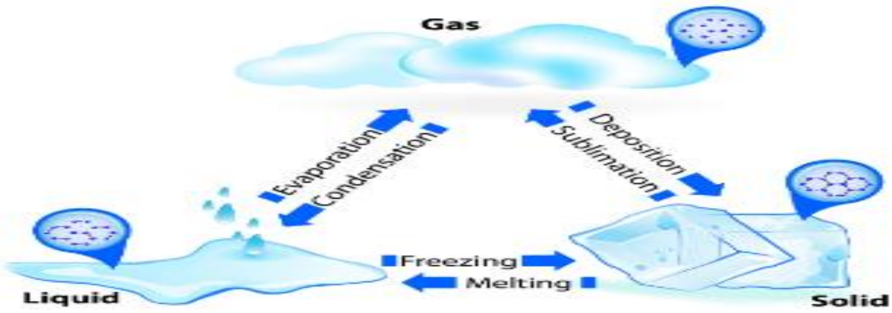


Figure I.1: States of matter.

I.2.2 Clarification of the concept of a system

A system is a part of the universe in which the studied transformation takes place and is delimited by real or imaginary boundaries. Everything outside the system constitutes the surroundings. The combination of the system and the external surroundings

forms the universe.

Sign Convention: By sign convention, what is received by the system (energies: work (W) or heat (Q)) will be considered positive, while what is given or lost by the system will be considered negative.

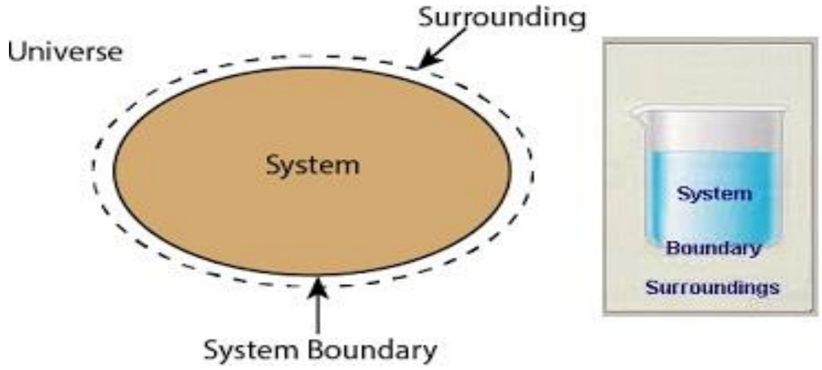


Figure I.2: Thermodynamic system.

I.2.3 Classification of Systems

Systems are categorized based on the type of interaction they have with their surroundings, particularly in terms of energy and matter exchange.

1-Open system: This type allows both energy and matter to be transferred across its boundaries.

Examples: living beings, boiling water in a pot, a lit candle, or an operating internal combustion engine.

2-Closed system: Energy can pass through the boundary, but matter cannot. *Examples*: a battery in use, a functioning refrigerator, or plants enclosed in a sealed glass container.

3-Isolated system: Neither energy nor matter is exchanged with the surroundings. Although perfect isolation is practically unattainable, some systems approximate this condition. *Examples*: an insulated thermos, a calorimeter, or a chemical reaction occurring within one.

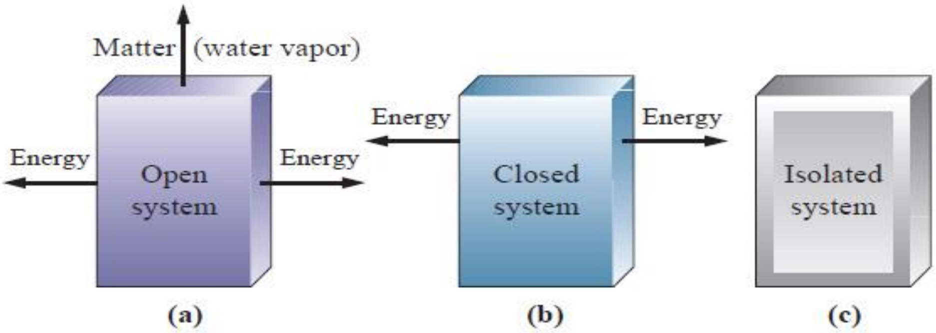


Figure I.3: Types of thermodynamic system.

According to the composition of the system:

Thermodynamic systems can be classified into two main categories: **homogeneous** and **heterogeneous** systems.

- **Homogeneous System**: Composed of only one phase-gas, liquid, or solid-with uniform physical properties throughout.
- **Heterogeneous System**: Involves more than one phase, or a single phase that displays varying properties across different regions.

Example:

For each of the systems listed below, determine whether it is homogeneous or heterogeneous.

A block of solid water → Homogeneous System

An unsaturated solution of sugar in water → Homogeneous System

Vinaigrette → Heterogeneous System

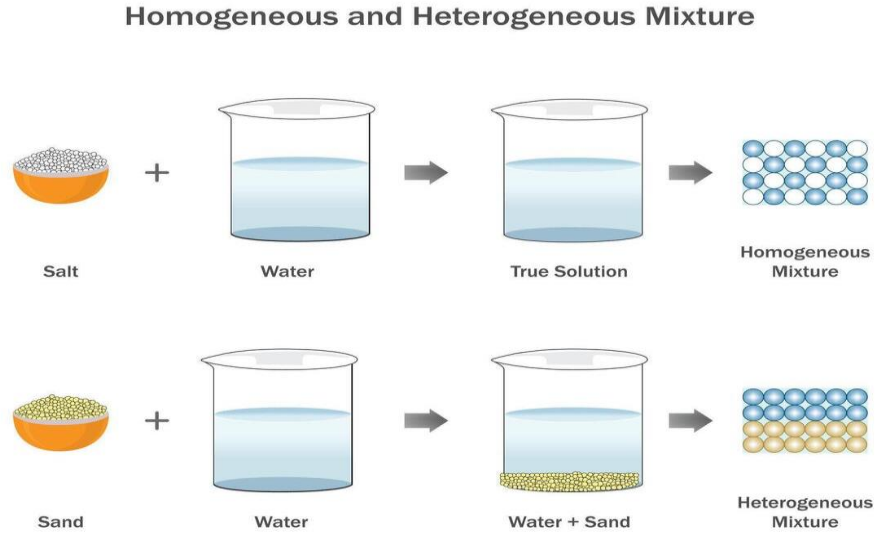


Figure I.4: Homogeneous and Heterogeneous Mixture.

I.3 Description of the state of a system

The condition of a system is defined by its state, which can be specified using a limited set of macroscopic variables known as state parameters.

Common examples include temperature (T), pressure (P), volume (V), and the amount of substance in moles (n). These variables are often interrelated and not all are independent-they are linked through what is known as the system’s equation of state.

Example:

$PV = nRT$

I.3.1 Intensive and extensive parameters

An extensive property depends on the amount of matter present and applies to the system as a whole. Examples include volume, mass, and quantity of matter.

An intensive property is defined at every point within a system and does not depend on the amount of substance present. Examples include mass density, pressure, concentration, and temperature.

Remarks:

Dividing one extensive variable by another always yields an intensive property, for example, mass divided by volume. Some quantities are neither extensive nor intensive (e.g., volume squared, as this is a nonlinear function of an extensive variable).

I.3.2 State functions

A state function (X) is a thermodynamic property whose value depends exclusively on the current state of the system, as defined by variables such as pressure, temperature, volume, and composition. It is path-independent, meaning that its variation (ΔX) between two states depends only on the initial and final conditions, not on the process used to reach them. Typical examples include internal energy (U), enthalpy (H), entropy (S), and Gibbs free energy (G).

$\Delta X = X_{\text{final}} - X_{\text{initial}}$.

Example:

The variable height (H) is a state function.

Work (W) is not a state function.

Internal energy (U) is a state function: $\int_1^2 \Delta U = dU$.

Heat (Q) does not qualify as a state function because its value depends on the specific process taken between two states, rather than solely on the initial and final states of the system.

$\Delta F = F_{\text{final}} - F_{\text{initial}} = F_2 - F_1$, regardless of the path taken (a, b, or c),

ΔF is independent of how the transformation is carried out.

If F is a state function (e.g., U, H, S), its differential dF is exact, meaning it depends only on the system's initial and final states and is independent of the path taken between them.

If F is a path-dependent quantity (e.g., Q, W), its differential δF is inexact, meaning its value depends on the specific path followed and cannot be determined solely from the state variables.

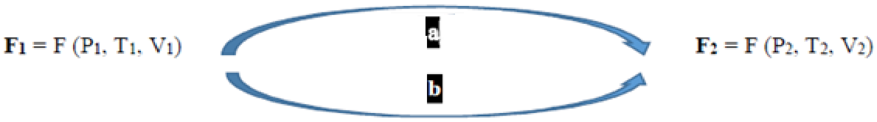


Figure I.5: The passage from state 1 to state 2.

If the value of F_2 remains identical regardless of whether the system transitions from state 1 to state 2 via path a or path b, then F is considered a state function.

I.4 Energy transfer or exchange (Work, Heat)

Energy transfer refers to the movement of energy from one location to another without altering its form. When interacting with its surroundings, a system may either absorb or release energy. By thermodynamic convention :

- **$Q > 0$**: Heat is absorbed by the system (endothermic process).
- **$Q < 0$**: Heat is released to the surroundings (exothermic process).
- **$W > 0$**: Work is done on the system (the system receives energy).
- **$W < 0$**: The system performs work on its surroundings (acts as a motor).

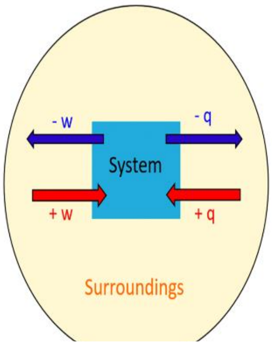


Figure I.6: Energy interaction with the external environment.

Units:

- Work [W]: Joules (J);
- Heat [Q]: Joules (J) or calories (cal), where **1 cal = 4.18 J.**

I.5 Thermodynamic equilibrium and system transformations

I.5.1 Definition and criteria of thermodynamic equilibrium

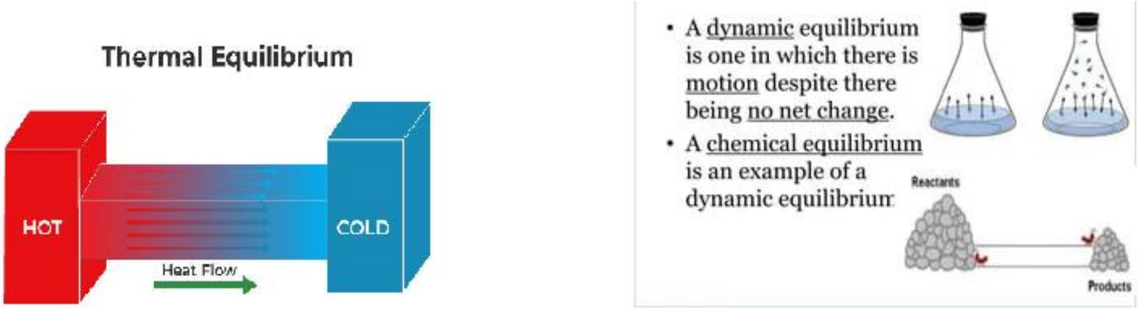
A system is in thermodynamic equilibrium when the values of state variables are the same at every point in the system and remain constant over time.

Three criteria must be simultaneously satisfied:

Thermal equilibrium: Achieved when the temperature is evenly distributed throughout the system and matches that of the surroundings, with no net heat flow over time.

Dynamic equilibrium: Established when pressure is uniform across the system and remains equal to the external pressure, indicating no net mechanical force or movement.

Chemical equilibrium, where the composition is uniform throughout the system (there should be no transfer of matter between different phases or chemical reactions) over time.



- A dynamic equilibrium is one in which there is motion despite there being no net change.
- A chemical equilibrium is an example of a dynamic equilibrium

Figure I.7: Types of thermodynamic equilibrium.

Example:

A reaction such as the combustion of propane with oxygen, stopping when one of the reactants is completely depleted, is termed a total, complete, or irreversible reaction.

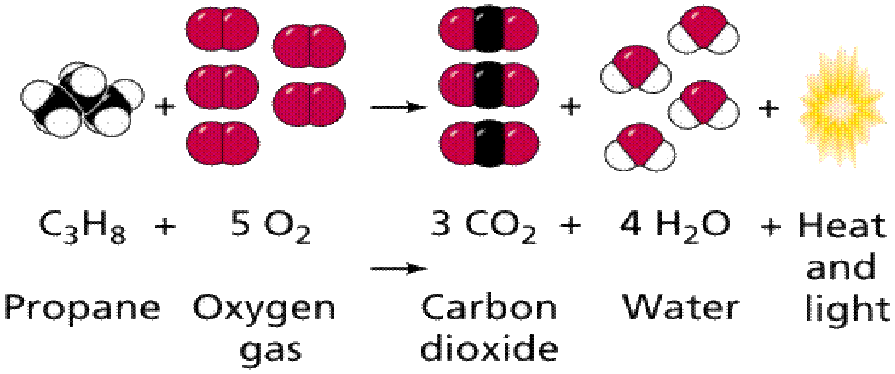


Figure I.8: The combustion of propane.

I.5.2 Thermodynamic state transformations

A transformation refers to the process by which a system evolves from an initial state to a final state as a result of an external disturbance or change in its surroundings. This evolution typically involves variations in one or more state variables that define the system's condition.

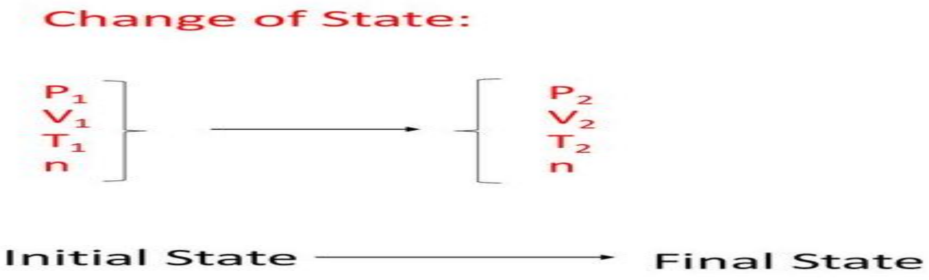


Figure I.9: Change of state.

In thermodynamics, there are four fundamental transformations:

1. **Isochoric transformation**: occurs at constant volume ($V=cst$ and $\Delta V=0$). (e.g., heating a fluid in a closed system).
2. **Isobaric transformation**: Isobaric transformation occurs at constant pressure ($P=cst$ and $\Delta P=0$). (e.g., heating a mass of water).
3. **Isothermal transformation**: Isothermal transformation occurs at constant temperature ($T=cst$ and $T=0$). (e.g., compression and expansion).
4. **Adiabatic transformation**: An adiabatic process takes place without any heat exchange between the system and its surroundings, meaning $\mathbf{Q = 0}$. Examples include the compression or expansion of a gas in a thermally insulated system.

5. **Reversible transformation:** A reversible transformation is an idealized process composed of an infinite succession of equilibrium states. If the process is reversed, the system retraces the same sequence of equilibrium states in the opposite direction.
   This is a model (does not actually exist), and it represents the limiting case where the transformation always remains close to the equilibrium state, essentially an infinitely slow transformation. It should not be confused with equilibrium.
6. **Irreversible transformation**: Every real transformation is irreversible; these are rapid and abrupt changes where the intermediate state variables are not known at each moment, with the exception of the initial and final equilibrium states.

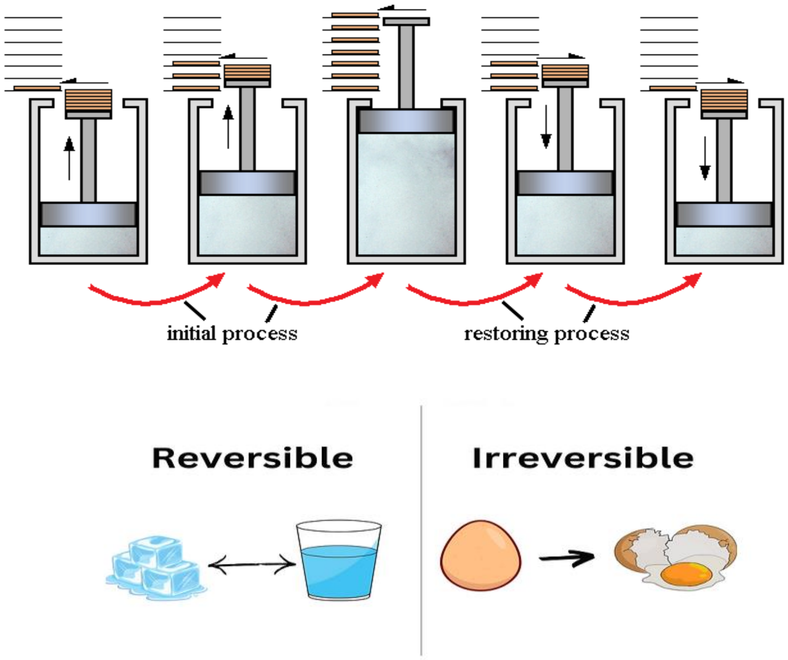


Figure I.10: Reversible and irreversible transformation.

I.6 Physical transformation or phase change

A phase change is a physical transformation in which a substance transitions from one state of matter to another, such as solid, liquid, or gas, without any alteration in its chemical composition. Throughout this process, the nature and quantity of the chemical species remain constant; however, their molecular arrangement and degree of mobility are modified, reflecting a change in their physical organization.

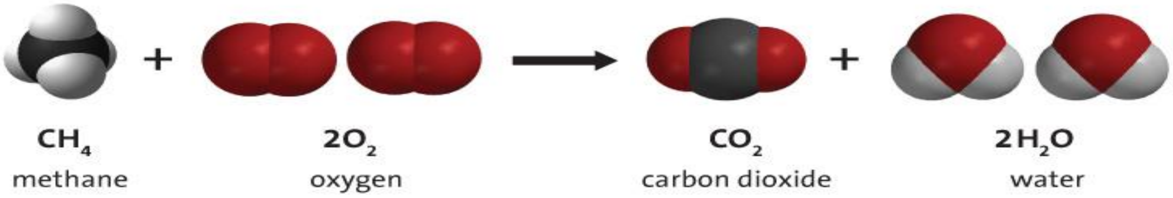


Figure I.11: Methane combustion.

I.7 Ideal gas model

I.7.1 Definition

An ideal gas is a theoretical model consisting of non-interacting particles that occupy all available volume and interact only through perfectly elastic collisions.

This model approximates the behavior of real gases under low-pressure conditions and obeys the ideal gas law, expressed as:

PV = nRT,

where *P* is pressure, *V* is volume, *n* is the amount of substance in moles, *R* is the ideal gas constant, and *T* is the absolute temperature.

I.7.2 Equation of State for an Ideal Gas

The behavior of an ideal gas is described by the equation PV = nRT, where:

P is the pressure exerted by the gas, commonly measured in atmospheres (atm), Pascals (Pa), or bars (bar). Conversion factors include:

1 atm = 1.0132×10^5 Pa,

1 bar = 10^5 Pa,

1 atm = 760 mmHg = 760 Torr.

V is the volume occupied by the gas, typically expressed in liters (L) or cubic meters (m^3), with the relation:

1 L = 1 dm^3 = 10^{-3} m^3.

n represents the amount of substance in moles (mol).

R is the universal gas constant, with common values depending on the units used:

R = 0.082 L.atm/(mol.K),

R = 8.32 J/(mol.K),

R = 2 cal/(mol.K).

T is the absolute temperature, expressed in Kelvin (K), and related to Celsius by:

T (K) = T (°C) + 273.15.

I.7.3 Processes of an ideal gas

There are several transformations for an ideal gas, defined as follows:

a. **Isochoric process of an ideal gas:** This is a transformation that occurs at constant volume $V_2 = V_1$ (final volume V_2 equals the initial volume V_1). In this transformation, no work is exchanged through pressure forces between the system and its surroundings, meaning W = 0.

$$W_{1-2} = -\int_1^2 P.dV = 0$$

b. **Isobaric process of an ideal gas:** This transformation occurs at constant pressure $P_1 = P_2$ (pressure of the final state P_2 is equal to the initial pressure P_1).

$$W_{1-2} = -\int_1^2 P.dV = -P\,(V_2 - V_1)$$

c. **Isothermal process of an Ideal Gas:** This process takes place at a constant temperature, meaning the final temperature T_2 is equal to the initial temperature T_1 ($T_2 = T_1$).

$$W_{1-2} = -\int_1^2 P.dV = -\int_1^2 nRT\,\frac{dV}{V} = nRT\,ln\frac{V_1}{V_2} = nRT\ln\frac{P_2}{P_1}$$

d. **Adiabatic process of an ideal gas:** This is a transformation that occurs without the exchange of heat with the external surroundings (Q = 0).

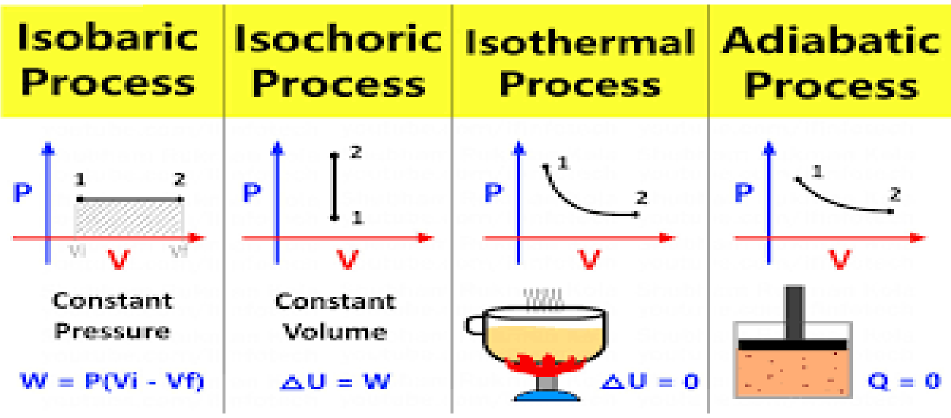


Figure I.12: The main thermodynamic transformations

e. **Processes (open, closed, or cyclic)**:

It is a transformation in which all state variables return to their original values, indicating that the final state is identical to the initial one ($T_2 = T_1$, $P_2 = P_1$, $V_2 = V_1$).

This typically involves a sequence of changes followed by a complete return to the starting conditions.

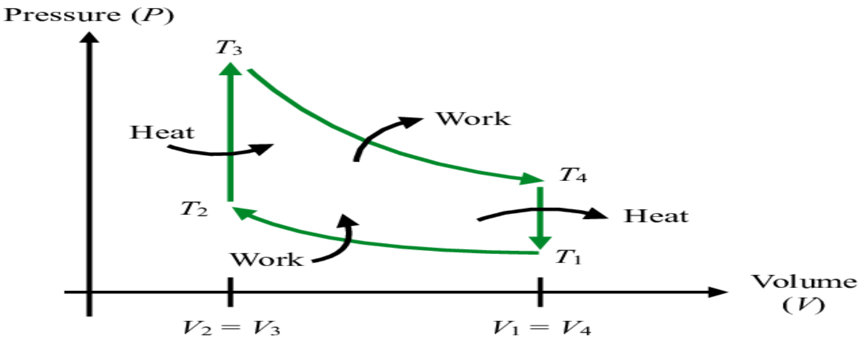


Figure I.13: Example of a thermodynamic cycle.

f. **Monothermic processes**: This is a process that occurs in a system at a constant external temperature. The temperature of the system can vary or may not be defined if the system is not in thermal equilibrium.

g. **Infinitesimal processes:** A transformation is considered infinitesimal when the system passes between two equilibrium states that are infinitely close to each other. In this case, the exchanged heat is given by the differential expression: $dQ = m.c.dT$, where m is the mass, c is the specific heat capacity, and dT is the infinitesimal change in temperature.

h. **Quasi-Static processes**: This is a transformation slow enough for the system to pass through a continuous sequence of equilibrium states infinitely close from i to f.

i. **Reversible and irreversible processes:** A transformation is considered reversible if it satisfies two conditions: It must be infinitely slow. It must be reversible, meaning the process follows the same sequence of equilibrium states, but in the reverse direction. (B →A) as in the forward direction (A→B). A real transformation is irreversible, either because it is fast (abrupt) or because, although slow, it is not reversible.

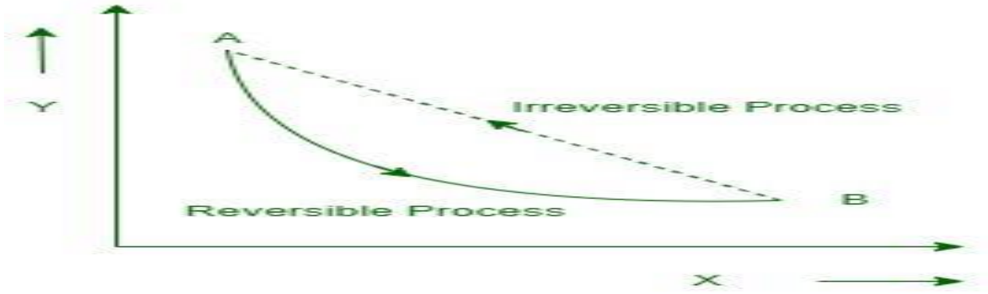


Figure I.14: Reversible and irreversible process.

Example of Application:

1. A sample of ideal gas undergoes an isothermal process starting from the state characterized by (P_1 = 1 atm, V_1 = 2 L, T_1 = 25 °C) to the state (P_2 = 12 atm). Calculate V_2?
2. This mass undergoes an isobaric transformation from its initial state to T = 267 °C. Calculate V_3?
3. We introduce this mass into a closed steel cylinder at 27 °C and 2 atm. What is its pressure P_4 if we heat it to 130 °C?

Solution :

$$P_1V_1 = P_2V_2 \Rightarrow V_2 = \frac{P_1V_1}{P_2} = \frac{1\,x\,2}{12} = 0.16\,L$$

$$\frac{V_1}{T_1} = \frac{V_3}{T_3} \Rightarrow V_3 = \frac{V_1T_3}{T_1} = \frac{540\,x\,2}{28} = 3.6L$$

$$\frac{P_1}{T_1} = \frac{P_4}{T_4} \Rightarrow P_4 = \frac{T_4P_1}{T_1} = \frac{403\,x\,2}{300} = 2.68\,atm$$

I.7.4 Graphical representation of ideal gas transformations

Changes in the state of a system resulting from a transformation can be illustrated using various thermodynamic diagrams, which help visualize the system's evolution over time. Different types of transformations, corresponding to specific forms of energy exchange with the surroundings, can be easily identified in these diagrams—often appearing as vertical or horizontal lines:

Isochoric transformation : constant volume (**V = constant**) ;
Isobaric transformation : constant pressure (**P = constant**) ;
Isothermal transformation : constant temperature (**T = constant**) ;
Isentropic (adiabatic) transformation: no heat exchange (**Q = 0**).

a. Clapeyron Diagram: P=f(V) in the (P, V) plane

It is a representation where the pressure P of a thermodynamic system is indicated as a function of its mass-specific volume V (in physics) or molar volume (in chemistry) to follow the evolution of a transformation.

Such a diagram can only be plotted when pressure is defined in the system, i.e., in a quasi-static transformation.

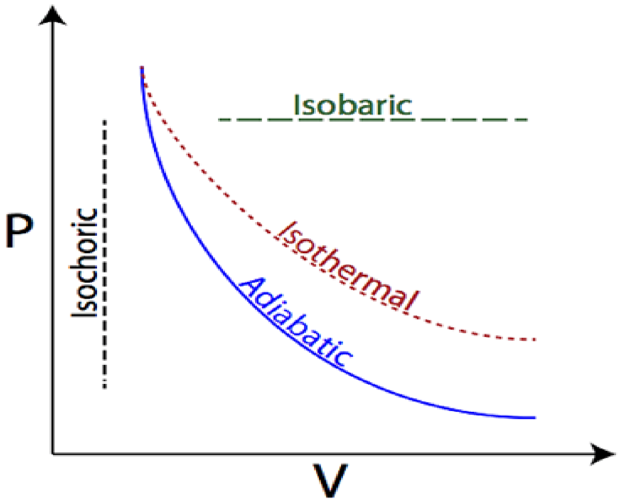


Figure I.15: Clapeyron Diagram.

b. Amagat Diagram: PV=f(P) in the (P, V) plane

This diagram is named after the French physicist Emile Amagat (1841-1915), who notably worked on high-pressure gases.

It is a thermodynamic diagram representing, for a given fluid and at constant temperature, the variation of the pressure–volume product can be analyzed as a function of the pressure applied to the fluid. This representation can also be used to illustrate how the compressibility factor evolves with changing pressure.

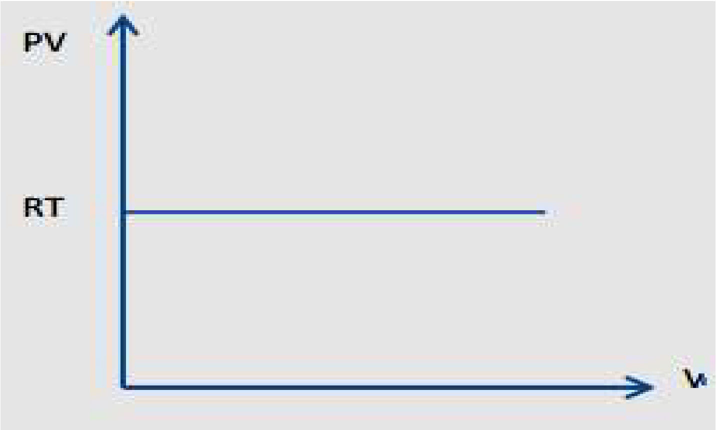


Figure I.16: Amagat Diagram.

I.7.5 Fundamental laws of ideal gases

An ideal gas must obey the following laws:

a. Boyle's law:

For a given mass of gas at constant temperature, the product of pressure and volume remains unchanged: **PV = constant**.

Considering two equilibrium states of the same gas at identical temperature:

- P_1 and V_1 are the pressure and volume in state (1),
- P_2 and V_2 are the pressure and volume in state (2),

Boyle's Law is written as: $P_1V_1 = P_2V_2$.

On a Clapeyron diagram where pressure (**P**) is plotted as a function of volume (**V**), the resulting curve is a hyperbola, illustrating that pressure is inversely proportional to volume.

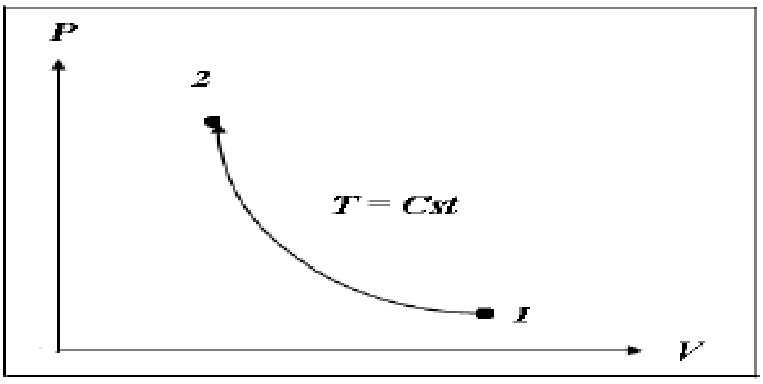


Figure I.17: The curve of Clapeyron Diagram.

b. Gay-Lussac's law:

Gay-Lussac's law states that, for a fixed amount of gas kept at constant volume, the pressure is directly proportional to the absolute temperature. This implies that the ratio **P/T** remains constant when comparing two different states of the same gas, provided the volume does not change.

The mathematical expression of the law is:

$P_1 / T_1 = P_2 / T_2$

Where:

- P_1 and T_1 are the pressure and temperature in the initial state (1),
- P_2 and T_2 are the pressure and temperature in the final state (2).

On the graph $P=f(T)$, it is observed that the curve is linear.

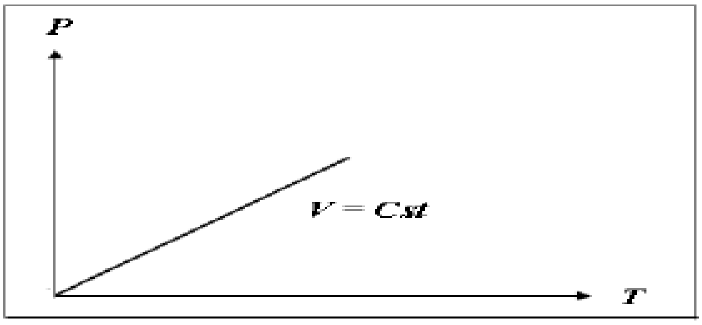


Figure I.18: The curve of $P=f(T)$.

c. Charles's law:

Charles's Law states that, for a fixed quantity of gas at constant pressure, the volume is directly proportional to the absolute temperature. This means the ratio **V/T** remains constant when comparing two states of the same gas under constant pressure.

The law is expressed as:

$\mathbf{V_1 / T_1 = V_2 / T_2}$

Where:

- $\mathbf{V_1}$ and $\mathbf{T_1}$ are the volume and temperature in the initial state (1),
- $\mathbf{V_2}$ and $\mathbf{T_2}$ are the volume and temperature in the final state (2).

The relationship will be: $V_1/T_1=V_2/T_2$. On the graph $V=f(T)$, it is observed that the curve is linear.

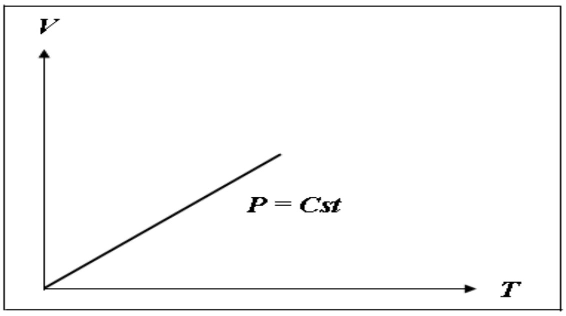


Figure I.19: The graph $V=f(T)$.

d. Avogadro's law:

Under identical conditions of pressure and temperature, all ideal gases occupy the same molar volume. This means that, at a given pressure and temperature, the molar volume V_m remains constant: V_m = constant.

e. Dalton's law:

Consider a mixture composed of several gases confined within a volume V, at temperature T and total pressure P. Let n_i represent the number of moles of the *i*-th gas. For an ideal gas mixture, the following relations apply:

PV=nRT;

The total pressure, P_{total}, is the sum of the partial pressures of each component gas: $P_{total} = \sum P_i$. Each P_i represents the partial pressure of gas i, which is the pressure it would exert if it occupied the entire volume alone at the same temperature T. $\mathbf{P_{total}= \Sigma P_i}$

For a gas, $P_iV=n_iRT$ (Equation 2). Dividing (2) by (1) yields:

$\mathbf{P/P_i=n/n_i=x_i}$

With x_i representing the mole fraction of component i. $P_i=x_i \cdot P$, and $\Sigma P_i=P$, and $\Sigma x_i=1$.

Example:

Given a gaseous mixture composed of O_2, N_2, and CO_2 at a total pressure of 1 atm and a temperature of 273.15 K. If the mixture contains 0.1 mole of N_2, 0.4 mole of CO_2, and a total of 2.0 moles of gas, determine the partial pressure of O_2 ($P(O_2)$).

Solution:

$$P(O_2) = X_{O_2}.P$$

$$n_T = n(N_2) + n(O_2) + n(CO_2)$$

$$n(O_2) = n_T - [n(N_2) + n(CO_2)]$$

$$n(O_2) = 2 - (0.1 + 0.4) = 1.5\, mole$$

$$x(O_2) = \frac{n(O_2)}{n_T} = \frac{1.5}{2} = 0.75$$

$$P(O_2) = x(O_2)\,.P = 0.75\, atm$$

I.8 Real gases

In real gases, intermolecular interactions occur and become particularly significant at short distances between molecules. As a result, the ideal gas model does not accurately describe the behavior of all gases under all thermodynamic conditions. Therefore, attempts have been made to modify the ideal gas law, which is too simple, to better adapt it to the reality observed in experimental results. Among the various equations presented in the literature, the Van der Waals equation of state will be considered. It applies to fluids and partially accounts for the intermolecular forces between their constituent particles.

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

In this equation, *n* represents the number of moles of gas, while *a* and *b* are empirical constants specific to each gas. The term a/V^2 reflects the contribution of intermolecular attractions (internal or cohesive pressure), and *b* represents the finite volume occupied by the gas molecules (covolume). When both correction terms are neglected, the equation simplifies to the ideal gas law.

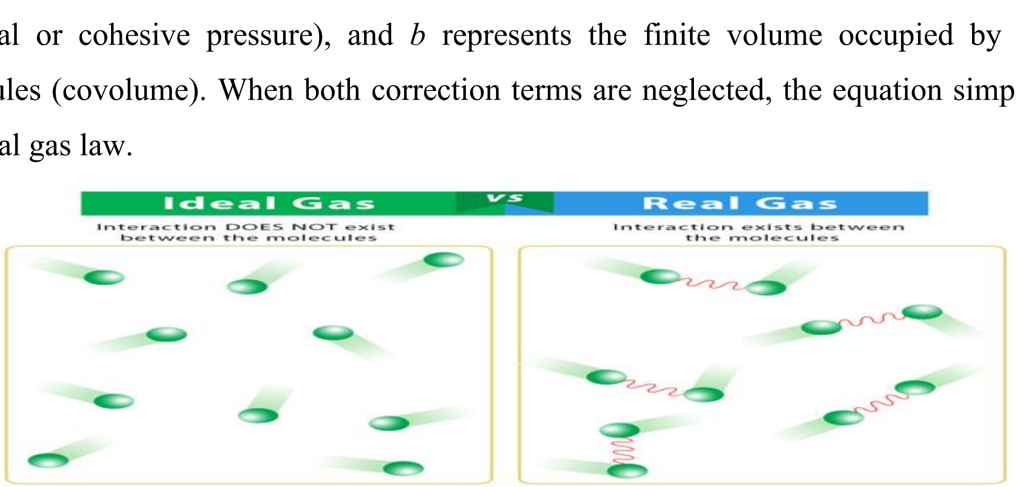


Figure I.20: Ideal vs Real gas.

Real-World Examples & Case Studies

- Steam Engine (Classical Thermodynamics): The efficiency of steam engines in the 18th century was analyzed using the laws of thermodynamics, paving the way for industrialization.
- Refrigerators & Heat Pumps (Technical Thermodynamics): Domestic refrigerators use a reversed Carnot cycle to maintain low temperatures inside while rejecting heat to the surroundings.
- Environmental Application: Gas laws are used in air quality monitoring stations to calculate pollutant concentrations from pressure, temperature, and volume measurements.
- Medical Example: Oxygen cylinders in hospitals are filled using principles from Boyle’s and Gay-Lussac’s laws to ensure correct dosage under varying temperatures.

Self-Assessment Quiz

1- Multiple Choice Questions

1. Which of the following is an extensive property?
   a) Temperature;
   b) Pressure;
   c) Volume;
   d) Density.
2. In an isothermal process for an ideal gas:
   a) Temperature remains constant;
   b) Pressure remains constant;
   c) Volume remains constant;
   d) Heat exchange is zero.

2- True/False

3. The Van der Waals equation applies only to ideal gases.
4. In a closed system, matter can cross the system boundary.

3- Short Answer

5. State the first condition for thermodynamic equilibrium.
6. Give an everyday example of an adiabatic process.

Chapter Summary:

This chapter introduced the fundamental concepts of thermodynamics, including the definition, branches, and classifications of systems. It explained the distinction between intensive and extensive variables, the concept of state functions, and the principles of energy exchange. The criteria for thermodynamic equilibrium were discussed, along with the main types of transformations (isochoric, isobaric, isothermal, adiabatic, reversible, irreversible). The ideal gas model and fundamental gas laws were presented, followed by real gas behavior and the Van der Waals equation.

Essential Formulas :

- Ideal Gas Law: $PV=nRT$;
- Boyle's Law : $P_1V_1=P_2V_2$ (T constant) ;
- Charles's Law : $V_1/T_1=V_2/T_2$ (P constant) ;
- Gay-Lussac's Law : $P_1/T_1=P_2/T_2$ (V constant) ;
- Avogadro's Law: V_m=constant at given P and T;
- Dalton's Law: $P_{total}=\sum P_i$, $P_i=x_i \cdot P_{total}$;
- Van der Waals Equation:

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

Corrected Exercises

Exercise 1:

At standard temperature and pressure (STP), one mole of an ideal gas occupies 22.4 liters, corresponding to a pressure of 1 atmosphere and a temperature of 0 °C (273.15 K).

A. Calculate the ideal gas constant in:

1. L.atm/mol.K;
2. J/mol.K;
3. cal/mol.K.

B. Compute the molar volume of one mole of an ideal gas under standard temperature and pressure (STP).

Exercise 2:

1. Classify the following systems as open, closed, or isolated, and specify the type of exchange (matter and/or energy) that occurs between each system and its surroundings:

You, a tree, a moving car, a turned-on TV, the liquid in a thermometer, hot coffee in a thermos bottle, the universe.

2. Among the following variables, identify which are intensive and which are extensive:

Pressure, Volume, Mass, Temperature, Mole fraction of component i, Molar concentration, Molar volume, Energy, Power, Surface area, Speed, Mass density.

Exercise 3:

A spherical balloon is inflated with helium (He) until its diameter reaches 25 meters.

If the pressure is 730 torr and the temperature is 82°F, what is the mass of helium (in kg) contained in the balloon.

Data: M(He) = 4 g. mol^{-1}; R = 0.082 L.atm/mol^{-1}.K^{-1}.

Exercise 4:

If the composition of air is given in percentages: N_2 = 79.04%, O_2 = 20.93%, and CO_2 = 0.03%. Determine the partial pressures of these components under standard conditions.

Exercise 5:

1. A cylinder holds 765 mL of propane gas under a pressure of 1.25×10^5 Pa. What volume will the gas occupy if the pressure is decreased to 1.00×10^5 Pa, assuming temperature remains constant?

2. A sample of oxygen gas is confined in a rigid container at a pressure of 1.63×10^5 Pa and a temperature of –50 °C. To double the pressure, to what temperature must the gas be heated, assuming volume remains constant?

3. A certain amount of helium gas occupies 22.4 L at 0 °C. What will be its volume if the temperature increases to 25 °C, while the pressure remains unchanged?

Exercise 6:

Three containers each contain H_2, O_2, and N_2 under the following conditions:

- H_2 ($V_1 = 2.25$ L, $P_1 = 0.33$ bar, $T_1 = 293$ K);
- O_2 ($V_2 = 5.5$ L, $P_2 = 250$ mmHg, $T_2 = 293$ K);
- N_2 ($V_3 = 1.4$ L, $P_3 = 1.013 \times 10^5$ N/m², $T_3 = 273$ K).

1. Calculate the masses of each gas (assuming ideal gases).
2. The gases are mixed in a single container of volume V = 18.5 L at temperature T = 273 K. Assuming the resulting gas mixture behaves ideally, calculate the following:
a. The total pressure of the mixture.
b. The mole fraction of each component gas.
c. The partial pressure of each gas in the mixture.

Correction

Exercise 1:

A. We have PV=nRT and P=1 atm et T=0 °C

1. ***In L.atm/mol.K ;***

$$R = \frac{PV}{nT} = \frac{1\ (\text{atm})22.4\ (\text{L})}{1\ (\text{mol})\ 273\ (\text{K})} = 0.082\ \text{L.atm/mol.K}$$

2. ***In J/mol.K ;***

$$R = \frac{PV}{nT} = \frac{1\,.101325\ (\text{Pa})\ 22.4\ 10^{-3}\ (\text{m}^3)}{1\ (\text{mol})\ 273\ (\text{K})} = 8.31\ \text{J/mol.K.}$$

3. ***In cal/mol.K***

1cal=4.18 J.

$$R = \frac{8.31}{4.18} = 2\ \text{cal/mol.K.}$$

B. *STP (Standard Temperature and Pressure): P = 1 atm and T = 0* °C

PV= n R T

$$V = \frac{nRT}{P} = \frac{1\,.\,0.082\,.\,298}{1} = 24.436\ \text{L/mol (Molar volume).}$$

Exercise 2:

1.

Open system: You, a tree, a moving car.

Closed system: A turned-on TV, the liquid in a thermometer.

Isolated system: Hot coffee in a thermos bottle, the universe.

2.

Intensive variables: Pressure, temperature, speed, mass density.

Extensive variables: Volume, mass, mole fraction, molar concentration, energy, power, surface area.

Exercise 3:

n=m/M ⟹ m= n . M

PV=nRT ⟹ n=PV/RT

$$m = \frac{P.V}{R.T}\,M$$

P=730 torr, T=82°F, V= $V_{\text{balloon}} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\,(\frac{D}{2})^3$ where **D** is the diameter and **r** the radius.

$$m = \frac{4.P}{3\,.\,R.T}\,\pi\,(\frac{D}{2})^3\ \text{M}$$

1 torr = 133.32 Pa (1 atm= 101325 Pa= 1.01325 Bar= 760 torr).

°C= (°F – 32) $\frac{5}{9}$ ⟹ 82°F= 27.77 °C= 300.77 k

$$m = \frac{4.\,730\,.\,133.32}{3\,.\,8.31\,.\,300.77}\ 3.14\,(\frac{25}{2})^3\ \ 4\ = \ 1273.62\ \text{Kg.}$$

Exercise 4:

Standard total pressure: P_{total}=1 atm.

Dalton's Law: the partial pressure of a gas in a mixture is equal to the mole fraction of the gas multiplied by the total pressure: $\mathbf{P_i = X_i\ P_T}$

Air composition:

N_2=79.04% ⇒ X_{N2}=0.7904.

O_2=20.93% ⇒ X_{O2}=0.2093

CO_2=0.03% ⇒ X_{CO2}=0.0003

Partial pressure of N_2:

$$P_{N2} = 0.7904 \cdot 1 \text{ atm} = 0.7904 \text{ atm}$$

Partial pressure of O_2: $P_{O2} = 0.2093 \cdot 1$ atm = 0.2093 atm

Partial pressure of CO_2: $P_{CO2} = 0.0003 \cdot 1$ atm = 0.0003 atm

Exercise 5:

1. The volume of the gas. This is an isothermal transformation: PV=Cost

We use Boyle–Mariotte's law: $P_1V_1=P_2V_2$

$V_2= P_1V_1/P_2 = 765 \ . \ 1.25 \ 10^5 / 10^5 = 956.25$ mL.

2. The temperature of the gas. This is an isochoric transformation: P/T= cost

We use Charles's law: $P_1/T_1=P_2/T_2$

$T_2 = P_2 T_1/ P_1 = 2 \ P_1 \ 223 / P_1 = 446$ K. (Temperature must be expressed in kelvin).

3. The volume of the gas. This is an isobaric transformation: V/T = cost

We use Gay-Lussac's law:: $V_1/T_1 = V_2/T_2$

$V_2 = V_1 \ T_2/T_1 = 22.4 \ 273 / 298 = 20.52$ L.

Exercise 6:

1. The mass of each gas

PV=nRT   n=PV/RT   m/M= PV/RT   m= PVM/RT

$$M(H_2) = \frac{0{,}33 \ . \ 10^5 \ Pa \ .2.25 \ 10^{-3} \ \ m^3 \ \ 2 \ g/mol}{8.31 \ \ 293} = 0.06 \text{ g}$$

$$M(O_2) = \frac{250 \ . \ 133{,}32 \ Pa \ . \ 5.5 \ 10^{-3} \ \ m^3 \ \ 32 \ \ g/mol}{8.31 \ \ 293} = 2.41 \text{ g}$$

$$M(N_2) = \frac{01{,}013 \ . \ 10^5 \ Pa \ . \ 1.4 \ 10^{-3} \ \ m^3 \ \ 28 \ \ g/mol}{8.31 \ \ 273} = 1.75 \text{ g} \qquad (N/m^2=Pa)$$

2.a. Total pressure

PV=nRT $P_T=n_TRT/V$

$n_T=\sum n_i = n(O_2) + n(H_2) + n(N_2) = (2.41/32) + (0.06/2) + (1.75/28)= 0.168$ mol

$P_T= 0.168 \ . \ 0.082 \ . \ 273 / 18.5 = 0.2$ atm.

2.b. Mole fraction of each gas Xi= ni/nT

$X(H_2)= nH_2/ n_T = (0.06/2)/0.168= 0.18$.

$X(O_2)= nO_2/ n_T = (2.41/32)/0.168= 0.45$.

$X(N_2)= nN_2/ n_T = (1.75/28)/0.168= 0.37$.

***2.c. Partial pressure of each gas* $P_i= X_i \ . \ P_T$**

$P(H_2)= 0.18 \ . \ 0.2 = 0.036$ atm

$P(O_2)$= 0.45. 0.2 = 0.09 atm

$P(N_2)$= 0.37 . 0.2 = 0.074 atm

Non-Corrected Problems for Training

1. A sample of nitrogen gas occupies 3 L at 2 atm and 300 K. It expands isothermally to 6 L. Calculate the final pressure.
2. A 2 mol sample of oxygen is heated at constant volume from 300 K to 500 K. Calculate the change in internal energy (C_v = 21 $J.mol^{-1}.K^{-1}$).
3. In a closed container, 5 mol of CO_2 follows the Van der Waals equation with a = 3.592 $L^2.atm.mol^{-2}$ and b = 0.0427 $L.mol^{-1}$. Calculate the pressure at T = 350 K and V = 10 L.
4. A cylinder contains helium gas at 1 atm and 25 °C. The gas is compressed adiabatically until its volume is reduced by half. Calculate the final temperature (γ = 1.66).

Chapter II:

First principle of Thermodynamics

Learning Objectives:

By the end of this chapter, students should be able to:

- State and apply the First Law of Thermodynamics to closed and open systems.
- Define and compute internal energy (U), work (W), and heat transfer (Q) for various thermodynamic processes.
- Interpret and use enthalpy (H) in energy balance calculations.
- Explain the concept of reversible and irreversible processes.
- Use P–V diagrams to describe and analyze processes such as isothermal, adiabatic transformations.
- Apply the energy balance equations to solve practical engineering problems involving heat and work interactions.

II.1 Introduction

Thermodynamics has applications in various industrial sectors.

An industrial facility produces or consumes energy and is the site of physico-chemical phenomena that evolve towards an equilibrium state, which can be predicted by thermodynamics.

Thermodynamics originally emerged as a framework for studying how heat could be converted into mechanical work. The French physicist Sadi Carnot was a key figure in this development, introducing foundational ideas in his 1824 work titled *Reflections on the Motive Power of Fire*.

We will now introduce, in a simplified formulation, the basics of thermodynamics necessary for understanding the conversion of heat into mechanical energy and vice versa.

Example: The brakes of a vehicle descending a hill at a constant speed heat up. External forces (gravity) provide the system with work that transforms into heat.

II.2 Notion of Temperature

Temperature is an intensive and measurable property that reflects the thermal state of a body whether it is hot or cold. It provides insight into the degree of molecular agitation within the substance. As the molecular speed (v_i) increases, so does the kinetic energy (E_k) of the particles, leading to higher thermal agitation. This relationship is described by Maxwell's distribution of molecular speeds, which shows that as temperature rises, the average molecular speed and thus the kinetic energy increases accordingly.

$$\frac{1}{2}m_t V_t^2 = \frac{1}{2}k_B T$$

Where:

- m is the mass of a molecule,
- T represents the absolute temperature,
- k is the Boltzmann constant, approximately $1.38064852 \times 10^{-23}\ \mathrm{J\cdot K^{-1}}$,
- v denotes the velocity of the particles.

II.2.1 Thermometry

Thermometry is the field of physics that focuses on the measurement of temperature. A thermometer derived from the Greek words thermos ("heat") and metron ("measure") is an instrument designed to detect and indicate temperature values.

II.2.2 Zeroth law of thermodynamics

Consider two systems, A and B, separated by a diathermal wall, while the combined system (A + B) is thermally isolated from the external environment. If the two systems initially differ in their thermal states, energy in the form of heat will be exchanged. Over time, this exchange ceases, indicating that the systems have reached thermal equilibrium.

This fundamental observation leads to the zeroth law of thermodynamics, which establishes the existence of a measurable intensive property temperature that characterizes the thermal state of a system. When two systems are in thermal equilibrium, they possess the same temperature, regardless of the nature of their interaction or composition.

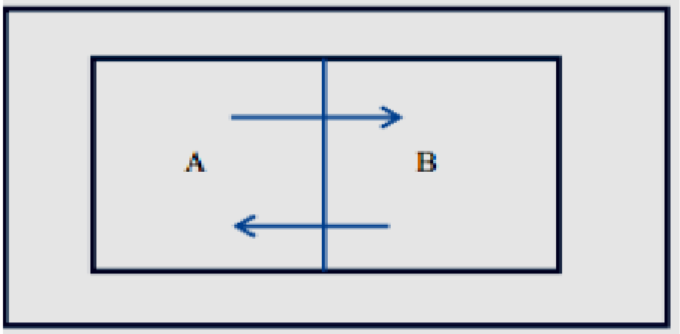


Figure II.1: Zeroth law of thermodynamics

II.2.3 Temperature scales: Centesimal, Absolute, and Fahrenheit

Different scales are used to measure temperature: the Newton scale (established around1700), Rømer (1701), Fahrenheit (1724), Réaumur (1731), Delisle (1738), centigrade (Celsius)(1742), Rankine (1859), Kelvin (1848), Leyden (circa 1894), Celsius (1948).

a. Centesimal

In the centesimal scale, the two phenomena are separated by 100 on this scale, and 1°C represents one hundredth of the reference range. It is, therefore, a centesimal scale.

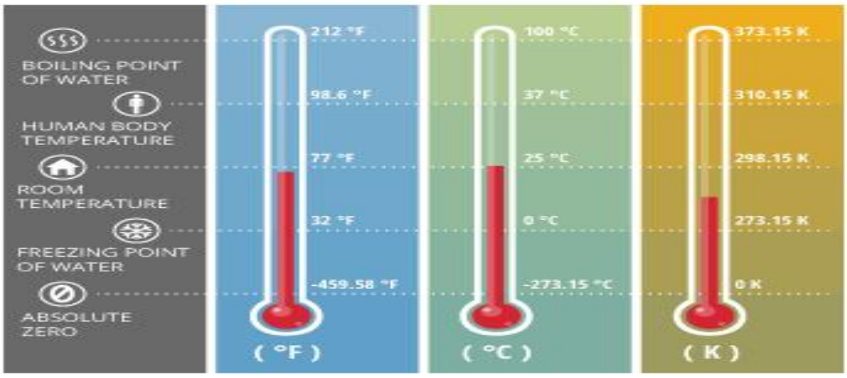


Figure II.2: Centesimal scale

b. Absolute

Absolute temperature expresses the energy intensity of matter. It is zero when matter contains no energy, has no heat.

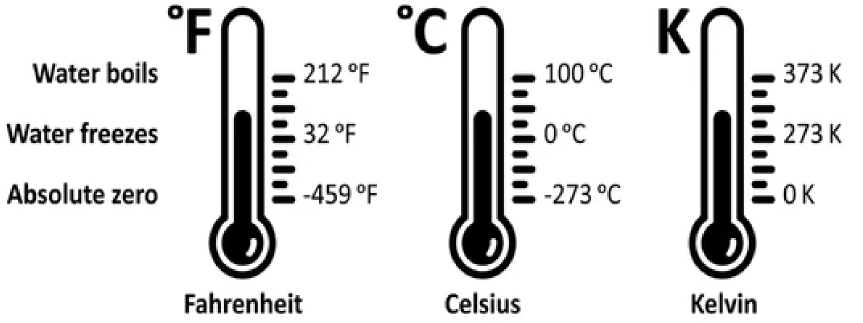


Figure II.3: Absolute zero temperature

c. Fahrenheit

The zero point on the Fahrenheit scale corresponds to the temperature at which a mixture of equal parts water and ammonium chloride begins to freeze. The chosen scale is a subdivision of the interval into 12 units, each subdivided into 8 degrees, making a total range of 96 degrees - the Fahrenheit degree.

II.2.4 Thermometry

Thermometry is the area of physics dedicated to the measurement of temperature. A thermometer derived from the Greek words *thermos* (“heat”) and *metron* (“measure”) is an instrument designed to detect and indicate temperature values.

a. Different types of thermometers

The most frequently used types of thermometers are:

Gas thermometer: Based on the principle of the volume change of gas at constant pressure and mass, or the change in pressure at constant volume and mass, it is sensitive to temperature variations and is used as a regulator to control others.

Dial and needle thermometer: Also known as a Bimetallic thermometer, it consists of a pair of strips with different coefficients of expansion.

Liquid crystal thermometer: By using the color change of liquid crystals depending on the temperature, an interval of temperature (but not an exact value) can be defined. This type of thermometer is often used in aquariums. The most common ones include:

Alcohol thermometer: Due to its very low freezing point ranging from -130 °C to 78 °C, it is used in the medical field for measuring body temperature and air temperature, especially in extremely low freezing temperatures.

Mercury thermometer: Often used in wall thermometers to measure air temperature.
Electronic thermometer: This type of thermometer remains the most accurate and efficient, usable in all conditions. It measures body temperature, air temperature, room temperature, liquid temperature, etc., and is the easiest to use just a simple click, and it displays the exact value on its screen.

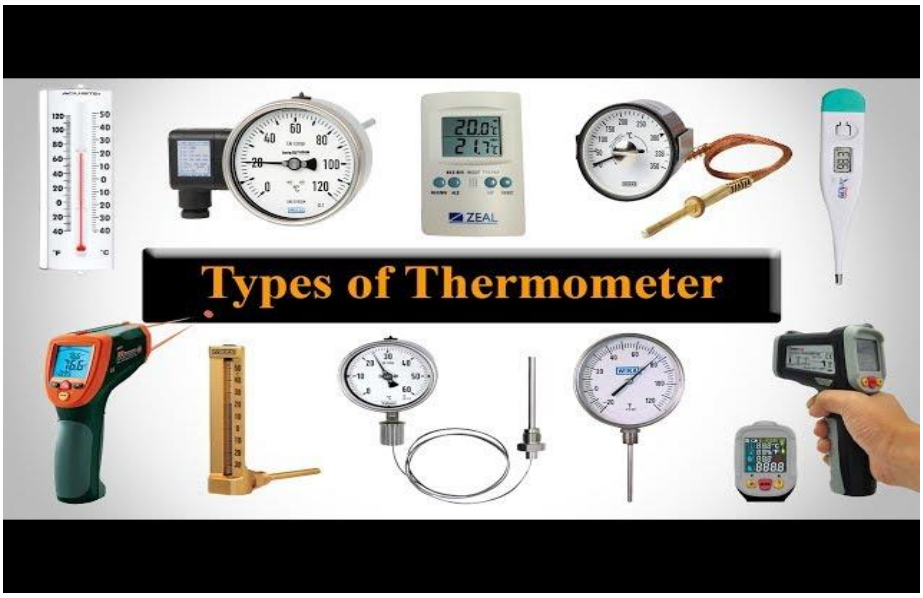


Figure II.4: Types of thermometers.

II.3 Concepts of heat or quantity of heat Q

II.3.1 Definition of heat

Heat can be most simply defined as the energy responsible for changing the temperature of a body. When a system absorbs heat from its surroundings, its temperature rises an effect that can be measured with high precision.

If ΔT represents the temperature change, the amount of heat absorbed by the system can be calculated using the following relation:

$$\delta Q = CdT$$

$$Q = \int_{Ti}^{Tf} CdT$$

dT represents the temperature change, and *C* is the thermal capacity or heat capacity expressed in $J \cdot K^{-1}$ or $cal \cdot K^{-1}$.

Remarks:

- Heat is considered positive when it is absorbed by the system, and negative when it is released to the surroundings.

- The unit of heat is the joule (J) in the SI system, though it may also be expressed in kilocalories (kcal).
- Like work, heat depends on the path taken during a process and not solely on the initial and final states hence, it is not a state function.
- Thermal energy naturally flows from a body at higher temperature to one at lower temperature, continuing until thermal equilibrium is reached between them.

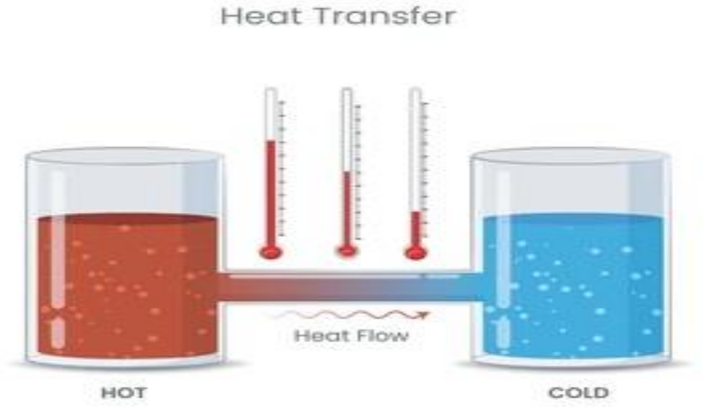


Figure II.5: Heat transfer.

II.3.2 Specific heat or molar heat of a pure substance

The specific heat capacity or molar heat capacity, denoted by c, refers to the amount of thermal energy required to raise the temperature of 1 gram or 1 mole of a pure substance by 1 kelvin (or 1 degree Celsius). Its units are J/g.K or J/mol.K.

a. For substances in the gaseous state, two types of specific heat are defined:

- c_p: specific heat at constant pressure;
- c_v: specific heat at constant volume.

  → Note that: $c_p \neq c_v$

b. For substances in the liquid or solid state, the difference between c_p and c_v is generally negligible, so we approximate:

  → $c_p \approx c_v \approx c$

II.3.3 Heat capacity (caloric)

Heat capacity, denoted by C, is defined as the amount of heat required to raise the temperature of an entire sample of a pure substance by 1 kelvin. It is calculated as the product of the specific heat and the mass, or the molar heat and the number of moles. Its unit is joules per kelvin (J/K).

$$C = mc = nc$$

For pure substances in the gaseous state, we define:

CP: Heat capacity at constant pressure. With: $c_p = m \cdot c_p \; or \; n \cdot c_p$

C_V: Heat capacity at constant volume. With: $C_V = m \cdot c_V \; or \; n \cdot c_V$

II.3.4 Type of heat

There are two types of heat:

a. Sensible heat with temperature change

In such cases, the quantity of heat exchanged between two bodies at different temperatures is directly proportional to the temperature difference (ΔT) and to the amount of substance involved expressed either as mass (m) or number of moles (n).

1. In the case of an isochoric transformation:

For an isochoric transformation of a gas, we have dV=0, therefore, the elementary amount of heat involved is:

For an infinitesimal transformation: $\delta Q = C_V dT$

During a finite transformation, the amount of heat transferred from state (1) to state (2) is given by:

$$\int_1^2 \delta Q = \int_{T_1}^{T_2} C_V\, dT \Rightarrow Q = Q_V = \int_{T_1}^{T_2} C_V\, dT = \int_{T_1}^{T_2} m\, C_V dT = \int_{T_1}^{T_2} n\, C_V dT$$

If C_V is constant between T_1 and T_2:

$$Q = Q_V = C_V(T_2 - T_1) = m\, C_V(T_2 - T_1) = n\, C_V(T_2 - T_1)$$

2. In the case of an isobaric transformation:

The amount of heat involved is: $\delta Q = CPdT$

$$\int_1^2 \delta Q = \int_{T_1}^{T_2} C_P\, dT \Rightarrow Q = \int_{T_1}^{T_2} C_P\, dT = \int_{T_1}^{T_2} m\, c_P dT = \int_{T_1}^{T_2} n\, c_P dT$$

If "C_P" is constant between T_1 and T_2:

$$Q = Q_P = C_P(T_2 - T_1) = m\, c_P(T_2 - T_1) = n\, c_P(T_2 - T_1)$$

In general, the relationship for the quantity of heat when the temperature changes from T_1 to T_2 is then written as:

$$Q = \int_{T_1}^{T_2} C\, dT = \int_{T_1}^{T_2} m\, c\, dT = \int_{T_1}^{T_2} n\, c\, dT$$

The specific (or molar) heat capacity varies with temperature and can be expressed as a function:

c=f(T)

However, if the heat capacity **C** remains constant over the temperature range **[T_1, T_2]**, the heat exchanged is given by:

$Q=C.(T_2-T_1)$;

$Q = m.c.(T_2 - T_1)$.

c: Specific heat capacity (J/kg.K or cal/kg.K).

$Q = n.c.(T_2-T_1)$;

c: Molar heat capacity (J/mol.K or cal/mol.K).

With:

Q: Amount of heat (J or Kcal).

C: Heat capacity of the system, expressed in joules per kelvin (J/K) or calories per kelvin (cal/K);

m: Mass of the substance, given in kilograms (kg);

n: Amount of substance, measured in moles (mol).

b. Variation of heat related to changes in physical state

A substance can exist in three physical states, also known as phases. Phase changes such as melting, freezing, vaporization, and condensation occur under conditions of constant pressure and temperature. During these transformations, the system requires or releases an additional amount of energy, known as latent heat. This energy does not change the temperature but enables the transition between phases.

The latent heat associated with a specific phase change is denoted as follows:

L_{fus}: latent heat of fusion.

L_{vap}: latent heat of vaporization.

L_{sub}: latent heat of sublimation.

We then define:

- Specific latent heat L (J/kg), where Q = m.L.
- Molar latent heat L (J/mol), where Q = n.L.

Note:

The heat required for a phase change is very high compared to the heat required to raise temperatures (sensible heat).

II.3.5 Calorimetry

Calorimetry deals with the measurement of heat quantities, allowing for the determination of specific heats, latent heats, and calorific powers. It is based on the principle of the equality of heat exchanges. When two bodies at different temperatures are brought into contact, heat is transferred from the hotter body to the colder one. Once thermal equilibrium is reached, both bodies attain the same final temperature, known as the equilibrium temperature (T_{eq}) of the mixture.

According to the principle of conservation of energy, the heat gained by one body ($Q_1 > 0$) is equal in magnitude to the heat lost by the other ($Q_2 < 0$), which is expressed by the principle of equality of heat exchange:

$Q_1 + Q_2 = 0$.

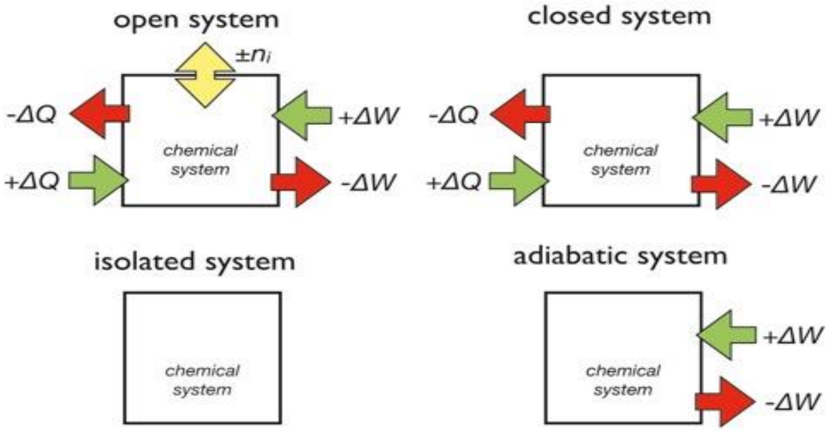


Figure II.6: System types.

The equilibrium temperature is obtained from the energy balance of the two systems. For these measurements, a calorimeter is used. The calorimeter is an enclosure that can be considered thermally isolated or adiabatic (no heat exchange with the external environment).

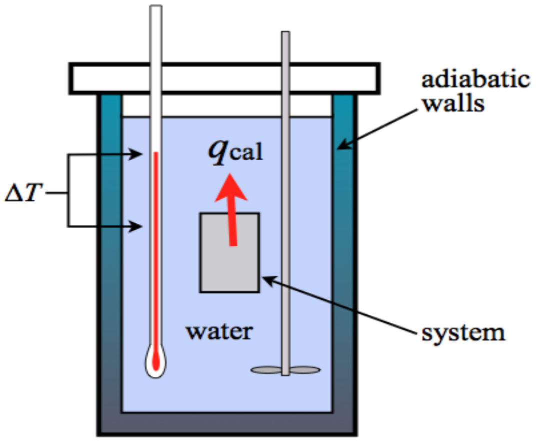


Figure II.7: The Berthelot calorimeter.

A system isolated adiabatically from the external environment:

$\Sigma\ Q = 0 \Longrightarrow Q_1 + Q_2 = 0$

$$\Longrightarrow m_a\, c_a \int_{T_a}^{T_m} dT \;+\; m_b\, c_b \int_{T_b}^{T_m} dT = 0$$

$$\Rightarrow m_a\, c_a(T_m - T_a) + m_b\, c_b\, (T_m - T_b) = 0$$

$$\Rightarrow T_m = T_{eq} = \frac{m_a\, C_a\, T_a + m_b\, C_b\, T_b}{m_a\, C_a + m_b\, C_b}$$

a. Water value 'μ' of the Calorimeter

In the calorimeter, heat exchange also occurs with the calorimeter and its accessories.

We designate 'μ' as the mass of water that exchanges the same amount of heat as the calorimeter and its accessories, known as the 'water value of the calorimeter'.

With: $Ccal = \mu . c_{eau}$.

$\boldsymbol{C_{cal}}$: Calorimeter heat capacity, expressed in joules per kelvin (J/K).

$\boldsymbol{\mu}$: Water value (kg).

Note: $C_P - C_V = R$: Mayer's relation

The Laplace coefficient "$\boldsymbol{\gamma}$" is defined as:

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

By combining Mayer's relation and the coefficient $\boldsymbol{\gamma}$, we can express molar heat capacities in terms of R and $\boldsymbol{\gamma}$.

$$C_V = \frac{R}{\gamma - 1} \qquad\qquad C_P = \frac{\gamma R}{\gamma - 1}$$

c_p *and* c_V: Molar heats, and $\boldsymbol{\gamma}$ is the Laplace coefficient.

Example 1:

A calorimeter initially holds 1 kg of water at a temperature of 20 °C, into which 0.5 kg of water at 60 °C is introduced. If we neglect the influence of the calorimeter on heat, calculate Teq?

Given: cm = 4185 J/kg.K.

Solution:

$Q = 0 => Q_1 + Q_2 = 0$

$Q_1 = m_1\, c_m\big(T_{eq} - T_1\big)$

$Q_2 = m_2\, c_m\big(T_{eq} - T_2\big)$

$\Rightarrow m_1\, c_m\big(T_{eq} - T_1\big) + m_2\, c_m\big(T_{eq} - T_2\big) = 0$

$$Teq = \frac{(m_1\, T_1 + m_2\, T_2)}{(m_1 + m_2)}$$

$m_1 = 1kg\, ;\, T_1 = 20°C$

$m_2 = 0.5kg\, ;\, T_2 = 60°C$

$$Teq = \frac{(1 \times (20 + 273) + 0.5 \times (60 + 273))}{(1 + 0.5)} = 306K = 43.33°C$$

Example 2:

1. A calorimeter initially contains 1 kg of water at 15 °C. When 1 kg of water at 65 °C is added, the system reaches a final temperature of 38.8 °C. Determine the heat capacity of the calorimeter.

2. Using the same calorimeter, now filled with 1 kg of water at 15 °C, 50 g of ice at 0 °C is introduced. The final temperature of the system is 10.87 °C. Calculate the latent heat of fusion (L_{fus}) for the ice.

3. Again, in the same calorimeter with 1 kg of water at 15 °C, 50 g of ice at -5 °C is added, and the final temperature is 10.76 °C. Calculate the specific heat capacity of the ice.

Solution:

1.

$$\sum Qi = 0 \Rightarrow Q_1 + Q_2 + Q_{cal} = 0$$

$$m_1 c_p(H_2O,l)(T_{eq} - T_1) + m_2 c_p(H_2O,l)(T_{eq} - T_2) + \mu c_p(H_2O,l)(T_{eq} - T_i) = 0$$

$$\mu = (T_{eq} - T_i) - m_1(T_{eq} - T_1) - m_2(T_{eq} - T_2) = 100.84g$$

2.

$$\sum Qi = 0 \Rightarrow Q1 + Qfus + Q2 + Qcal = 0$$

$$m_1 c_p(H_2O,l)(283.87 - 288) + m_2 Lfus + m_2 c_p(H_2O,l)(Teq - 273) + \mu c_p(H_2O,l)(283.87 - 288) = 0$$

$$Lfus = \frac{-m_1 c_p(H_2O,l)(283.87 - 288) - m_2 c_p(H_2O,l)(Teq - 273) - \mu c_p(H_2O,l)(283.87 - 288)}{m_2}$$

$$Lfus = \frac{-1000(283.87 - 288) - 50(283.87 - 273) - 100.84(283.87 - 288)}{50}$$

$$Lfus = 80.05\ cal/g$$

3.

$$\sum Qi = 0 \Rightarrow Q_1 + Q_{solide} + Q_{fus} + Q_{cal} = 0$$

$$m_1 c_p(H_2O,l)(283.76 - 288) + m_2 c_p(H_2O,s)(273 - 268) + m_2 L_{fus} + m_2 c_p(H_2O,l)(283.76 - 288) + \mu c_p(H_2O,l)(283.76 - 288) = 0$$

$$c_p(H_2O,s) = \frac{-m_1 c_p(H_2O,l)(283.76 - 288) - m_2 L_{fus} - m_2 c_p(H_2O,l)(283.76 - 288) - \mu c_p(H_2O,l)(283.76 - 288)}{m_2(273 - 268)}$$

$$cp(H_2O,s) = \frac{-1000(283.76-288) - 50\times 80.05 - 50\,(283.76-288) - 100.84(283.76-288)}{50(273-268)}$$

$c_p(H_2O,s) = 0.5\ cal/gK$

II.4 Mechanical work of pressure forces (Mechanical Energy)

II.4.1 Definition

Work is performed by an object when it applies a force over a distance. In thermodynamics, the work done by pressure forces refers to the energy expended to displace or deform a system under the action of pressure.

II.4.2 Expression of Work

Let's consider the classic example of a gas in a cylinder with a movable piston.

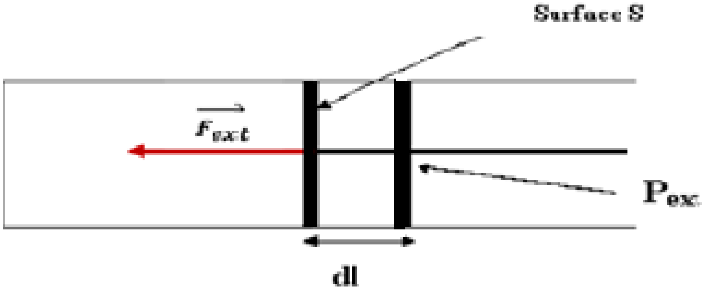


Figure II.8: Work pressure forces.

When pressure is exerted on a piston, the gas is compressed over an infinitesimal displacement dl. The force applied to the gas in this case is denoted by F = Pext S, and the elementary work of this force during this displacement is: $\boldsymbol{\delta W = F_{ext} \cdot dl}$

Where:

- dl: Elementary displacement of the point of application.
- $\boldsymbol{Pext}$: Pressure exerted on the system (gas).
- We have: $\boldsymbol{Fext} = -\boldsymbol{P_{ext} \cdot S}$
- So, we get: $\boldsymbol{\delta W = -P_{ext} \cdot S \cdot dl}$ $\quad S \cdot dl = dV$
- Therefore: $\boldsymbol{\delta W = -P_{ext} \cdot dV}$ As this is work (W) done on the external environment (ME), the sign is <0:
- During compression $\boldsymbol{dV}<0$, the gas receives work, and $\boldsymbol{\delta W}>0$.
- During expansion $\boldsymbol{dV}>0$, the gas does work on the external environment, and $\boldsymbol{\delta W}<0$. We have: $\boldsymbol{\delta W = -P_{ext} \cdot dV}$

The work W is then obtained by integrating the previous relation. The work of pressure forces is given by:

$$W = -\int_{V_1}^{V_2} P_{ext}.dV$$

In the International System of Units (SI), the unit of work is the joule (J).

II.4.3 Geometric interpretation of work

In the Clapeyron diagram, the work W will be represented by the area enclosed between the curve P = f(V), the volume axis, and the lines parallel to the pressure axis passing through the abscissas $V_{initial}$ and V_{final}.

$$W = -\int_{V_1}^{V_2} P_{ext}.dV = -A$$

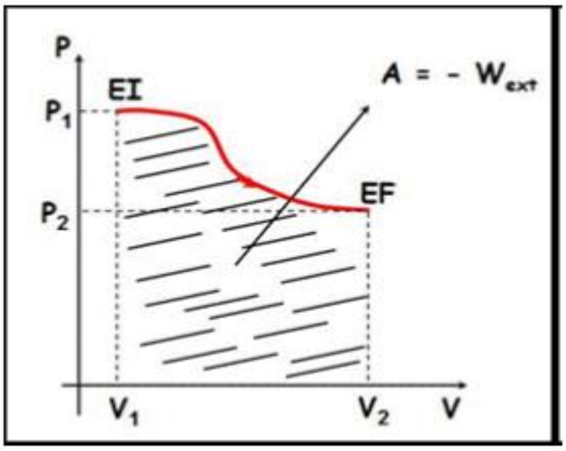


Figure II.9: Graphical representation of work (curve P = f(V)).

Note:

Work is path-dependent; it varies according to the specific process followed between the initial and final states. As a result, it is not considered a state function.

II.4.4 Work of a reversible transformation

We have: $\delta W = -P_{ext}.\,dV$ During a reversible transformation, at any instant, we can write :

$$P_{ewt} = P_{int} = P = \frac{nRT}{V}$$

Therefore:

$$W = -\int_{V_1}^{V_2} P_{ext}.dV$$

a. Case of an isothermal transformation (T= Const)

$$W = -\int_{V_1}^{V_2} P.dV$$

We replace P with $P=nRT/V$, and we get:

$$W = -\int_{V_1}^{V_2} \frac{nRT}{V}.dV$$

$$W = -nRT\int_{V_1}^{V_2} \frac{dV}{V} \Rightarrow W = -nRT\ln\frac{V_2}{V_1}$$

For an isothermal transformation, we have: $T_1= T_2=T$, and $P_1V_1=P_2V_2$

$\Rightarrow V_2/V_1= P_1/P_2$.

So:

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

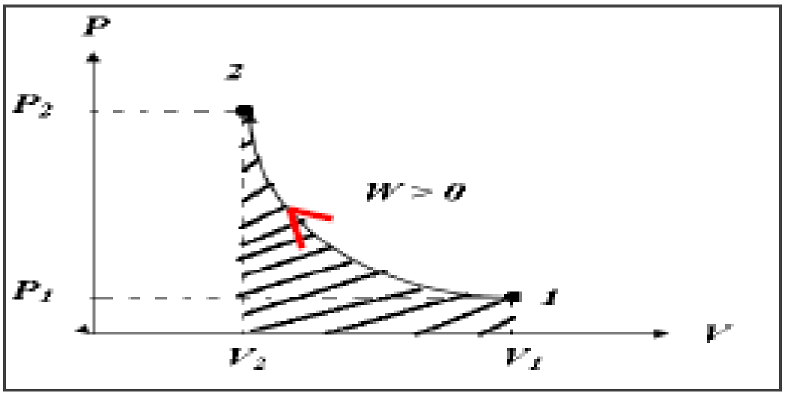


Figure II.10: Isothermal process.

b. Case of an isobaric transformation (P = Constant)

$$W = -\int_{V_1}^{V_2} P.dV = -P\int_{V_1}^{V_2} dV = -P\,(V_2-V_1) = -nR(T_2-T_1)$$

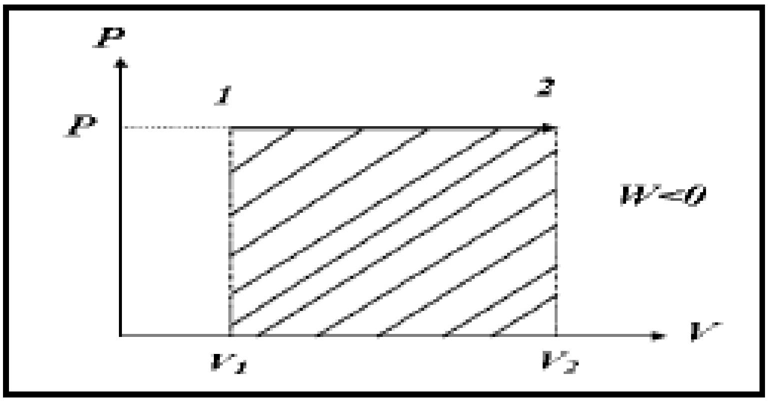


Figure II.11: Isobaric process.

c. Case of an isochoric transformation (V = Constant)

$V=Cst \Rightarrow dV=0$

So:

$$W = -\int_{V_1}^{V_2} P_{ext}.dV = 0$$

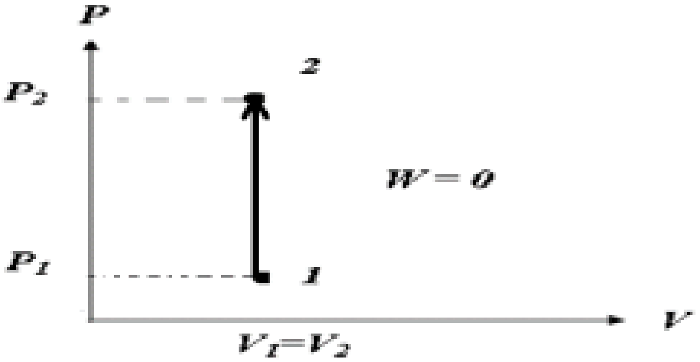


Figure II.12: Isochoric process.

d. Case of an adiabatic transformation Q=0

$$pV^{\gamma} = P_1V_1^{\gamma} = P_2V_2^{\gamma} = cst \Rightarrow P = \frac{cst}{V^{\gamma}}$$

$$\delta W = -PdV = \frac{cst}{V^{\gamma}}\, dV$$

$$\Rightarrow W_{1,2} = -\int_{V_1}^{V_2} P.dV = -\int_{V_1}^{V_2} \frac{cst}{V^{\gamma}}.dV = -cst\int_{V_1}^{V_2} \frac{dV}{V^{\gamma}} = -\frac{cst}{1-\gamma}\,(V_2^{1-\gamma} - V_1^{1-\gamma})$$

Based on the relation $P=cst/V^{\gamma}$, we obtain $V^{1-\gamma}= PV/cst$, and by substituting this into the work expression, we get:

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

Example:

Two moles of an ideal diatomic gas (with $\gamma = 1.4$) undergo adiabatic compression, with the pressure increasing from 5 atm to 10 atm. The initial volume is $V_1 = 7$ L.

a. Calculate the final volume V_2 and the final temperature T_2.

b. Determine the work exchanged between the gas and the surroundings during this compression.

c. Discuss its sign.

Solution:

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \Longrightarrow V_2^{\gamma} = \frac{P_1}{P_1}\,V_1^{\gamma} \;\Rightarrow\; V_2 = \left(\frac{P_1}{P_1}\right)^{\frac{1}{\gamma}} V_1 \Rightarrow\; V_2 = \left(\frac{5}{10}\right)^{\frac{1}{1.4}} 7 = 4.3\,L$$

The work is positive because during compression, the system receives work. Adiabatic reversible compression from state 1 to state 2:

$$P_2V_2 = nRT_2 \;\Rightarrow\; T_2 = \frac{10\,x\,4.3}{2\,x\,0.082} = 262.2\,K$$

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{nR}{\gamma - 1}\,(T_2 - T_1) = \frac{10\,x\,4.3 - 5\,x7}{1.4 - 1} \Longrightarrow W = 12.5\,L.atm$$

e. Work of an irreversible transformation

We have: $\delta W = -P\text{ext}dV$ In this case, $\mathbf{P_{ext}} \neq \mathbf{P_{int}}$, and P_{ext} is a constant equal to P_{final}. So,

$$W = -\int_{V_1}^{V_2} P_{ext}.dV = -\int_{V_1}^{V_2} P_{final}.dV \Longrightarrow W = -\,P_{final}\,(V_2 - V_1)$$

For an ideal gas at constant temperature, we will have:

$$W = -\,P_{final}\left(\frac{1}{P_2} - \frac{1}{P_1}\right) nRT; \left(P_{final} = P_2\right) \Longrightarrow W = -nRT\,(1 - \frac{P_2}{P_1})$$

Example:

A 1.00 m^3 volume of air, treated as an ideal gas at an initial pressure of 10 bar, undergoes an isothermal expansion until the pressure drops to 1 bar.

1. Determine the work resulting from the expansion of the air.
2. Determine the amount of heat exchanged by the air during its evolution.

Solution:

The transformation of the considered air being isothermal: at constant n and T, we write:

$$P_1V_1 = nRT_1$$

$$P_2V_2 = nRT_2$$

With $T_1 = T_2$ (isothermal expansion), therefore:

$$P_1V_1 = P_2V_2$$

Hence,

$$V_2 = \frac{P_1V_1}{P_2} = \frac{10\ x\ 10^5\ x\ 1}{1\ x\ 10^5} = 10\ m^3$$

The work resulting from the expansion of air:

$$W_{1,2} = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \Rightarrow W = -nRT \ln \frac{V_2}{V_1}$$

With:

$$nRT = P_1V_1 = P_2V_2\ and\ P_1 = 10^6 Pa;\ V_1 = 1\ m^3$$

Therefore:

$$W_{1,2} = -10^6\ ln10 = -2.3\ 10^6\ J$$

The amount of heat exchanged by the air:

$$Q_{1,2} = \int_{T_1}^{T_2} m.c\,dT = m.c \int_{T_1}^{T_2} dT = m.c\,(T_2 - T_1) = 0$$

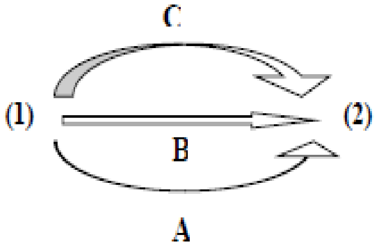
Knowing that: $T_2 = T_1$ (isothermal transformation).

II.5 Internal Energy

Internal energy (U) is a state function, meaning that its variation ΔU depends solely on the initial and final states of the system, regardless of the process or path followed during the transformation.

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

According to the first law of thermodynamics, the change in internal energy (ΔU) between two states remains the same, regardless of the type of transformation undergone. That is, for any set of processes taking the system from state (1) to state (2), the value of ΔU depends only on these two states and not on the path taken.



Path A: $U_2 - U_1 = Q_A + W_A$.

Path B: $U_2 - U_1 = Q_B + W_B$.

Path C: $U_2 - U_1 = Q_C + W_C$.

Therefore: $U_2 - U_1 = Q_A + W_A = Q_B + W_B = Q_C + W_C$.

Thus, the sum Q+W is independent of the path taken and depends only on the initial and final states of the transformation. With: $Q_A \neq Q_B \neq Q_C$, and $W_A \neq W_B \neq W_C$.

Sign convention:

If $\Delta U > 0$, the system gains energy.
If $\Delta U < 0$, the system loses energy.
The same interpretation applies to Q (heat) and W (work):
$Q > 0$ or $W > 0$ indicates energy is received by the system,
$Q < 0$ or $W < 0$ indicates energy is released by the system.
The unit of ΔU is Joule or Calorie, and it is the same unit for Q and W.
To indicate the state function nature of U, we write, for an infinitesimal variation:
$dU = \delta Q + \delta W$

Special case:

- In a cyclic transformation: initial state ≈ final state $\Rightarrow \Delta U_{cycle} = 0 \Longrightarrow W + Q = 0$
- For an isolated system, there is no exchange of energy (neither work nor heat) with the surroundings, meaning $W = 0$ and $Q = 0$, which leads to:

$\Delta U = 0$

II.6 First Law of Thermodynamics

The first law postulates that the algebraic sum of the work "W" and the heat "Q" exchanged by the system with the external environment is equal to the change ($U_2 - U_1$) in its internal energy, which is a state function, meaning it depends only on the initial and final states, not on the path taken. In contrast, W and Q individually are generally path-dependent and not state functions.

II.6.1 First Law of Thermodynamics

For any transformation occurring in a non-isolated system, the variation in internal energy corresponds to the total energy exchanged with the surroundings, in the form of heat (thermal transfer) and work (mechanical transfer).

Example:

During a period, the electric motor of an aquarium pump (system) performs 555 kJ of work on the pump and releases 124 kJ of heat to the external environment. What is the change in energy?
$\Delta U = U_2 - U_1 = Q + W = -125 - 555 = -679$ kJ.

II.7 Enthalpy "H"

It represents energy exchanged between a system and its surroundings, combining into a single thermodynamic potential both the system's internal energy (dependent on its temperature and amount of substance) and the boundary work needed to occupy a given volume (linked to pressure). This is a state function and an extensive property.

II.7.1 Differential expression of H

This function is defined by the following relations:
$H=U+PV \quad dH=dU+d(PV) \quad dH=dU+PdV+VdP$ (1)
For a quasi-static transformation:
$dU=dQ+dW \quad dW=-PdV \Rightarrow dU=dQ-PdV$ (2)
Replacing (2) into (1) $\Rightarrow dH=dQ-PdV+VdP+PdV \quad dH=dQ+VdP$ (3)

a. Joule's law

The adiabatic expansion of a gas in a vacuum, known as the Joule-Gay-Lussac expansion, is an expansion with constant internal energy.
$\Delta U=Q+w \Rightarrow \Delta U=0.$

1. **First Joule's law:** the internal energy U is a function that depends on temperature:

$U = f(T) \Rightarrow dU=C_v\,dT.$

2. **Second Joule's Law Enthalpy** is a function of temperature:

$H = f(T) \Rightarrow dH=C_p dT.$

Note :

The variations of internal energy and enthalpy depend exclusively on the initial and final states. Consequently, for a cyclic process, we have:

Cycle⟹ $\Delta U=0$ and $\Delta H=0$.

b. Mayer's relation

This relation can be readily derived from the definition of enthalpy. For one mole of an ideal gas, we have:

$H=U+PV$ and $PV=nRT$.

Differentiating gives:

$dH=dU+d(PV)$ and since $d(PV)=nR\,dT$, it follows that:

$nC_P\,dT = nC_V\,dT + nR\,dT$

$C_P=C_V+R$

Hence: Mayer's Relation: $C_P-C_V = R$

II.8 Application of the first law to the ideal gas

For each transformation, we define the initial state (1) described by the parameters (P_1, T_1,V_1) and the final state (2) described by the parameters (P_2, T_2, V_2).

We also provide the expressions for work, internal energy, enthalpy, and heat for each transformation.

II.8.1 Isothermal transformation (dT = 0)

$\Delta U=U_2-U_1 \Longrightarrow \Delta U = Q+ w \Longrightarrow \Delta U = 0$

$\Delta U= nC_V\,dT$

$W=-Q$

$\Delta H= H_2 - H_1 \Longrightarrow \Delta H= 0$……… $\Delta H= nC_p\,dT$

II.8.2 Isochoric transformation (dV = 0)

$\Delta U=U_2-U_1 \Longrightarrow \Delta U = Q+ w$

$W=0 \Longrightarrow \Delta U = Q \Longrightarrow \Delta U = \int_{T_1}^{T_2} nC_V\,dT$

II.8.3 Isobaric transformation (dP = 0)

$\Delta U=U_2-U_1 \Longrightarrow \Delta U = Q_p+ w$

$W = -\int_{V_1}^{V_2} P_{ext}.dV$ $P_{ext}=P_1=P_2$

$$\Delta U = Qp - P_1 \int_{V_1}^{V_2} dV \Rightarrow \Delta U = Qp - P_1(V_2 - V_1)$$

$\Delta U=U_2-U_1 \Longrightarrow U_2-U_1 = Qp - P_1V_2 - P_1V_1)$

$Qp = (U_2 + P_1V_2) - (U_1 + P_1V_1)$

$Qp = H_2 - H_1 \Longrightarrow Qp = \Delta H$

II.8.4 Adiabatic transformation

The first principle is written as follows:

$$P_{ext} = P_{int} = \frac{nRT}{V}$$

dU= nC_V dT = - P_{ext} dV

$$\frac{nR\ dT}{\gamma - 1} = -P_{ext}dV$$

The differential expression becomes: Integration of the differential equation:

$$\frac{d\ (PV)}{\gamma - 1} = -PdV$$

$$d(PV) = -\gamma\ PdV + PdV$$

$$PdV + VdP = -\gamma\ PdV + PdV$$

$$VdP = -\gamma\ PdV$$

$$\frac{dP}{P} = -\gamma\ \frac{dV}{V}$$

$$ln\frac{P_2}{P_1} = -\gamma \ln\frac{V_2}{V_1} = \gamma \ln\frac{V_1}{V_2}$$

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

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = cst$$

Hence, the Laplace's law : $PV^{\gamma} = cst$

The use of the ideal gas law leads to coupling equations for the pairs (T, V) and (T, P):

$TV^{\gamma-1} = cst$ and $T^{\gamma}P^{1-\gamma} = cst$

Example of application:

One mole of nitrogen gas (N_2), assumed to behave as an ideal gas, is heated from 20 °C to 100 °C. Determine the amount of heat Q absorbed by the system, as well as the changes in its internal energy and enthalpy, for each of the following two scenarios:

when the transformation is isochoric (constant volume)

when the transformation is isobaric (constant pressure)

Given: Cp (N_2, g) = 33 $J.mol^{-1}.K^{-1}$ and R = 8.31 $J.mol^{-1}.K^{-1}$

Solution:

1. At constant volume, the change in internal energy is equal to the heat absorbed. Using the relation $C_P - C_V = R$, we obtain:

$C_V = C_P - R$

$C_V = 33 - 8.31 = 24.69$ J/mol.K

$Q_V = 1975.2$ J

2. The change in enthalpy corresponds to the heat absorbed under constant pressure. Given that the transformation is isobaric, it follows that:

$$Qp = \Delta H = n \int_{T_1}^{T_2} C_P dT$$

$Q_P = 2640$ J

Case Studies

- **Power plants:** Conversion of heat energy from combustion into mechanical work to drive turbines, following energy conservation principles.
- **Refrigeration and air conditioning:** Transfer of heat from a low-temperature zone to a high-temperature zone using work input, demonstrating $Q+W=\Delta U$.
- **Internal combustion engines:** Fuel combustion releases heat, part of which is converted into piston work, while the rest is rejected as waste heat.
- **Industrial steam systems:** Boilers convert chemical energy in fuel into steam enthalpy, then turbines convert part of that energy into work.
- **Human metabolism:** Food chemical energy is transformed into mechanical work, heat, and stored energy, respecting the conservation of energy.

Self-Assessment Quiz

1- MCQs

1. In an isothermal process, the internal energy change (ΔU) is:
   a) Positive
   b) Negative
   c) Zero
   d) Depends on pressure
2. For an ideal gas undergoing reversible isothermal expansion from V_1 to V_2, the work is:
   a) $W=nR(T_2-T_1)$;
   b) $W=-nRT\ln V_2/V_1$;
   c) $W=P(V_2-V_1)$;
   d) None of the above.

2- True/False

1. The First Law of Thermodynamics states that energy can be created as long as it is balanced by work.
2. In an adiabatic process, there is no heat exchange between the system and its surroundings.

3- Short Question

Question: In an adiabatic compression of an ideal gas, why does the temperature increase?

Recap & Key Formulas

- **Key Concepts**

  Internal Energy (U): Energy stored in the microscopic motions and interactions of molecules.

  Enthalpy (H): $H=U+pV$.

- **First Law of Thermodynamics:** $\Delta U=Q+W$.

  Q: Heat added to the system;

  W: Work done by the system.

- **Work in Isothermal Process (ideal gas):** $W = -nRT \ln \frac{V_f}{V_i}$

- **Work in Adiabatic Process (ideal gas):** pV^{γ}=constant; $TV^{\gamma-1}$=constant.

- **Important Notes :**

  Sign convention: $Q>0$ when heat enters the system; $W>0$ when work is done by the system.

  For ideal gases, internal energy depends only on temperature.

  The First Law is an energy conservation principle, not a statement about process direction.

Corrected Exercises

Exercise 1:

A system consists of 10 g of gaseous N_2 at 0 °C and 1 atm. When 2025 joules are supplied to this system at ***constant pressure***, the resulting expansion produces 800 joules of work. Calculate:

1. The initial volume.
2. The volume and temperature at the final state.

Exercise 2:

A fuel–air mixture undergoes a transformation from state (1) to state (2) following three different paths:

- Path (a): an isochoric process followed by an isobaric process;
- Path (b): an isobaric process followed by an isochoric process;
- Path (c): a transformation at constant PV.

The initial and final states are defined as follows:

State (1): P_1=1 bar, V_1=3 L.

State (2): P_2=3 bar, V_2=1 L.

Questions:

1. Represent the three transformation paths on a P-V (Clapeyron) diagram.
2. Calculate the variation in internal energy ΔU between states (1) and (2).
3. Determine the work performed in each of the three cases, and deduce the heat exchanged. Specify whether the heat is absorbed or released by the system.

Exercise 3:

1. An adiabatic calorimeter initially contains 1000 g of water at 15 °C. When 1000 g of water at 65 °C is added, the system reaches thermal equilibrium at a final temperature of 28.8 °C. Determine the heat capacity of the calorimeter.
2. Using the same calorimeter, now containing 1000 g of water at 15 °C, 50 g of ice at 0 °C is introduced. The final equilibrium temperature is 10.87 °C. Calculate the latent heat of fusion of ice.
3. In the same calorimeter setup, 1000 g of water at 15 °C is mixed with 50 g of ice initially at –5 °C. The system reaches equilibrium at 10.69 °C. Determine the specific heat capacity of ice.

Data: C_{water} = 1 cal/g.K.

Exercise 4:

During an isothermal compression of 56g of Nitrogen (N_2) (considered as an ideal gas) from the pressure P_1=1 atm to a pressure P_2=20 atm at a temperature of 25 °C.

1. Calculate the work exchanged with the external environment in:
   - Reversible
   - Irreversible processes; Compare the results obtained and conclude.

Exercise 5:

A monoatomic ideal gas in its initial state A is characterized by the parameters P_A= 1 atm, T_A=300 K, V_A=10 L, undergoes the following reversible transformations:

- An adiabatic expansion to state B, doubling its volume.
- An isochoric heating to state C.
- An isobaric cooling returning it to the initial state.

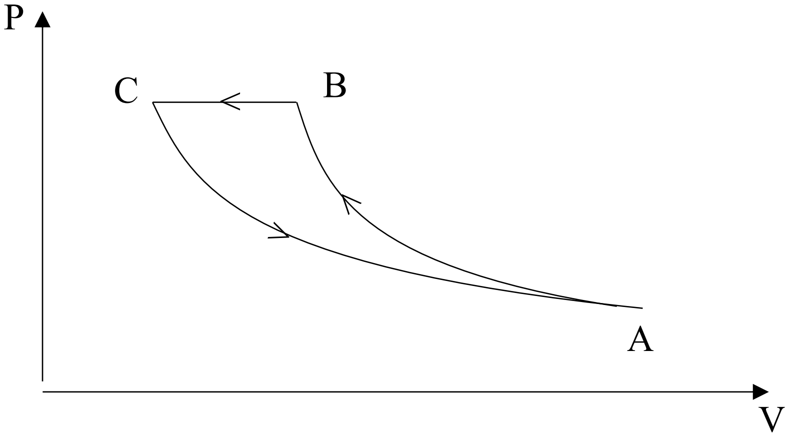
1. Determine the coordinates (P, V, and T) of each state.
2. Represent the different transformations on the Clapeyron diagram.
3. Calculate for each transformation the work, heat, change in internal energy, and enthalpy.
4. Determine the changes in internal energy and enthalpy of the cycle, conclude.

Exercise 6:

A mass m=1kg of oxygen occupies a volume V_A at temperature T_A=320 K under a pressure $P_A=8.10^4$ Pa.

1. Calculate V_A.
2. The gas undergoes the cycle ABCA (below), deduce the nature of transformations AB, BC, and CA. Justify.
3. Calculate V_B, V_C, and T_B.
4. What is the representation in coordinates (T, V).
5. Calculate W_{cycle} and Q_{cycle}.

Data: $P_B= 80.10^4$ Pa, γ=1.4. M(O)= 16g/mol.



Correction

Exercise 1:

1. Initial Volume V1

First, calculate the number of moles:

$$n = \frac{m}{M} = \frac{10}{28} = 0.3571\,\text{mol}$$

Using the **ideal gas law**:

$$PV = nRT \Rightarrow V1 = \frac{nRT1}{p}$$

$$V1 = \frac{0.3571 \times 8.314 \times 273.15}{1.013 \times 10^5} = 7.999 \times 10^{-3}\, m^3 = 7.999L$$

2. Final Temperature and Volume

$$W = -\int PdV = -P\int dV = -P\,(V_f - V_i)$$

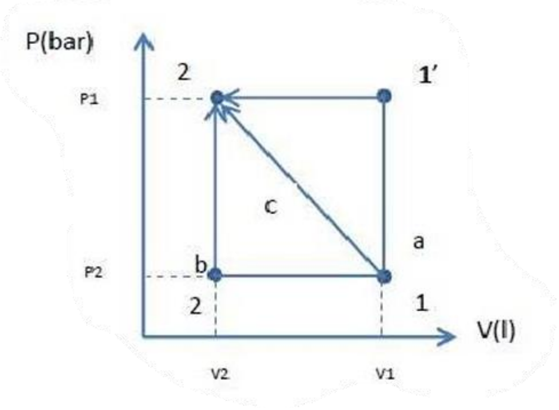
$$\Longrightarrow W = -P\,V_f + PV_i$$

$$\Longrightarrow V_f = \frac{PV_i - W}{P} = \frac{1\,.\,7.999\,10^{-3} - (-800)}{1.1.013 \times 10^5} = 15.9\,10^{-3}\,m^3 = 15.9\,L$$

$$P_f V_f = nRT_f \Longrightarrow T_f = \frac{P_f V_f}{nR} = \frac{1\,.\,15.9}{0.3571\,.\,0.082} = 538.6\,K$$

Exercise 2:

1. P=f(V): Clapeyron Diagram



2. ΔU

The variation of internal energy does not depend on the path taken since it is a state function. Therefore:

$\Delta U = \Delta Q - W = nc_p\Delta T = 0\,J$ (for path C, where the transformation is isothermal).

3. Work calculation for the three paths (a, b, and c):

For path (a):

$W_a = W_{11'} + W_{1'2} = -P_2 (V_2 - V_{1'})$

$W_{11'} = 0 W$

$W_{1'2}$ (isobaric)

$W_a = -P_2 (V_2 - V_{1'}) = -P_2 (V_2 - V_1) = P_2 (V_1 - V_2)$

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

For path (b):

$W_b = W_{12'} + W_{2'2} = -P_1 (V_{2'} - V_1)$

$W_{2'2} = 0$ W

$W_b = -P_1 (V_{2'} - V_1) = P_1 (V_1 - V_2)$

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

For path (c):

Isothermal transformation:

$$Wc = \int_{V2}^{V1} P\,dV = \int_{V2}^{V1} \frac{nRT}{V} dV = nRT ln\frac{V_1}{V_2}$$

$$\Rightarrow Wc = P_1V_1 ln\frac{V_1}{V_2} = 10^5 \cdot 3.10^{-3}.\ln 3 = 327\,J.$$

Heat quantities for paths a, b, and c:

Since ΔU=0, then W=−Q, thus:

- Qa=−600 J
- Qb=−200 J
- Qc=−327 J

Exercise 3:

1 – Calculation of the calorimeter's heat capacity:

Let Q_1 be the amount of heat absorbed by the calorimeter and cold water:

$Q_1 = (m_1 \cdot c_e + C) \cdot (t_{eq} - t_1)$

Let Q_2 be the amount of heat released by the hot water:

$Q_2 = m_2 \cdot c_e \cdot (t_{eq} - t_2)$

We have: $Q_1 + Q_2 = 0 \Rightarrow (m_1 \cdot c_e + C)(t_{eq} - t_1) + m_2 \cdot c_e \cdot (t_{eq} - t_2) = 0$

$\Rightarrow C = -[m_2 \cdot c_e \cdot (t_{eq} - t_2)] / (t_{eq} - t_1) - m_1 \cdot c_e$

$= -[1000 \times 1 \cdot (38.8 - 65)] / (38.8 - 15) - 1000 \times 1$

$= 100.84$ cal/K

2 – Calculation of the latent heat of fusion of ice:

Let Q_1 be the amount of heat released by the calorimeter and hot water:

$Q_1 = (m_1 \cdot c_e + C) \cdot (t_{eq} - t_1)$

Let Q_2 be the amount of heat absorbed by the ice to go from 0 °C to the equilibrium temperature:

$Q_2 = Q_2' + Q_2'' = m_2 \cdot L_f + m_2 \cdot c_e \cdot (t_{eq} - t_f)$

We have:

$Q_1 + Q_2 = 0 \Rightarrow (m_1 \cdot c_e + C)(t_{eq} - t_1) + m_2 \cdot L_f + m_2 \cdot c_e \cdot (t_{eq} - t_f) = 0$

$\Rightarrow L_f = -[(m_1 \cdot c_e + C)(t_{eq} - t_1) + m_2 \cdot c_e \cdot (t_{eq} - t_f)] / m_2$

$= -[(1000 \times 1 + 100.84)(10.87 - 15) + 50 \times 1(10.87 - 0)] / 50$

$= 80.05$ Cal/g

3 – Calculation of the specific heat of ice:

Let Q_1 be the amount of heat released by the calorimeter and hot water:

$Q_1 = (m_1 \cdot c_e + C) \cdot (teq - t_1)$

Let Q_2 be the amount of heat absorbed by the ice to go from -5 °C to the equilibrium temperature (t_{eq}= 10.69 °C):

$Q_2 = m_2 \cdot c_g \cdot (t_f - t_2) + m_2 \cdot L_f + m_2 \cdot c_e \cdot (t_{eq} - t_f)$

We have:

$Q_1 + Q_2 = 0$

$\Rightarrow (m_1 \cdot c_e + C)(t_{eq} - t_1) + m_2 \cdot c_g \cdot (t_f - t_2) + m_2 \cdot L_f + m_2 \cdot c \cdot (t_{eq} - t_f) = 0$

$$\mathrm{cg} = -\frac{(\mathrm{m_1 \cdot c_e} + \mathrm{C})(\mathrm{teq} - \mathrm{t_1}) + \mathrm{m_2 \cdot Lf} + \mathrm{m_2 \cdot c \cdot (teq - tf)}}{\mathrm{m_2 \cdot (tf - t2)}}$$

$$\mathrm{cg} = -\frac{(1000 \times 1 + 100.84)(10.69 - 15) + 50 \times 80.05 + 50\,\mathrm{x}1\,(10.69 - 0)}{50\,(0 + 5)}$$

= 0.83 cal/g.K

Exercise 4:

1. Calculation of work during a reversible compression. The relation of work exchanged with the external environment ⇒ $W = -\int_1^2 P_{ext} dV$

During a reversible transformation, at any instant, the external pressure is equal to the pressure of the gas inside the piston.

At all times ⇒ $Pext = P = \frac{nRT}{V}$

Since the process is isothermal, we deduce that:

$$W_{rev} = -nRT \int_1^2 \frac{dV}{V} = -nRT\ Log\ \frac{V_2}{V_1} = nRT\ Log\ \frac{V_1}{V_2}$$

Knowing that $P_1 \cdot V_1 = P_2 \cdot V_2 \Rightarrow \frac{P_2}{P_1} = \frac{V_1}{V_2}$

$$W_{rev} = nRT\ Log\ \frac{V_1}{V_2} = nRT\ Log\ \frac{P_2}{P_1} = \frac{56}{28}\ .8.32\,.298\,.\ Log\ \frac{20\,.\,1.03\ 10^5}{1.03\ 10^5}$$

$\Longrightarrow W_{rev} = 14919.226\,J = 14.92\ KJ$

Calculation of work during an irreversible compression.

The pressure being previously equilibrated to one atmosphere ⇒P_1

The external pressure is abruptly increased to P_2=20 atm

$$W_{irrev} = -P_{ext} \int_1^2 dV = -P_{ext}\,(V_2 - V_1) = nRT\,(\frac{V_1}{V_2} - 1) = nRT\,(\frac{P_2}{P_1} - 1)$$

$$W_{irrev} = \frac{56}{28}\,.8.32\,.298\,.\left(\frac{20}{1} - 1\right) = 95.5\ KJ$$

Exercise 5:

Monoatomic ideal gas, therefore:

- $\gamma = 5/3$
- $Cv = \frac{3}{2}R$
- $Cp = \frac{5}{2}R$

Initial state A: P_A=1 atm=101325 Pa, T_A=300 K, V_A=10 L=0.010 m^3

Calculation of the number of moles (n):

Using the ideal gas equation for state A:

$$P_AV_A=nRT_A \Longrightarrow n = \frac{P_AV_A}{RT_A} = \frac{101325 \text{ x } 0.010}{8.314 \text{ x } 300} = 0.406\, mol$$

Calculation of molar heat capacities:

$$C_V=\frac{3}{2}R=\frac{3}{2}\times 8.314=12.471 \text{ J/mol.K}$$

$$C_p=\frac{5}{2}R=\frac{5}{2}\times 8.314=20.785 \text{ J/mol.K}$$

1. Determine the coordinates (P, V, and T) of each state:

State A (Initial): P_A=1 atm, V_A=10 L, T_A=300 K.

Transformation A → B (Reversible Adiabatic Expansion):

The volume is doubled: $V_B=2V_A=2\times10$ L=20 L

Using the adiabatic relation $P_AV_A^{\gamma} = P_BV_B^{\gamma}$:

$$P_B = P_A(\frac{V_A}{V_B})^{\gamma} = 1\,(\frac{10}{20})^{5/3} = 0.315\, atm$$

Using the adiabatic relation $T_AV_A^{\gamma-1} = T_BV_B^{\gamma-1}$:

$$T_B = T_A(\frac{V_A}{V_B})^{\gamma-1} = 300\,(\frac{10}{20})^{(\frac{5}{3})-1} = 189\,K$$

State B: P_B=0.315 atm, V_B=20 L, T_B=189.0 K.

Transformation B → C (Isochoric Heating): the volume remains constant, so $V_C=V_B$=20 L.

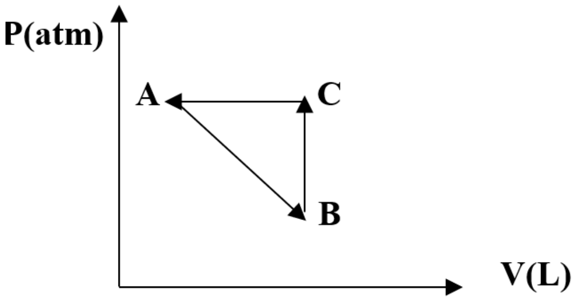
The problem states that an isobaric cooling returns the gas to the initial state A. This means $P_C=P_A$=1 atm.

Using the Ideal Gas Law for state C:

$$T_C = \frac{P_CV_C}{n\,R} = \frac{1\,.\,20}{0.406\;0.082} = 600K$$

State C: P_C=1 atm, V_C=20 L, T_C=600 K

2. Representation on the Clapeyron Diagram



3. Work, Heat, Change in Internal Energy, and Enthalpy for Each Transformation

Transformation A → B (Adiabatic Expansion):

Heat (Q_{AB}): For an adiabatic process, Q=0 J

Work (W_{AB}): $W=\Delta U = n\,C_v\,\Delta T= n\,C_v\,(T_B-T_A) = 0.406\ .\ 12.471\ (189-300) = -562.43$ J

Change in Enthalpy (ΔH_{AB}): $\Delta H_{AB}=\gamma\,\Delta U = \frac{5}{3}\,(-562.43) = -937.38$ J

Transformation B → C (Isochoric Heating)

Work (W_{BC}): For an isochoric process (constant volume), W=0 J

Change in Internal Energy (ΔU_{BC}): $\Delta U_{BC}=nC_v\Delta T = 0.406\ 12.471\ (600 - 189) = 2082.54$ J

Heat (Q_{BC}): For an isochoric process, Q=ΔU. $Q_{BC}=2082.54$ J

Change in Enthalpy (ΔH_{BC}): $\Delta H_{BC}=\gamma\,\Delta U = \frac{5}{3}\,(2082.54) = 3470.9$ J

Transformation C → A (Isobaric Cooling)

Work (W_{CA}): $W_{CA} = -P\int dV = -P\,(V_A - V_C) = -1\ 1.013\ 10^5\ (10 - 20) = 1013$ J

Change in Internal Energy (ΔU_{CA}): $\Delta U_{CA}=n\,C_v\,\Delta T = 0.406\ 12.471\ (300 - 600) = -1520.10$ J

Change in Enthalpy (ΔH_{CA}): $\Delta H_{CA}=\gamma\,\Delta U = \frac{5}{3}\,(-1520.10\,) = -2533.5$ J

Change in Internal Energy (ΔU_{CA}): $\Delta U_{CA}= W_{CA} + Q_{CA}$

$\Longrightarrow Q_{CA} = \Delta U_{CA} - W_{CA} = -1520.10 - 1013 = -2533.10$ J

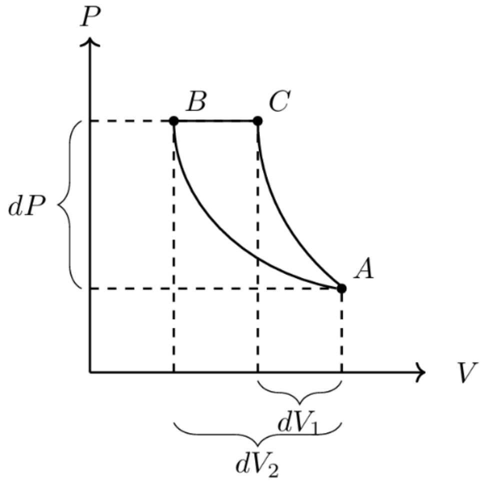
4. Changes in Internal Energy and Enthalpy of the Cycle

$\Delta U_{cycle}=\Delta U_{AB}+\Delta U_{BC}+\Delta U_{CA}=-562.43 + 2082.54 - 1520.10 = 0$J

$\Delta H_{cycle}=\Delta H_{AB}+\Delta H_{BC}+\Delta H_{CA}= -937.38 + 3470.9 - 2533.5 = -0$J

Exercise 6:

1. Calculate VA



$$n = \frac{m}{M} = \frac{1000}{32} = 31.25\,mol$$

We can use the ideal gas law: $P_AV_A=nRT_A$

$$\Rightarrow V_A = \frac{nRT_A}{P_A} = \frac{31.25\ .8.314\ .\ 320}{8\ 10^4} = 1.039\,m^3$$

2. Deduce the nature of transformations AB, BC, and CA

dV_1, the change in volume of transformation AB.

dV_2, the change in volume of transformation CA.

$$dV_1 < dV_2 \Rightarrow \frac{dV_1}{dP} < \frac{dV_2}{dP} \Rightarrow \frac{dP}{dV_1} > \frac{dP}{dV_2}$$

$\Longrightarrow$ $the\ slopeAB\ >\ the\ slopeCA$

AB: Adiabatic transformation.

BC: Isobaric transformation.

CA: isothermal transformation.

3. Calculate V_B, V_C, and T_B.

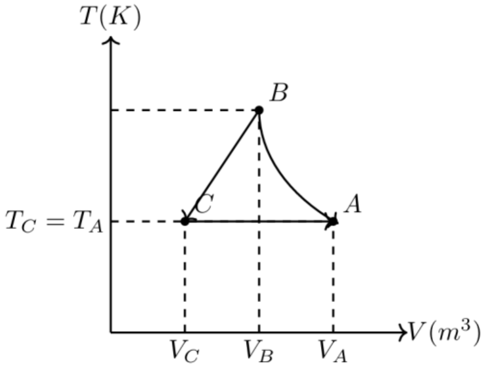
AB: Adiabatic transformation $\Rightarrow P_AV_A^{\gamma} = P_BV_B^{\gamma} \Rightarrow V_B^{\gamma} = \frac{P_A}{P_B}\, V_A^{\gamma} \Rightarrow V_B = (\frac{P_A}{P_B})^{\frac{1}{\gamma}}\, V_A$

$$\Rightarrow V_B \ = \ (\frac{8\ 10^4}{80\ 10^4})^{\frac{1}{1.4}} . 1039 = 0.2004\, m^3$$

$$P_CV_C = nR\ T_C \ \Longrightarrow\ V_C = \frac{nR\ T_C}{P_C} = \frac{31.25\ .\ 8.314\ .\ 320}{80\ 10^4} = 0.1038\, m^3$$

$$P_BV_B = nR\ T_B\ \ \Rightarrow T_B \ = \frac{P_BV_B}{nR} = \frac{80\ 10^4\ 0.2}{31.25\ .\ 8.314} = 616.12\ K$$

4. The representation in coordinates (T, V)



5. Calculate Q_{cycle} and W_{cycle}

$W_{cycle}=W_{AB}+W_{BC}+W_{CA}$

$Q_{cycle}=Q_{AB}+Q_{BC}+Q_{CA}$

Adiabatic transformation (AB)

$Q_{AB}=0 \Longrightarrow \Delta U=Q$

$$\frac{\mathrm{Cp}}{\mathrm{Cv}} = \gamma$$

$$\mathrm{Cp} - \mathrm{Cv} = \mathrm{R} \Rightarrow \mathrm{p} = \mathrm{R} + \mathrm{Cv}$$

$$\frac{\mathrm{Cv} + \mathrm{R}}{\mathrm{Cv}} = \gamma\ \Rightarrow \mathrm{Cv} + \mathrm{R} = \mathrm{Cv}\,\gamma\ \Rightarrow \mathrm{Cv}\ (\gamma - 1) = \mathrm{R}$$

$$\Rightarrow\ \mathrm{Cv}\ = \frac{\mathrm{R}}{\gamma - 1} = \frac{8.314}{1.4 - 1} = 20.775\frac{\mathrm{J}}{\mathrm{mol}}.\mathrm{K}$$

$\Delta U=nC_v\Delta T$

$\Delta U = 31.25 \,.\, 20.775\,(616.12 - 320) = 192246.65\ \text{J} = W_{AB}$

Isobaric transformation (BC)

$\Delta U = W + Q = nC_v\,\Delta T$

$W_{BC} = -P\,(V_C - V_B) = -80\ 10^4\,(0.1038 - 0.2004) = 77280\text{J}$

$\Delta U_{BC} = nC_v\,\Delta T = nC_v\,(T_C - T_B) = 31.25 \,.\, 20.775\,(320 - 616.12) = -1922246.65\ \text{J}$

$Q_{BC} = \Delta U_{BC} - W_{BC} = -1922246.65 - 77280 = -269526.65\ \text{J}$

Isothermal transformation (CA)

$\Delta U_{CA} = W_{CA} + Q_{CA} = nCv\,\Delta T = 0\ (T = cst)$

$Q_{CA} = -W_{CA}$

$$\mathrm{PV} = \mathrm{nRT} \Rightarrow \mathrm{P} = \frac{\mathrm{nRT}}{\mathrm{V}}$$

$$W_{CA} = -\int PdV = -\int \frac{\mathrm{nRT}}{\mathrm{V}}dV = -\mathrm{nRT}\int \frac{dV}{\mathrm{V}} = -\,\mathrm{nRT}\ln\frac{V_A}{V_C} = \mathrm{nRT}\ln\frac{V_C}{V_A}$$

$$W_{CA} == 31.25\,.8.314\,.320\ln\frac{0.1038}{1.038} = -191344.82\,J$$

$$Q_{CA} = +191344.82\,J$$

$W_{cycle} = W_{AB} + W_{BC} + W_{CA} = 192246.65 + 77280 + -191344.82 = 78181.835\ \text{J}$

$Q_{cycle} = Q_{AB} + Q_{BC} + Q_{CA} = 0 - 269526.65 + 191344.82\,J = -\ 78181.835\ \text{J}$

Non-Corrected Problems for Practice

1. A piston contains 2 mol of an ideal gas at 300 K, initially at 2 bar. The gas expands isothermally to 1 bar. Calculate the work done.
2. A gas is compressed isothermally from 5 L to 2 L at 298 K. Determine the work and heat exchanged.
3. A sample of oxygen undergoes isothermal expansion from 1.5 m^3 to 3 m^3 at 310 K. Find the work done by the gas.
4. Compare the work for isothermal expansion of an ideal gas and a real gas (using van der Waals equation) for the same initial and final states.

Chapter III:

Applications of the First Law of Thermodynamics to Thermochemistry

Learning Objectives

After completing this chapter, the student will be able to:

- Define thermochemistry and explain the link between the first law of thermodynamics and chemical transformations;
- Calculate the heat of reaction at constant volume and constant pressure, and relate Q_V to Q_P for gases;
- Explain the concept of standard state and apply it to solids, liquids, and gases;
- Define and calculate different types of enthalpy changes:
  - Standard enthalpy of formation ($\Delta H_f°$);
  - Enthalpy of combustion ($\Delta H_{comb}°$);
  - Enthalpy of dissociation;
  - Enthalpy of phase change (fusion, vaporization, sublimation);
- Apply Hess's Law to determine enthalpy changes using standard enthalpies of formation or reaction combinations;
- Use Kirchhoff's Law to evaluate the effect of temperature on reaction enthalpy.

III.1 Introduction

Thermochemistry is a branch of thermodynamics that deals with the various heats associated with chemical transformations, particularly chemical reactions.

A chemical reaction is a system that evolves from an initial state to a final state with the absorption or emission of heat. The evolution occurs either at constant volume or constant pressure.

Most often, chemical transformations are considered as thermodynamic systems that evolve at constant pressure.

III.2 Concept of a chemical reaction

A chemical reaction refers to the transformation of a system from an initial state, consisting of reactants, to a final state, composed of products. It is typically represented in the form:

$\nu_1 A + \nu_2 B \longrightarrow \nu_3 C + \nu_4 D$

A and B are reactants, C and D are products.

ν_1, ν_2, ν_3, and ν_4 are stoichiometric coefficients.

III.3 Heat of a Chemical Reaction

The heat of a chemical reaction is defined as the amount of thermal energy exchanged between the system and its surroundings during the course of the reaction. In practical applications, reactions are generally carried out either at constant volume or at constant pressure. Accordingly, the associated heat changes are defined as follows:

According to the first principle, we have:

$dU = dQ + dW$ $\qquad$ $dH = dU + d(PV)$

Isochoric transformation (V = constant):

$\Delta U=0$ $\qquad$ $\Delta H = Q + \int V\, dP$

Isobaric transformation (P = constant):

$\Delta U = Q_p - P_1 (V_2-V_1)$ $\qquad$ $\Delta H = Q_p$

Relationship between Q_V and Q_P

In the case of a chemical reaction carried out in the gaseous phase at a given temperature 'T', a relationship between Q_V and Q_P can be established. We have:

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

For an ideal gas: $PV=nRT \Rightarrow \Delta(PV)=\Delta(nRT) \Rightarrow \Delta H= \Delta U+ \Delta(nRT)=\Delta U+ RT\Delta n$

Where: $\qquad$ $\boldsymbol{\Delta n}= \Sigma \boldsymbol{n_i}$ **Produ**cts(**g**)$-\Sigma \boldsymbol{n_i}$**R**eactants(**g**).

Note

- If all substances are solids or liquids, $Q_P = Q_V$
- If in the reaction there are gaseous, solid, and liquid substances, the number of moles of solids and liquids is neglected.

Example

$$H_2(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(g)$$

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

Therefore:

$$Q_p = Q_V - \frac{1}{2}RT$$

$$H_2(g) + \frac{1}{2}O_2\,(g) \rightarrow H_2O\,(l)$$

$V_l << V_g$

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

III.4 Standard state

The behavior of a real system is analyzed by comparison with an associated hypothetical system known as the **standard system**.

For a gas or a gas mixture, the standard state corresponds to that of an ideal gas obeying the equation PV=nRT, at a pressure of 1 bar and a given temperature T.

For a substance in the condensed phase (liquid or solid), the standard state refers to the pure substance in the same physical state, at temperature T and pressure P=1 bar.

The standard reference state of a chemical element is defined as the standard state of its simplest pure form, in the most stable physical state at temperature T and P=1 bar.

Note: 1 bar=10^5 Pa=1 N/m^2, and 1 atm=1.013 bar.

- **Examples:**

Gaseous phase: O_2(g), Cl_2(g), H_2(g)
Liquid phase: Br_2(l), Hg(l)
Solid phase: C (graphite), S(s), Fe(s), Cu(s),...

The **standard enthalpy of reaction**, denoted $\Delta H_R°$or $\Delta H_{298}°$ corresponds to the enthalpy change associated with a chemical reaction conducted under standard conditions.

III.5 Enthalpy H

Enthalpy H is a function depending on the initial and final states of a system, expressing the amount of heat involved in a thermodynamic transformation.

This thermodynamic quantity is defined as the sum of the internal energy and the product of pressure and volume. The variation in enthalpy represents the amount of heat absorbed or released by the system when the only work involved is due to pressure forces.

H= U+PV

During an isobaric transformation (constant pressure), the change in enthalpy ΔH is equal to the heat exchanged with the surroundings, denoted Q_P.

Enthalpy H is a state function and is typically expressed in units of joules (J) or calories (cal).

III.5.1 Standard enthalpy of formation $\Delta H_f°$

The standard enthalpy of formation is defined as the enthalpy change associated with the formation of one mole of a compound in its standard state, starting from its constituent elements in their standard reference states.

$$H_2(g) + \frac{1}{2}O_2\,(g) \rightarrow\ H_2O\,(l) \qquad \Delta H^{\circ}_{f(298)} = -285.1\,kJ/mol$$

In general, the standard enthalpy of formation is negative, indicating an exothermic process. However, it may be positive for thermodynamically unstable compounds.

Note: The standard enthalpy of formation of a pure element in its reference state is defined as zero.

$\Delta H_f°$ (O_2, H_2, N_2, C (s), S(s)…) = 0.

III.5.2 Enthalpy of combustion

The standard enthalpy of combustion, denoted $\Delta H_{comb}°$, refers to the amount of heat released when one mole of a compound or an element undergoes complete combustion in the presence of oxygen (O_2), resulting in the formation of carbon dioxide gas (CO_2) and liquid water (H_2O).

Example:

Determination of the enthalpy of combustion of benzene: What is the numerical value of the standard enthalpy of combustion of benzene (C_6H_6)?

Data:

$\Delta H_f°(C_6H_6)$=80 kJ.mol^{-1} ;

$\Delta H_f°(CO_2)$=-400 kJ.mol^{-1} ;

$\Delta H_f°(H_2O)$=-240 kJ.mol^{-1} .

$$C_6H_6\ (g) + \frac{15}{2}\ O_2 \xrightarrow{\Delta H^°_{com}} 6CO_2(g) + 3\ H_2O\ (l)$$

$$\Delta H^°_{com} = \ \Delta H^°_f\ (product) - \Delta H^°_f\ (reactant)$$

$$\Delta H^°_{com} = \ 6\,\Delta H^°_f\ (CO_2) + \ \ 3\,\Delta H^°_f\ (H_2O) - \Delta H^°_f\ (C_6H_6) - \ \frac{15}{2}\ \Delta H^°_f\ (O_2)$$

$$\Delta H^°_{com} = 6\ (-400) + 3\ (-240) - 80 - \frac{15}{2}\ (0) = 13200\ kJ/mol$$

$\Delta H^°_{com}$<0 : Exothermic reaction

III.5.3 Enthalpy of dissociation

The enthalpy of dissociation, denoted $\Delta H_{dissociation}$, represents the enthalpy change associated with the cleavage of chemical bonds within a substance. This process generally involves the decomposition of a compound into its constituent atoms or simpler molecules. It quantifies the amount of energy either absorbed or released during bond dissociation. A positive enthalpy change indicates an endothermic process, requiring energy input to break the bonds. In contrast, a negative value reflects an exothermic process, in which energy is released. The exact form of the dissociation reaction depends on the chemical nature of the substance. For instance, the dissociation of a diatomic molecule AB into its atomic components A and B is represented as:

$AB(g) \rightarrow A(g)+B(g)$

The enthalpy of dissociation is a key parameter in understanding the energetics of chemical reactions and is often determined experimentally.

It provides insight into the strength of chemical bonds within a compound and how much energy is involved in breaking those bonds.

$$H_2(g) + \frac{1}{2}O_2\ (g)\ \underset{-\Delta H^°_d}{\overset{\Delta H^°_f}{\rightarrow}}\ H_2O\ (g) \qquad\qquad \Delta H^°_f = \ -\Delta H^°_d$$

III.5.4 Enthalpy of phase change

During a phase transition of a pure substance such as melting, vaporization, condensation, sublimation, or solidification the temperature remains constant throughout the entire process.

ΔH_{fus} = -ΔH_{sol}

ΔH_{vap} = - ΔH_{liq}

ΔH_{sol} = - ΔH_{con}

The enthalpy of one mole of a pure substance (A) undergoing melting and vaporization from T_1 to T_2 is given by the following diagram:

$$\underset{T_1}{A(sol)} \xrightarrow{\Delta H_1} \underset{T_{fus}}{A(sol)} \xrightarrow{\Delta H_{fus}} \underset{T_{fus}}{A(liq)} \xrightarrow{\Delta H_2} \underset{T_{vap}}{A(liq)} \xrightarrow{\Delta H_3} \underset{T_{vap}}{A(vap)} \xrightarrow{\Delta H_{vap}} \underset{T_2}{A(vap)}$$

$$\Delta H_{T1\to T2} = \int_{T1}^{Tfus} C_{p\,(sol)}\mathrm{dT} + \Delta H_{fus} + \int_{Tfus}^{Tvap} C_{p\,(liq)}\mathrm{dT} + \Delta H_{vap} + \int_{Tvap}^{T2} C_{p\,(vap)}\mathrm{dT}$$

$$\Delta H_{T1\to T2} = \int_{T1}^{Tfus} n\, C_{p\,(sol)}\mathrm{dT} + n\,\Delta H_{fus} + \int_{Tfus}^{Tvap} n\, C_{p\,(liq)}\mathrm{dT} + n\,\Delta H_{vap} + \int_{Tvap}^{T2} nC_{p\,(vap)}\mathrm{dT}$$

$\boldsymbol{\Delta H_{fus}}$ **or** $\mathbf{L_{fus}}$: Latent heat of fusion.

$\boldsymbol{\Delta H_{vap}}$ **or** $\mathbf{L_{vap}}$: Latent heat of vaporization.

Example:

Calculate the enthalpy change associated with heating one mole of iodine from 300 K to 500 K at a constant pressure of one atmosphere. The process may involve phase transitions. The molar heat capacities of iodine in its various physical states are provided:

Cp (I_2, solid) = 5.4 $\mathrm{cal.mol^{-1}.k^{-1}}$

Cp (I_2, liquid) = 19.5 $\mathrm{cal.mol^{-1}.k^{-1}}$

Cp (I_2, gas) = 9.0 $\mathrm{cal.mol^{-1}.k^{-1}}$

The molar enthalpies of phase changes (latent heats) are:

$\Delta H^{\circ}_{vap}\ 475°K = 6.1\ K\mathrm{cal/mol}$

$\Delta H^{\circ}_{fus}\ 387°K = 3.74\ K\mathrm{cal/mol}$

Solution:

The change in enthalpy when one mole of iodine goes from 300K to 500K under a pressure of one atmosphere.

$$\underset{T_1 = 300K}{I_2(sol)} \xrightarrow{\Delta H_1} \underset{387\ k}{I_2(sol)} \xrightarrow{\Delta H_2} \underset{387\ K}{I_2(liq)} \xrightarrow{\Delta H_3} \underset{457\ K}{I_2(liq)} \xrightarrow{\Delta H_4} \underset{457\ K}{I_2(g)} \xrightarrow{\Delta H_5} \underset{T_2}{I_2(g)}$$

T4=500K The enthalpy of heating for solid iodine is:

$\Delta H^{\circ}_1 = \int_{300}^{387} n\, C_{p\,(I_2\,sol)}\mathrm{dT}$= 5.4 (387-300) = 469.8 cal = 0.4698 kcal

The enthalpy of fusion is:

$$\Delta H^{\circ}_2 = n\Delta H^{\circ}_{fus\,(I2,sol)} = 3.74\ kcal$$

The enthalpy of heating for liquid iodine is:

$\Delta H^{\circ}_3 = \int_{T2}^{T3} n\, C_{p\,(I_2\,lid)}\mathrm{dT}$= -19.5 (457-387) = 1.365 kcal

The enthalpy of vaporization is:

$$\Delta H_4^\circ = n\Delta H_{vap\ (I2,liq)}^\circ = 6.10\ kcal$$

The enthalpy of heating for gaseous iodine is:

$\Delta H_5^\circ = \int_{T3}^{T4} n\ C_{p\ (I_2\ g)}$dT= 9 (500-457) = 0.387 kcal

The change in enthalpy for the transformation from initial to final state is:

$$\Delta H^\circ = \sum \Delta H_i^\circ = 12.062\ kcal$$

a. Enthalpy of fusion ΔH_{fus}

The enthalpy of fusion is defined as the amount of heat absorbed by a substance during its transition from the solid phase to the liquid phase, under constant temperature and pressure conditions.

The enthalpy of solidification (the reverse transformation) is the opposite of the enthalpy of fusion: ΔH(solidification) = -ΔH(fusion).

b. Enthalpy of vaporization ΔH_{vap}

The enthalpy of vaporization refers to the enthalpy change associated with the phase transition of one mole of a substance from the liquid phase to the vapor phase.

The enthalpy of liquefaction (the reverse transformation) is the opposite of the enthalpy of vaporization: ΔH(liquefaction) = -ΔH(vaporization).

c. Enthalpy of sublimation ΔH_{sub}

The enthalpy of sublimation, formerly known as the latent heat of sublimation, is the heat absorbed by a substance when it changes from the solid to the gaseous state at constant temperature and pressure. The enthalpy of deposition (the reverse transformation) is the opposite of the enthalpy of sublimation: ΔH(deposition) = -ΔH(sublimation).

III.6 Standard enthalpy of reaction

There are two methods to calculate the standard enthalpy of reaction:

III.6.1 Direct reaction (Hess's Law)

The enthalpy change of a reaction is calculated as the sum of the standard enthalpies of formation of the products, minus the sum of the standard enthalpies of formation of the reactants.

$n_1R_1+n_2R_2 \rightarrow n_3P_1+ n_4P_2$

$\Delta H_R^\circ = (n_3\ \Delta H^\circ(P_1)+ n_4\ \Delta H^\circ(P_2))-(n_1\ \Delta H^\circ(R_1)+ n_2\ \Delta H^\circ(R_2))$

n_1, n_2, n_3, and n_4 are stoichiometric coefficients.

R_1 and R_2 are the reactants.

P_1 and P_2 are the products.

In general: $\Delta H_R° = (\Sigma n_{iP}\, \Delta H_{if}^{\circ}$ (products)) - ($\Sigma n_{iR}\, \Delta H_{if}^{\circ}$ (reactants))

Example 1:

$$CO\ (g) +\ H_2O\ (g) \rightarrow CO_2(g) +\ H_2\ (g)$$

$$\Delta H_R =\ \Delta H_f^{\circ}\ (CO_2) -\ \Delta H_f^{\circ}\ (CO) +\ \Delta H_f^{\circ}\ (H_2O)$$

With:

$\Delta H_f^{\circ}\ (CO_2) =\ -94.1\ kcal/mol$

$\Delta H_f^{\circ}\ (H_2O) =\ -57.8\ kcal/mol$

$\Delta H_f^{\circ}\ (CO) =\ -26.4\ kcal/mol$

$\Delta H_R =\ -94.1 + 26.4 + 57.8 =\ -9.9\ kcal$

Example 2:

Calculate the standard enthalpy change for the following reaction:

$$Ca_3(PO_4)_2(s) +\ 3\ H_2SO_4(\ell) \rightarrow 3\ CaSO_4(s) +\ 2\ H_3PO_4(s)$$

C	$Ca_3(PO_4)_2(s)$	$H_2SO_4(\ell)$	$CaSO_4(s)$	$H_3PO_4(s)$
$\Delta H_f^{\circ}\ (Kcal/mol)$	-986.2	-342.42	-193.91	-306.2

Solution:

According to Hess's Law:

ΔH_R° =($\Sigma n_{i,P}\, \Delta H_{i,f}^{\circ}$ (produits))−($\Sigma n_{i\ ,R}\, \Delta H_{i,f}^{\circ}$ (réactifs))

ΔH_R° =**3** ΔH_f° ($CaSO_4$(s))+ **2** ΔH_f °(H_3PO_4(s)) −ΔH_f °($Ca_3(PO_4)_2$(s))−**3** ΔHf °(H_2SO_4(ℓ))

ΔH_R° = −71,73 kcal $\Delta H_R° < 0$ (Exothermic reaction)

Example 3:

Determine the standard enthalpy of combustion of naphthalene in the presence of oxygen. The following standard enthalpies of formation are provided:

$C_{10}H_8$+ 12 O_2(g)→10 CO_2(g)+ 4 H_2O (ℓ)

C	$C_{10}H_8$	$CO_2(g)$	$H_2O\ (\ell)$
$\Delta H_f^{\circ}\ (Kcal/mol)$	-5157	-393.5	-285.8

Solution:

According to Hess's Law:

$\Delta H^{\circ}_{\text{comb}} = (\sum n_{i.P}\ \Delta H^{\circ}_{\text{f}}$ (products))$-$($\sum n_{i.R}\ \Delta H^{\circ}_{\text{f}}$ (reactants))

$\Delta H^{\circ}_{\text{comb}}{}^{\circ}$ $= \mathbf{10}\ \Delta H^{\circ}_{\text{f}}$ ($CO_2(g)$)+ $\mathbf{4}\ \Delta H^{\circ}_{\text{f}}$($H_2O\ (\ell)$) $-\Delta H^{\circ}_{\text{f}}$($C_{10}H_8$)$-\mathbf{12}\ \Delta H^{\circ}_{\text{f}}$($O_2(g)$)

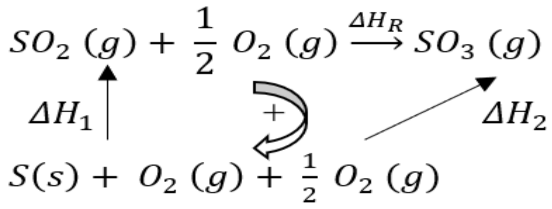
$\Delta H^{\circ}_{\text{f}}$ ($O_2\ (g)$)=0 (O_2 is a simple substance)

$\Delta H^{\circ}_{\text{comb}}$78,8 kJ.mol$^{-1} > 0$ (Endothermic reaction)

Hess's Cycle: $\Delta H_R = \sum \nu_i\ \Delta H_i$

The Hess's cycle is founded on Hess's Law, which states that the total enthalpy change of a reaction depends only on the initial and final states, not on the specific pathway taken. Since enthalpy is a state function, the cycle introduces an alternative reaction pathway that connects the same initial and final states, allowing the enthalpy change to be calculated indirectly.

Example:



$\Delta H_1 + \Delta H_R - \Delta H_2 = 0 \implies \Delta H_R = \Delta H_2 - \Delta H_1 = -23.49\ kcal/mol$

III.6.2 Reaction in Stages

When the standard enthalpies of formation of the substances involved in a reaction are not available, the target reaction can be obtained by combining several known reactions in such a way that their sum yields the overall desired reaction.

The thermodynamic equation system follows the same rules as an algebraic equation system.

Note:

The thermal effect of a reverse reaction is equal in magnitude but opposite in sign to that of the corresponding forward reaction.

Example:

Determine the standard enthalpy change associated with the following thermochemical reaction:

$2\ Al + Fe_2O_3 \rightarrow 2\ Fe + Al_2O_3$

Given that:

$$2\,Al + \frac{3}{2}\,O_2(g) \rightarrow\ Al_2O_3 \qquad \Delta H_1^\circ =\ -399\ \text{kcal}$$

$$2\,Fe + \frac{3}{2}\,O_2(g) \rightarrow\ Fe_2O_3 \qquad \Delta H_2^\circ =\ -196\ \text{kcal}$$

Solution:

$$2\,Al + \frac{3}{2}\,O_2(g) \rightarrow\ Al_2O_3 \qquad \Delta H_1^\circ =\ -399\ \text{kcal}$$

$$(-)x\left(2\,Fe + \frac{3}{2}\,O_2(g) \rightarrow\ Fe_2O_3\right) \qquad -\Delta H_2^\circ = (-) - 196\ \text{kcal} = 195\ \text{kcal}$$

$$\Delta H_R =\ \Delta H_1^\circ -\ \Delta H_2^\circ =\ -203\ kcal$$

III.7 Effect of Temperature on the Standard Enthalpy of Reaction (Kirchhoff's Law)

The variations in enthalpies are generally given at T_1=298K, and there may be a need to know the enthalpy value at a temperature T_2. Kirchhoff's Law allows us to do this.

$$\Delta H_{T2} =\ \Delta H_{\mathrm{R}}^\circ + \int \Delta C_{p(T)}\ dT$$

$\Delta C_{p(T)}$=($\sum n_p\ C_p$ (products)) − ($\sum n_R\ C_p$ (reactants))

$$\Delta H_{T2} =\ \Delta H_{\mathrm{R}}^\circ + \int_{298}^{T2} (\textstyle\sum n_P\ Cp\ \text{products}) - \textstyle\sum n_R\ Cp\ \text{reactants})\ \mathrm{dT}$$

If $\Delta C_{p(T)}$=0, the enthalpy of the reaction is independent of temperature.

If $\Delta C_{p(T)} \neq 0$, the enthalpy varies with temperature, $\Delta H_{T2} \neq \Delta H_{\mathrm{R}}^\circ$.

Example 1:

Calculate the enthalpy change of the reaction at 1000K:

$N_2(g)$+ 3 $H_2(g) \rightarrow 2\ NH_3(g)$ $\quad \Delta H_{\mathrm{R}}^\circ$= 26420 kcal

Corps	$N_2(g)$	$H_2(g)$	$NH_3(g)$
Cp cal/K.mol	$6.6+0.8\ 10^{-3}\ T$	$6.6+0.8\ 10^{-3}\ T$	$8.1+8\ 10^{-3}\ T - 6.3\ 10^{-6}\ T^2$

Solution:

According to Kirchhoff's Law:

$$\Delta H_{1000} =\ \Delta H_{\mathrm{R}}^\circ + \int \Delta C_{p(T)}\ dT$$

$\Delta C_{p(T)}$=($\sum n_p\ C_p$ (products)) − ($\sum n_R\ C_p$ (reactants))

$\Delta C_{p(T)}$= 2 C_p ($NH_3(g)$) - C_p ($N_2(g)$) - 3 C_p ($H_2(g)$)

$\Delta C_{p(T)} = 2\ (8.1 + 8\ 10^{-3}\ T - 6.3\ 10^{-6}\ T^2) - (6.6 + 0.8\ 10^{-3}\ T) - 3\ (6.6 + 0.8\ 10^{-3}\ T)$

$\Delta C_{p(T)} = 8.1 + 0.8\ 10^{-3}\ T - 6.3\ 10^{-6}\ T^2$

$$\Delta H_{1000} = \Delta H^{\circ}_{\mathrm{R}} + \int_{298}^{1000} (8.1 + 0.8\ 10^{-3}\ \mathrm{T} - 6.3\ 10^{-6}\ \mathrm{T}^2)\ \mathrm{dT}$$

$$\Delta H_{1000} = \Delta H^{\circ}_{\mathrm{R}} + \int_{298}^{1000} (8.1 + 0.8\ 10^{-3}\ \mathrm{T} - 6.3\ 10^{-6}\ \mathrm{T}^2)\ \mathrm{dT}$$

$$\Delta H_{1000} = \Delta H^{\circ}_{\mathrm{R}} + 8.1 \int_{298}^{1000} \mathrm{dT} + 0.8\ 10^{-3} \int_{298}^{1000} \mathrm{T\ dT} - 6.3\ 10^{-6} \int_{298}^{1000} \mathrm{T}^2\ \mathrm{dT}$$

$$\Delta H_{1000} = \Delta H^{\circ}_{\mathrm{R}} + 8.1\ [T]_{298}^{1000} + 0.8\ 10^{-3} \left[\frac{T^2}{2}\right]_{298}^{1000} - 6.3\ 10^{-6} \left[\frac{T^3}{3}\right]_{298}^{1000}$$

$$\Delta H_{1000} = -20.3\ 10^{\ 5}\ cal$$

Example 2:

The enthalpy of combustion of methane at 25 °C is $\Delta H_{298}° = -890.34$ kJ.

Determine the enthalpy of the reaction at 100 °C in the case where the formed water is always liquid and, in the case, where it is gaseous.

Given: C_p (CH_4) = 35.31 ($J.mol^{-1}.K^{-1}$).
C_p (CO_2) = 37.2 ($J.mol^{-1}.K^{-1}$).
C_p (O_2) = 29.4 ($J.mol^{-1}.K^{-1}$).
C_p (H_2O (liquid)) = 75.28 ($J.mol^{-1}.K^{-1}$).
C_p (H_2O (gas)) = 33.6 ($J.mol^{-1}.K^{-1}$).
ΔH_{vap}= 43.89 (K $J.mol^{-1}$).

Solution:

1. In the case where the formed water is liquid

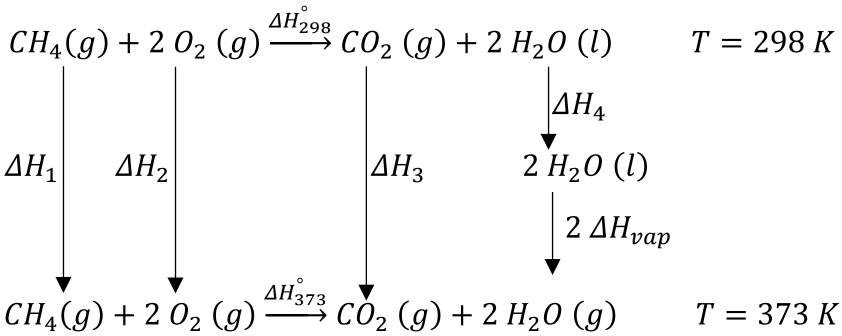
$$\begin{tikzcd}
CH_4(g) \arrow[d, "\Delta H_1"'] & + & 2\ O_2\ (g) \arrow[d, "\Delta H_2"'] \arrow[r, "\Delta H^{\circ}_{298}"] & CO_2\ (g) \arrow[d, "\Delta H_3"] & + & 2\ H_2O\ (l) \arrow[d, "\Delta H_4"] & T = 298\ K \\
CH_4(g) & + & 2\ O_2\ (g) \arrow[r, "\Delta H^{\circ}_{373}"] & CO_2\ (g) & + & 2\ H_2O\ (l) & T = 373\ K
\end{tikzcd}$$

$$\Delta H_{373} = \Delta H^{\circ}_{\mathrm{R}} + \int_{298}^{373} \Delta C_{p(T)}\ dT = \Delta H^{\circ}_{298} + \Delta C_p\ \Delta T$$

$\Delta C_{p(T)}$= 2 Cp (H_2O(l)) + Cp (CO_2) – 2 Cp (O_2) – Cp (CH_4) = 93.65 J/K

$$\Delta H_{373} = -890.34 + 93.65\ 10^{-3}\ (373 - 298) = -883.316\ kJ$$

2. In the case where the formed water is gaseous



$$\Delta H_{373} = \Delta H^\circ_{298} + \int_{298}^{373} \Delta C_p\ dT = \Delta H^\circ_{298} + \Delta C_p\ \Delta T + \Delta H_{vap\ (H_2O)}$$

$\Delta C_{p(T)}$= 2 Cp (H_2O(g)) + Cp (CO_2) – 2 Cp (O_2) – Cp (CH_4) = 10.29 J/K

$$\Delta H_{373} = -890.34 + 10.29\ 10^{-3}\ (373 - 298) + 2\ 43.89 = -801.79\ kJ$$

III.8 Bond Energy

During a chemical reaction, there is a breaking and forming of chemical bonds.

The enthalpy change is attributed to the overall bonds involved in the chemical process. To calculate bond energy:

1. Write the formation reaction from the simple pure substances.
2. Write the cycle where monoatomic elements appear in the gaseous state.
3. Write the balance of the formed bonds.
4. Apply Hess's Law in the case of the cycle: $\Sigma \Delta H_i = 0$.

The formation of the bond is always exothermic, the breaking of an endothermic bond.

In tables, bond enthalpies are given at 298K:

Bond	Dissociation Energy (kcal/mol)
Cl–Cl	57.9
Br–Br	46.1
I–I	36.1
H–Cl	103.0
H–Br	88.0
H–I	71.0

Example 1:

Calculate the bond energies C−H using the following data:

C(s)→C (g) $\Delta H^{\circ}_{sublimation}$ =715 kJ.mol^{-1}

H_2(g)→2 H(g) $\Delta H^{\circ}_{\text{disociation}}$= 436 kJ.mol^{-1}

ΔH°_{f} (CH_4 (g))= −74.85 kJ.mol^{-1}

Solution:

1. Bond Energy C-H

$$\begin{tikzcd}
C\ (s) + 2\ H_2\ (g) \arrow[rr, Rightarrow, "\Delta H^{\circ}_{f}"] \arrow[d, "\Delta H^{\circ}_{sub}"'] \arrow[d, phantom, shift left=6ex, "2\ x\ \Delta H^{\circ}_{dis}\ +"] & & CH_4\ (g) \\
C\ (g) + 2\ x2\ H\ (g) \arrow[urr, "4\ E_{C-H}"'] & &
\end{tikzcd}$$

$\sum_i \Delta H_i = 0 \ \Rightarrow\ \Delta H^{\circ}_{f}\ \left(CH_4\ (\text{g})\right) - \Delta H^{\circ}_{sublimation} - 2x\ \Delta H^{\circ}_{\text{disociation}}$ - 4 E_{C-H}= 0

$$E_{C-H} = \frac{\Delta H^{\circ}_{f}\ (CH_4\ (\text{g})) - \Delta H^{\circ}_{sublimation} - 2x\ \Delta H^{\circ}_{\text{disociation}}}{4} = \frac{-74.85-715-\ 2\ x\ 436}{4} = -415.46\ kJ$$

$E_{C-H} = -415.46\ kJ$

Example 2:

The standard enthalpy of formation of ethanol C_2H_5OH, ΔH°_{f} =−239 kJ.mol^{-1}.

Calculate the bond energy of C-O in ethanol.

Data:

$\Delta H^{\circ}_{sub}(c)$= 717 kJ.mol^{-1}.

A-B	H-H	O-H	C-H	C-C
$\Delta H^{\circ}_{f(A-B)}$	-435	-460	-414	-347

From the expanded formula of the ethanol molecule, we have:

C-C bond: ΔH°_{f} (C-C), C-O bond: ΔH°_{f} (C-O), O-H bond: ΔH°_{f} (O-H), C-H bonds: ΔH°_{f} (C-H)

$$\begin{tikzcd}
2C\ (s) + 3\ H_2\ (g) + \frac{1}{2}\ O_2\ (g) \arrow[rr, "\Delta H^{\circ}_{f}"] \arrow[d, "2\ \Delta H^{\circ}_{sub}\quad -3\Delta H^{\circ}_{f\ (H-H)}\quad -\frac{1}{2}\Delta H^{\circ}_{f\ (O-O)}"'] & & C_2H_5OH\ (g) \\
2C\ (g) + 6\ H\ (g) + \ O\ (g) \arrow[urr, "5\ \Delta H^{\circ}_{f\ (C-H)} + \Delta H^{\circ}_{f\ (C-O)} + \Delta H^{\circ}_{f\ (C-C)} + \Delta H^{\circ}_{f\ (O-H)}"'] & &
\end{tikzcd}$$

$$\Delta H_f^{\circ} = 2\Delta H_{sub}^{\circ} - 3\Delta H_{f\,(H-H)}^{\circ} - \frac{1}{2}\Delta H_{f(O-O)}^{\circ} + 5\,\Delta H_{f(C-H)}^{\circ} + \Delta H_{f(C-O)}^{\circ} + \Delta H_{f(C-C)}^{\circ} + \Delta H_{f(O-H)}^{\circ}$$

$$\Delta H_{f(C-O)}^{\circ} = \Delta H_f^{\circ} - 2\Delta H_{sub}^{\circ} + 3\Delta H_{f\,(H-H)}^{\circ} + \frac{1}{2}\Delta H_{f(O-O)}^{\circ} - 5\,\Delta H_{f(C-H)}^{\circ} - \Delta H_{f(C-C)}^{\circ} - \Delta H_{f(O-H)}^{\circ}$$

$$\Delta H_{f(C-O)}^{\circ} = -200\ kJ/mol$$

Practical Case Studies

- **Industrial Energy Recovery:** Using waste heat from steel manufacturing to power turbines through the Rankine cycle.
- **Environmental Remediation:** Endothermic dissolution of ammonia salts in water for soil cooling in agriculture.
- **Food Industry:** Exothermic caramelization reactions in sugar processing.
- **Power Generation:** Combustion of natural gas in combined cycle plants and its thermochemical efficiency.

Self-Assessment Quizzes

1- MCQs

1. Which of the following is an endothermic process?
   a) Combustion of methane;
   b) Dissolution of NH_4NO_3 in water;
   c) Condensation of steam;
   d) Formation of ice from water.
2. The unit of enthalpy change in the SI system is:
   a) J/s;
   b) J/mol;
   c) W;
   d) Pa.

2- True/False

1. In an exothermic reaction, ΔH is negative.
2. Specific heat capacity is independent of temperature.

3- Short Questions

1. Define Hess's Law and provide one industrial example.
2. How does thermochemistry help improve energy efficiency in power plants?

Recap & Key Formulas

- **Essential Concepts**

  Thermochemistry studies heat changes in chemical reactions, often at constant pressure.

  Heat of reaction: energy exchanged with surroundings when a chemical system changes from reactants to products.

  Standard state: reference condition (P = 1 bar, given T) for substances in thermodynamic tables.

  Enthalpy $H=U+PV$ is a state function; at constant pressure, $\Delta H=Q_P$.

  Hess's Law: ΔH depends only on initial and final states.

  Kirchhoff's Law: accounts for temperature dependence of ΔH using heat capacities.

- **Key Formulas**

  First Law: $dU=dQ+dW$

  Isobaric Process: $\Delta H=Q_P$

  Isochoric Process: $\Delta U=Q_V$

  Relation between Q_V and Q_P (ideal gases): $Q_P=Q_V+RT\Delta n$

  Standard Enthalpy of Reaction: $\Delta H_R°=\sum n_P \Delta H_f°(\text{products})-\sum n_R \Delta H_f°(\text{reactants})$

  Kirchhoff's Law: $\Delta H_{T2} = \Delta H^{\circ}_{R} + \int \Delta C_{p(T)}\, dT$

Corrected Exercises

Exercise 1:

Calculate the standard enthalpy change ($\Delta H°$) for the reaction: $2C\ (graphite)+O_2\ (g)\rightarrow 2CO\ (g)$

Given the following thermochemical equations:

1. $C\ (graphite)+O_2\ (g)\rightarrow CO_2\ (g)$ $\Delta H_1°=-93.69$ kcal;
2. $2CO\ (g)+O_2\ (g)\rightarrow 2CO_2\ (g)$ $\Delta H_2°=-136.58$ kcal.

Exercise 2:

Consider the reaction:

$C(s) + H_2O\ (g) \longrightarrow CO_2\ (g) + H_2\ (g)$

1. Calculate the standard enthalpy of this reaction.
2. Calculate the heat of reaction at constant volume (Q_v) at 25 °C.

Data: $\Delta H_f°\ (CO_2) = -110$ kJ/mol ; $\Delta H_f°\ (H_2O) = -242$ kJ/mol.

Exercise 3:

The standard enthalpy of combustion of one mole of liquid methanol ($CH_3OH(l)$) under standard conditions (1 bar, 25 °C) is given as:

$\Delta H_{comb}°(CH_3OH)=-725$ kJ.

1. Write the balanced chemical equation for the complete combustion of methanol.
2. Determine the standard enthalpy of formation of liquid methanol.
3. Calculate the enthalpy change of the combustion reaction at 60 °C. Indicate whether the reaction is endothermic or exothermic, and justify your answer.
4. Estimate the average bond enthalpy of the C–H bond in liquid methanol.

Data: $\Delta H_f°\ (H_2O,l) = -68.32$ kcal/mol ; $\Delta H_f°\ (C_2O,g) = -94.05$ kcal/mol,

$\Delta H_{sub}°\ (C, s) = 171.66$ kcal/mol; $\Delta H_f°\ (O{=}O) = -119$ kcal/mol ;

$\Delta H_f°\ (H\text{-}H) = -1103$ kcal/mol;

$\Delta H_f°\ (O\text{-}H) = -107$ kcal/mol ; $\Delta H_f°\ (C\text{-}O) = -82$ kcal/mol.

$C_p(H_2O, l) = 75.2$ J/mol.K ; $C_p(CH_3OH)$ lid= 81.61 J/mol.K ; $C_p(O_2,g) = 34.71$ J/mol.K, $C_p(CO_2,g) = 36.4$ J/mol·K.

Exercise 4:

1. Write the formation reaction of **liquid** ethanol (C_2H_5OH) at 25 °C from its constituent elements.

2. Determine the standard enthalpy of formation of ethanol in the gaseous state.
3. Estimate the bond dissociation energy of the O–H bond in ethanol vapor.
4. Calculate the molar heat capacity (**C_p**) of liquid methanol.

Element	C_p (kJ/mol.K)
C(s)	8.56
H_2	20.59
O_2	20.93

Data:

$\Delta H_f°$ (C_2H_5OH, l) = -278 kJ/mol;

$\Delta H_{vap}°$ (C_2H_5OH, l) = 38.5 kJ/mol;

$\Delta H_{sub}°$ (C)= 714 kJ/mol;

ΔH_f (CH_3OH, l) = -238 kJ/mol (à 328K);

Bond	H-H	O-O	C-O	C-C	C-H
$\Delta H_{dis}°$ kJ/mol	436	495	351	347	414

Exercise 5:

Using the data in the table below, calculate the bond energies E(C–C), E(C=C), and E(C–H) in the gaseous compounds CH_4, C_2H_4, and C_2H_6.

Compound	**CH_4**	**C_2H_4**	**C_2H_6**	**H(g)**	**C(g)**
ΔH (kJ/mol)	-76	52	-58	218	718

Exercise 6:

Calculate the standard enthalpies of formation (**ΔH_f**) of the compounds CH_4(g), CH_3Cl(g), and HCl(g) from the following reactions:

1.

$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$ $\Delta H_1 = -42$ kcal/mol

2.

$C(s) + 2\ H_2(g) \rightarrow CH_4(g)$ $\Delta H_2 = -17.89$ kcal/mol

3.

$2\ C(s) + 3\ H_2(g) + Cl_2(g) \rightarrow 2\ CH_3Cl(g)$ $\Delta H_3 = -30.60$ kcal/mol

Then, calculate the reaction enthalpy ΔH_r (or heat of reaction Q_R) for the following reaction using two different methods:

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$

Exercise 7:

Calculate the reaction enthalpy **ΔH_r** at **353 K** and **383 K** for the following reaction:

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

Given data at 25 °C (298 K):

- ΔH_f° (H_2O, l) = –68.32 kcal/mol;
- ΔH_{vap}° (H_2O, l) = 10 kcal/mol;
- C_p (H_2, g) = 6.85 cal/mol.K;
- C_p (O_2, g) = 8.11 cal/mol.K;
- C_p (H_2O, g) = 7.8 cal/mol.K;
- C_p (H_2O, l) = 18 cal/mol.K.

Correction

Exercise 1:

2 x (2C (graphite)+O_2 (g)→2CO (g)) **2 x** ΔH_1° = **2 x** (-93.69) = - 187.38 kcal.

- (2CO (g)+O_2 (g)→2CO_2 (g)) $-\Delta H_2^\circ = -(-136.58)$ = 136.58 kcal.

$\Delta H_R^\circ = 2\,.\,\Delta H_1^\circ - \Delta H_2^\circ = -187.38 + 136.58 = -50.8$ kcal

Exercise 2:

1. Calculate the standard enthalpy of this reaction ΔH_R°

$\Delta H_R^\circ = \Sigma\, n_{ip}\, \Delta H_{i.fP}^\circ - \Sigma\, n_{iR}\, \Delta H_{i.fR}^\circ$

$\Delta H_R^\circ = \Delta H_f^\circ\, CO_2 + \Delta H_f^\circ H_2 - \Delta H_f^\circ C(s) - \Delta H_f^\circ\, H_2O(g)$

$\Delta H_f^\circ H_2 = \Delta H_f^\circ C(s) = 0$

$\Delta H_R^\circ = \Delta H_f^\circ\, CO_2 - \Delta H_f^\circ\, H_2O(g) = -110 + 242 = 132\ kJ$

2. Calculate (Qv) at 25 °C

$Q_p = Q_v + \Delta n\, RT \Longrightarrow Q_v = Q_p - \Delta n\, RT = \Delta H_R^\circ - \Delta n\, RT$

$\Delta n = \Sigma ni\ Products\ (g) - \Sigma ni\ Reactants\ (g) = \Delta H_f^\circ CO_2 + n\, H_2 - n\, H_2O(g)$

$\Delta n = 1 + 1 - 1 = 1\ mol$

$Qv = 132\ 10^3 - 1\,.0.314\,.298 = 129.5\ kJ$

Exercise 3:

1. Combustion Reaction of Methanol

$$CH_3OH\ (l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(l)$$

2. Standard Enthalpy of Formation of Liquid Methanol

$$\Delta H^\circ_R = \Sigma\ n_{ip}\ \Delta H^\circ_{i.fP} - \Sigma\ n_{iR}\ \Delta H^\circ_{i.fR}$$

$$\Delta H^\circ_R = \Delta H^\circ_f\ CO_2 + 2.\Delta H^\circ_f\ H_2O\ (l) - \Delta H^\circ_f CH_3OH\ (l) - \frac{3}{2}\Delta H^\circ_f\ O_2(g)$$

$$\Delta H^\circ_f CH_3OH\ (l) = \Delta H^\circ_f\ CO_2 + 2.\Delta H^\circ_f\ H_2O\ (l) - \Delta H^\circ_R$$

$$\Delta H^\circ_f CH_3OH\ (l) = 2\ (-68.32) + (-94.05) - \frac{-725.2}{4.18} = -57.197\frac{kcal}{mol} = -239.084\frac{kJ}{mol}$$

3. Enthalpy of Reaction at 60 °C (333 K)

$$\Delta H_{333} = \Delta H^\circ_{298} + \int_{298}^{333} \Delta C_p\ dT = \Delta H^\circ_{298} + \Delta C_p \int_{298}^{333} dT$$

$$\Delta Cp = (\textstyle\sum n_P\ C_p\ (products)) - (\textstyle\sum n_R\ C_p\ (reactants))$$

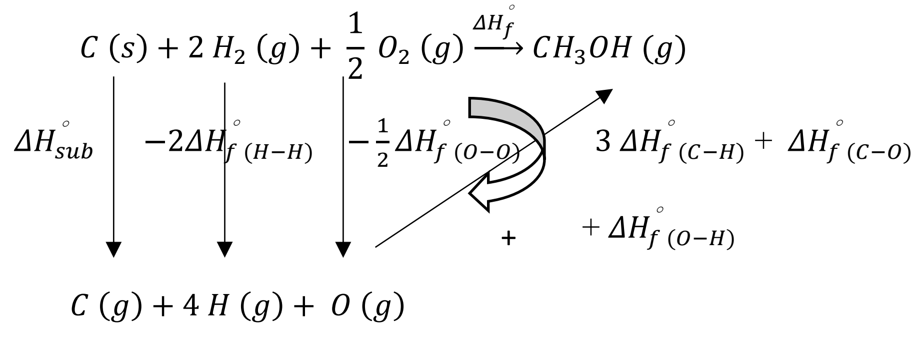
$$\Delta Cp = C_p\ CO_2 + 2\ C_p\ H_2O\ (l) - C_p\ CH_3OH\ (l) - \frac{3}{2}C_p\ O_2(g)$$

$$\Delta Cp = 37.2 + 2\ .\ 75.2 - 81.6 - \frac{3}{2}\ 29.4 = 61.9\frac{J}{K}$$

$$\Delta H_{333} = -725.2 + 61.9\ 10^{-3}\ (333 - 298) = -723.033\ kJ$$

Since ΔH<0, the **reaction is exothermic**.

4. Estimating the Enthalpy of the C–H Bond in $CH_3OH(l)$



$$\Delta H^\circ_f\ CH_3OH - \Delta H^\circ_{sub} + 2\Delta H^\circ_{f\ (H-H)} + \frac{1}{2}\Delta H^\circ_{f(O-O)} - 3\ \Delta H^\circ_{f(C-H)} - \Delta H^\circ_{f(C-O)} - \Delta H^\circ_{f(O-H)} = 0$$

$$\Delta H_f^\circ\ CH_3OH - \Delta H_{sub}^\circ + 2\Delta H_{f\,(H-H)}^\circ + \frac{1}{2}\Delta H_{f(O-O)}^\circ - \Delta H_{f(C-O)}^\circ - \Delta H_{f(O-H)}^\circ = 3\,\Delta H_{f(C-H)}^\circ$$

$$\Delta H_{f(C-H)}^\circ = \frac{\Delta H_f^\circ\ CH_3OH - \Delta H_{sub}^\circ + 2\Delta H_{f\,(H-H)}^\circ + \frac{1}{2}\Delta H_{f(O-O)}^\circ - \Delta H_{f(C-O)}^\circ - \Delta H_{f(O-H)}^\circ =}{3}$$

$$\Delta H_{f(C-H)}^\circ = 75.43\ Kcal$$

Exercise 4:

1. Formation Reaction of Liquid Ethanol ($C_2H_5OH(l)$) at 25 °C

$$C\ (s) + 3\ H_2\ (g) + \frac{1}{2}\ O_2\ (g) \xrightarrow{\Delta H_f^\circ\ C_2H_5OH\ (l)} C_2H_5OH\ (l)$$

2. Standard Enthalpy of Formation of Gaseous Ethanol

$$\begin{tikzcd}
C\ (s) + 3\ H_2\ (g) + \frac{1}{2}\ O_2\ (g) \arrow[rr, "\Delta H_f^\circ\ C_2H_5OH\ (g)"] \arrow[d, "\Delta H_f^\circ\ (C_2H_5OH\ (l))"'] & & C_2H_5OH\ (g) \\
C_2H_5OH\ (l) \arrow[urr, "\Delta H_v^\circ\ (C_2H_5OH)"'] & + &
\end{tikzcd}$$

$$\Delta H_f^\circ\ (C_2H_5OH\ (g)) = \Delta H_f^\circ\ (C_2H_5OH\ (l)) + \Delta H_v^\circ\ (C_2H_5OH) = -278 + 38.5$$

$$\Delta H_f^\circ\ (C_2H_5OH\ (g)) = -239.5\frac{kJ}{mol}$$

3. Dissociation Energy of the O–H Bond in Gaseous Ethanol

$$\begin{tikzcd}
2C\ (s) \arrow[d, "2\,\Delta H_{sub}^\circ"'] & + 3\ H_2\ (g) \arrow[d, "-3\Delta H_{f\,(H-H)}^\circ"'] & + \frac{1}{2}\ O_2\ (g) \arrow[d, "-\frac{1}{2}\Delta H_{f\,(O-O)}^\circ"'] \arrow[r, "\Delta H_f^\circ"] & C_2H_5OH\ (g) \\
2C\ (g) & + 6\ H\ (g) & +\ O\ (g) \arrow[ur, "-5\,\Delta H_{d\,(C-H)}^\circ - \Delta H_{d\,(C-O)}^\circ - \Delta H_{d\,(C-C)}^\circ - \Delta H_{d\,(O-H)}^\circ"'] &
\end{tikzcd}$$

$$\Delta H_f^\circ - 2\Delta H_{sub}^\circ + 3\Delta H_{f\,(H-H)}^\circ + \frac{1}{2}\Delta H_{f(O-O)}^\circ + 5\,\Delta H_{d(C-H)}^\circ + \Delta H_{d(C-O)}^\circ + \Delta H_{d(C-C)}^\circ + \Delta H_{d(O-H)}^\circ = 0$$

$$-\Delta H_{d(O-H)}^\circ = \Delta H_f^\circ - 2\Delta H_{sub}^\circ + 3\Delta H_{f\,(H-H)}^\circ + \frac{1}{2}\Delta H_{f(O-O)}^\circ + 5\,\Delta H_{d(C-H)}^\circ + \Delta H_{d(C-O)}^\circ + \Delta H_{d(C-C)}^\circ$$

$$-\Delta H_{d(O-H)}^\circ = -239.5 - 2\,.\,714 + 3\,(-436) + \frac{1}{2}\,(-495) + 5\,.\,414 + 351 + 347$$

$$-\Delta H_{d(O-H)}^\circ == -455\ kJ/mol$$

$$\Delta H_{d(O-H)}^\circ = 455\ kJ/mol$$

4. Molar Heat Capacity (Cp) of Liquid Methanol

$$C\,(s) + 2\,H_2 + \frac{1}{2}\,O_2 \xrightarrow{\Delta H_f^{\circ}\,(CH_3OH\,(l))} CH_3OH\,(l)$$

We use **Kirchhoff's law** to estimate Cp of methanol assuming:

$$\Delta H_{328} = \Delta H^{\circ}_{298} + \int_{298}^{328} \Delta C_p\, dT$$

$$\Delta Cp = \left(\sum np\ Cp\ (products)\right) - \left(\sum nR\ Cp\ (reactants)\right)$$

$$\Delta Cp = Cp\ CH_3OH\,(l) - \frac{1}{2} Cp\ O_2(g) - 2\ Cp\ \ H_2 - Cp\ C(s)$$

$$\Delta H_{328} = \Delta H^{\circ}_{298} + \int_{298}^{328} \left(C_{p,CH_3OH\,(l)}\,(l) - \frac{1}{2} C_{p,O_2\,(g)} - 2\ C_{p,H_2} - C_{p,C\ \ (s)}\right) dT$$

$$\Delta H_{328} = \Delta H^{\circ}_{298} + \left(C_{p,CH_3OH\,(l)} - \frac{1}{2} C_{p,O_2\,(g)} - 2\ C_{p,H_2} - C_{p,C\ \ (s)}\right)(328 - 298)$$

$$C_{p,CH_3OH\,(l)} = \frac{\Delta H_{328} - \Delta H^{\circ}_{298}}{328 - 298} + \frac{1}{2} C_{p,O_2\,(g)} + 2\ C_{p,H_2} + C_{p,C\ \ (s)}$$

$$C_{p,CH_3OH\,(l)} = \frac{(-238 + 239)10^3}{328 - 298} + \frac{1}{2}20.93 + 2\,.\,20.59 + 8.56 = 93.53\ J/mol.K$$

Exercise 5:

CH_4

$$\begin{tikzcd}
C\,(graphite) + \arrow[d, "\Delta H^{\circ}_{sub}"'] & 2\,H_2\,(g) \arrow[r, "\Delta H^{\circ}_{f,CH_4}"] \arrow[d, "-2\,\Delta H^{\circ}_{f\,(H-H)}"] & CH_4(g) \\
C\,(g) + & 4\,H\,(g) \arrow[ur, "4\,E_l(C-H)"', "+"] &
\end{tikzcd}$$

$$\Delta H^{\circ}_{f,CH_4} + 4\,E_l(C-H) - \Delta H^{\circ}_{sub} - 4\,\Delta H^{\circ}_{d\,(H)} = 0$$

$$4\,E_l(C-H) = -\Delta H^{\circ}_{f,CH_4} - \Delta H^{\circ}_{sub} - 4\,\Delta H^{\circ}_{d\,(H)} = -76 - 718 - 4x\,(218)$$

$$E_l(C-H) = -416.5\ kJ$$

C_2H_4

$$\begin{tikzcd}
2C\,(graphite) \arrow[d, "2\,\Delta H^{\circ}_{sub}"'] & +\,2\,H_2\,(g) \arrow[r, "\Delta H^{\circ}_{f,C_2H_4}"] \arrow[d, "-2\Delta H^{\circ}_{f\,(H-H)}"] & C_2H_4(g) \\
2C\,(g)\,+ & 4\,H\,(g) \arrow[ur, "4\,E_l(C-H)+\;E_l(C=C)"', "+"] &
\end{tikzcd}$$

$$\Delta H^{\circ}_{f,C_2H_4} -\ 4\,E_l(C-H) -\ E_l(C=C) -\ 2\,\Delta H^{\circ}_{sub} + 2\,\Delta H^{\circ}_{f\,(H-H)} = 0$$

$$E_l(C=C) - = \Delta H^{\circ}_{f,C_2H_4} -\ 4\,E_l(C-H) -\ 2\,\Delta H^{\circ}_{sub} + 2\,\Delta H^{\circ}_{f\,(H-H)}$$

$$E_l(C=C) = 52 - 4\,(-307.5) - 2\,(718) + 2\,(-218)\ kJ$$

$$E_l(C=C) = -590\ kJ$$

C_2H_6

$$\begin{tikzcd}
2C\,(graphite) \arrow[d, "2\,\Delta H^{\circ}_{sub}"'] & +\,3\,H_2\,(g) \arrow[r, "\Delta H^{\circ}_{f,C_2H_6}"] \arrow[d, "-3\Delta H^{\circ}_{f\,(H-H)}"] & C_2H_6(g) \\
2C\,(g)\,+ & 6\,H\,(g) \arrow[ur, "6\,E_l(C-H)+\;E_l(C-C)"', "+"] &
\end{tikzcd}$$

$$\Delta H^{\circ}_{f,C_2H_6} -\ 6\,E_l(C-H) -\ E_l(C-C) -\ 2\,\Delta H^{\circ}_{sub} + 3\,\Delta H^{\circ}_{f\,(H-H)} = 0$$

$$E_l(C-C) = \Delta H^{\circ}_{f,C_2H_6} -\ 6\,E_l(C-H) -\ 2\,\Delta H^{\circ}_{sub} + 3\,\Delta H^{\circ}_{f\,(H-H)}$$

$$E_l(C-C) = -58 - 6\,(-307.5) - 2\,(718) + 3\,(-218)\ kJ$$

$$E_l(C-C) = -303\ kJ$$

Exercise 6:

Calculate the standard enthalpies of formation

$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$ $\Delta H_1 = -42$ kJ/mol $\Rightarrow \Delta H^{\circ}_{f,HCl} = \frac{1}{2}\ \Delta H^{\circ}_1\ = -21\ kcal$

$C(s) + 2\,H_2(g) \rightarrow CH_4(g)$ $\Delta H_2 = -17.89$ kJ/mol $\Rightarrow \Delta H^{\circ}_{f,CH_4} = \Delta H^{\circ}_2\ = -17.89\ kcal$

$2\,C(s)+3H_2(g)\ Cl_2(g)\rightarrow 2\,CH_3Cl(g)$ $\Delta H_3 = -30.60$ kJ/mol $\Rightarrow \Delta H^{\circ}_{f,CH_3Cl} = \frac{1}{2}\ \Delta H^{\circ}_3\ = -15.3\ kcal$

Calculate the reaction enthalpy ΔH_R°

The first method

$$\Delta H_R^\circ = \Delta H_{f,CH_3Cl(g)}^\circ + \Delta H_{f,HCl(g)}^\circ - \Delta H_{f,CH_4\,(g)}^\circ = -15.3 - 21 + 17.89 - 18.41\ kcal$$

The second method

$$\begin{tikzcd}
CH_4(g) + Cl_2(g) \arrow[r, "\Delta H_R^\circ"] & CH_3Cl(g) + HCl(g) \\
C\ (graphite) + 2\,H_2\ (g) + Cl_2\ (g) \arrow[u, "\Delta H_2^\circ"] \arrow[ur, "\frac{1}{2}\ \Delta H_1^\circ + \frac{1}{2}\ \Delta H_3^\circ"'] \arrow[ur, phantom, "\circlearrowright +", bend left] &
\end{tikzcd}$$

$$\Delta H_R^\circ - \frac{1}{2}\ \Delta H_1^\circ - \frac{1}{2}\ \Delta H_3^\circ + \Delta H_2^\circ = 0$$

$$\Delta H_R^\circ = \frac{1}{2}\ \Delta H_1^\circ + \frac{1}{2}\ \Delta H_3^\circ - \Delta H_2^\circ = \frac{1}{2}(-42) + \frac{1}{2}(-30.6) - (-17.89)$$

$$\Delta H_R^\circ = -18.41\ kcal$$

Exercise 7:

$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$

$$\Delta H_{R,298}^\circ = \Delta H_{f,H_2O\,(l)}^\circ = -68.32\ kcal$$

$$\Delta H_{R,T}^\circ = \Delta H_{R,298}^\circ + \Delta Cp\ (T - 298)$$

T=353K

$$\Delta Cp = C_{p,H_2O\,(l)} - C_{p,H_2\,(g)} - \frac{1}{2} C_{p,O_2\,(g)} = 18 - 6.85 - \frac{1}{2}\ 8.11 = 7.08\ cal/K$$

$$\Delta H_{R,353}^\circ = -68.32 + 7.08\ 10^{-3}\ (353 - 298) = -67.93\ kcal$$

T=383K

At this temperature (383 K= 110 °C), water is in the gaseous state.

$$H_2(g) + ½\ O_2(g) \xrightarrow{\Delta H_R^\circ} H_2O(l) \xrightarrow{\Delta H_{vap}^\circ} H_2O(g)$$

$$H_2(g) + ½\ O_2(g) \xrightarrow{\Delta H_R'^\circ} H_2O(g)$$

$$\Delta H_{R,298}'^\circ = \Delta H_R^\circ + \Delta H_{vap}^\circ = -68.32 + 10 = -58.32\ kcal$$

$$\Delta H^{\circ}_{R,383} = \Delta H'^{\circ}_{R,298} + \Delta C_P\,(T - 298)$$

$$\Delta Cp = C_{p,H_2O\,(g)} - C_{p,H_2\,(g)} - \frac{1}{2}C_{p,O_2\,(g)} = 7.8 - 6.85 - \frac{1}{2}\,8.11 = -3.1\,cal/K$$

$$\Delta H^{\circ}_{R,383} = -58.32 - 3.1\,10^{-3}\,(383 - 298) = -58.58\,kcal$$

Non-Corrected Problems for Practice

1. Calculate the amount of heat released when 10 g of methane is completely combusted. *(Data: $\Delta H^{\circ}_{combustion}$ (CH_4) = –890 kJ/mol) ;*
2. 100 g of water is heated from 25 °C to 75 °C. Calculate the heat absorbed. *(c = 4.18 J/g·°C);*
3. A reaction has ΔH = +120 kJ. Is the reaction endothermic or exothermic? Justify your answer.
4. Using Hess's Law, determine ΔH for the reaction:
   $CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$
   Given:
   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$, ΔH = –890 kJ.

Chapter IV:
Second Law of Thermodynamics

Learning objectives

After completing this chapter the student will be able to:

- State the Second Law in its Clausius and Kelvin forms and explain their equivalence;
- Define entropy S and use the differential relation $dS=\delta Q_{rev}/T$ to compute entropy changes.;
- Distinguish reversible and irreversible processes and state the entropy-production sign rule ($\Delta S_{total}\geq 0$);
- Compute ΔS for common ideal-gas processes (isothermal, isobaric, isochoric, adiabatic) and for phase changes;
- Apply entropy balance to isolated systems and mixing problems (entropy of mixing).
- Explain the Carnot cycle, derive Carnot efficiency $\eta_{rev}=1-T_c/T_h$, and compare ideal and real heat-engine performance;
- Use Kirchhoff-type relations to estimate temperature dependence of reaction entropies where needed;
- Assess spontaneity for processes at constant T, P using the entropy perspective (and link to Gibbs free energy when appropriate).

IV.1 Introduction

The first principle, which is a principle of energy conservation, allows for the energy balance of systems. However, it provides no information about the direction of evolution or the spontaneity of transformations within these systems.

Hence, the need for a second principle, known as the principle of evolution. It introduces a new state function called "Entropy," denoted as "S".

Example 1:

When two containers, each containing a different gas, are brought into communication, the mixing of the two gases occurs spontaneously.

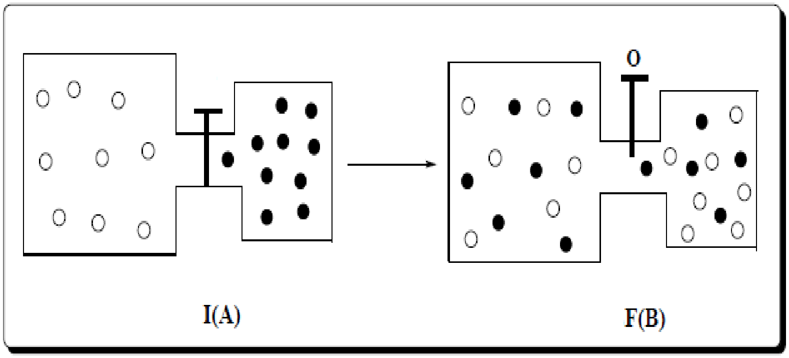


Figure IV.1: Illustration of the mixing of two gases.

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

Example 2:

Natural gas CH_4 undergoes a spontaneous combustion reaction in the air:

CH_4 (g) + $2O_2$ (g) → CO_2 (g) + 2 H_2O (g)

The reverse reaction is not spontaneous. If it were, one could produce a fuel from abundant and inexpensive products, eliminating energy crises.

Example 3:

$HCl + NaOH \rightarrow NaCl + H_2O$

$2HCl + Zn \rightarrow ZnCl_2 + H_2$

However, the reverse reactions are never observed to occur. That is to say:

$NaCl + H_2O \rightarrow HCl + NaOH$

$ZnCl_2 + H_2 \rightarrow 2HCl + Zn$

Example 4: Experiments show that when a hot body A at temperature T_A is brought into contact with a cold body B at temperature T_B, immediately body A cools while body B warms up. This continues until both bodies reach the same temperature (thermal equilibrium).

A+B → (A+B)

$T_A + T_B$ T_e

The reverse transformation below is not prohibited by the first principle; hence the need to have a second principle that can inform us about the direction of system evolution.

(A+B) → A+B

T_e $T_A + T_B$

IV.2 Statement of the Second Law of Thermodynamics

Consider a closed system undergoing a transformation from state A to state B. Assume the system remains at a uniform temperature at any given moment, though this temperature may change over time. If the system exchanges a total quantity of heat Q with the surroundings, this exchange can be broken down into infinitesimal amounts δQ, transferred over time intervals dt at temperature T:

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

IV.2.1 Clausius statement

Heat cannot spontaneously flow from a colder body to a hotter one without external intervention.

IV.2.2 Kelvin statement

It is impossible to extract heat from a system and convert it entirely into work without any other effect on the surroundings.

IV.3 Concept of Entropy

IV.3.1 Introduction to the entropy function S of a system

Consider a closed thermodynamic system, as illustrated in the following figure. We postulate the existence of an extensive state function known as entropy (S). For a transformation between two equilibrium states namely, the Initial State (IS) and the Final State (FS), the change in entropy ΔS of the system is given by:

$dS_{sys} = \delta S_c + \delta S_e$

- **$\delta S_{created}$:** Variation of entropy related to internal modifications within the system (entropy creation).

- **$\delta S_{exchanged}$:** Variation of entropy exchanged between the system and the external environment, due to heat exchanges δQ. It is not a state function; it is given by:

$$\delta S_e = \frac{\delta Q_e}{T_{ext}}$$

T_{ex}t is the temperature of the external environment.

$\delta S_c=0$ for a reversible transformation, in which the system remains in thermodynamic equilibrium at all time.

$\delta S_c>0$ for an irreversible transformation (entropy is created).

IV.3.2 Calculation of entropy variations

If we perform the entropy balance during a transformation, we can write:

$$\Delta S = \int_i^f ds = \int_i^f \delta S_c + \int_i^f \delta S_e = \int_i^f \delta S_c + \int_i^f \frac{\delta Q}{T}$$

S is a state function, and we can then write:

$$\Delta S_{i\to f} = S_f - S_i = \int_i^f \delta S_c + \int_i^f \frac{\delta Q}{T}$$

The integral is path-independent, as entropy is a state function; it depends solely on the initial and final states of the system.

Example:

Heat 10 g of dioxygen from 20 °C to 100 °C at constant pressure. Calculate the corresponding change in entropy.

Given: $C_p(O_2(g)) = 29.26$ J/K.kg.

Solution:

$$\Delta S = S_2 - S_1 = \int \frac{\delta Q}{T} = \int m\, C_p \frac{dT}{T} = m\, C_p\, ln\frac{T_2}{T_1} \Rightarrow \Delta S = 10.10^{-3}.29.26 \ln\frac{100}{20} = 0.47\, J/K$$

a. Reversible transformations ($\delta S_c=0$)**:**

If the transformation takes place reversibly between the initial state (i) and the final state (f), the entropy change is given by:

$\delta S_c=0 \Longrightarrow dS=\delta S_e$

$$\Delta S_{i\to f} = S_f - S_i = \int_i^f dS = \int_i^f \frac{\delta Q_{rev}}{T}$$

$$\Delta S_{i \to f} = \Delta S_{rev} = \int_i^f \frac{\delta Q_{rev}}{T}$$

b. Irreversible or spontaneous transformation at T ($\delta S_c>0$**):**

If the transformation occurs irreversibly from the initial state (i) to the final state (f):

$\delta Sc>0 \Rightarrow dS=\delta S_c+\delta S_e$

$$\Delta S_{i \to f} = S_f - S_i = \int_i^f dS = \int_i^f \delta S_c + \delta S_e \qquad > 0$$

$$\Delta S_{i \to f} = \int_i^f \delta S_e \qquad \delta S_e = \frac{\delta Q_{irrev}}{T}$$

Therefore, according to the Clausius inequality:

$$\Delta S_{i \to f} > \int_i^f \frac{\delta Q_{irrev}}{T}$$

Increase in disorder $\Delta S>0 \Rightarrow$Increase in disorder

Decrease in disorder $\Delta S<0 \Rightarrow$Decrease in disorder

IV.4 Entropy change of an isolated system

An isolated system does not exchange heat or work with the surroundings.

$\delta Q=0 \Rightarrow$Reversible transformation$\Rightarrow$ $\delta S_{int}=0$ et $dS = \delta S_e=0$.

$\delta W=0$ Irreversible transformation $\Rightarrow \delta S_{int}>0$ and $dS>0$.

The Universe = system + surroundings (The Universe is an isolated system)

Applying the previous relation: If the isolated system evolves irreversibly between A and B:

$$\Delta S = S_B - S_A > \int_A^B \frac{\delta Q_{irrev}}{T}, \ \delta Q_{irrev} = 0 \Rightarrow \Delta S > 0 \Rightarrow \quad S_B > S_A$$

If the isolated system evolves reversibly between A and B:

$$\Delta S = S_B - S_A > \int_A^B \frac{\delta Q_{rev}}{T}, \ \delta Q_{rev} = 0 \Rightarrow \Delta S = 0 \Rightarrow \quad S_B = S_A$$

In a reversible transformation, the entropy of an isolated system remains constant.

IV.5 Calculation of entropy variations for ideal gases

IV.5.1 Isobaric Transformation

The entropy change of an ideal gas during a transformation at constant pressure is given by:

$$\delta Q_p = nC_p dT = dH$$

$$dS = \frac{Q_{rev}}{T} = nC_p \frac{dT}{T} \Longrightarrow \Delta S = n \int_{T1}^{T2} C_p \frac{dT}{T}$$

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

IV.5.2 Isochoric Transformation

$$\delta Q_{rev} = nC_v dT = dU$$

$$dS = \frac{Q_{rev}}{T} = nC_v \frac{dT}{T} \Longrightarrow \Delta S = n \int_{T1}^{T2} C_v \frac{dT}{T}$$

And the entropy change becomes:

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

IV.5.3 Isothermal Transformation

The entropy change of an ideal gas during a transformation at constant temperature is given by:

$$dU = 0 \Longrightarrow \delta Q = -\delta W$$

$$dS = \frac{\delta Q}{T} = -\frac{\delta W}{T} = \frac{PdV}{T}$$

$$dS = nR \frac{dV}{V} \Longrightarrow \Delta S = nR \int_{V1}^{V2} \frac{dV}{V}$$

And the entropy change becomes:

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

The entropy change of a system depends solely on its initial and final states and is independent of the path taken during the transformation, as entropy is a state function. The change in entropy can be determined using one of the following three expressions:

IV.5.4 Entropy of an Ideal Gas as a Function of Variables (T, V)

$$dU = \partial W + \partial Q = \partial Q - P\,dV$$

$$dS = \frac{\partial Q}{T} \Longrightarrow \partial Q = T\,dS$$

$$dU = T\,dS - P\,dV$$

$$T\,dS = dU + P\,dV$$

$$dS = \frac{(dU + P\,dV)}{T}$$

$$dS = \frac{dU}{T} + \frac{P}{T}\,dV$$

$$dS = n\,C_V\,\frac{dT}{T} + \frac{nR}{V}dV$$

$$\varDelta S = n\,C_V \int_{T1}^{T2} \frac{dT}{T} + nR \int_{V1}^{V2} \frac{dV}{V}$$

$$\varDelta S = n\,C_V \ln\frac{T_2}{T_1} + nR\,\ln\frac{V_2}{V_1}$$

IV.5.5 Entropy of an Ideal Gas as a Function of Variables (T, P)

dH = dU + Δ(PV)

dU = ∂W + ∂Q = ∂Q - P dV = T dS - P dV

dH = T dS - P dV + V dP + P dV

dH = T dS + V dP

$$dS = \frac{dH + V\,dP}{T} = n\,C_p\,\frac{dT}{T} - nR\frac{dP}{P}$$

$$\varDelta S = n\,C_p \int_{T1}^{T2} \frac{dT}{T} + nR \int_{P1}^{P2} \frac{dP}{P}$$

$$\varDelta S = n\,C_P \ln\frac{T_2}{T_1} + nR\,\ln\frac{P_2}{P_1}$$

IV.5.6 Entropy of an Ideal Gas as a Function of Variables (P, V)

PV = nRT

P dV + V dP = nR dT

$$dT = \frac{P}{nR}\,dV + \frac{V}{nR}\,dP$$

$$\frac{dT}{T} = \frac{P}{nRT}dV + \frac{V}{nRT}dP$$

$$\frac{dT}{T} = \frac{dV}{V} + \frac{dP}{P}$$

$$dS = n\,C_P\,\frac{dV}{V} + n\,C_V\,\frac{dP}{P}$$

$$\Delta S = n\,C_P \int_{V1}^{V2} \frac{dV}{V} + n\,C_V \int_{P1}^{P2} \frac{dP}{P}$$

$$\Delta S = n\,C_P\,ln\frac{V2}{V1} + n\,C_V\,ln\frac{P2}{P1}$$

IV.5.7 Adiabatic Transformation

a. Reversible Adiabatic Transformation

If the transformation is a reversible adiabatic process, we can write throughout the process:

$$\Delta S_{sys} = \Delta S_c + \Delta S_e$$

No heat exchange with the surroundings: Q=0; Reversible transformation:

$\Delta S_e = 0$

$\Delta S_c = 0$

$\Delta S_{sys} = 0$

b. Irreversible Adiabatic Transformation

There is no heat exchange with the surroundings, i.e., Q=0.

$\Delta S_e = 0$

$\Delta S_c \neq 0$

$\Delta S_{sys} = \Delta S_c$

Although entropy is a state function meaning its change depends only on the initial and final states the entropy variation differs between reversible and irreversible adiabatic transformations. The appropriate expression for calculating the entropy change can be selected from the three previously introduced formulations.

IV.5.8 Entropy Change in a Mixture of Two Ideal Gases

Consider an ideal gas A characterized by P_A, T_A, and V_A, and an ideal gas B characterized by P_B, T_B, and V_B. Let n_A and n_B be the number of moles of each. The mixture of the two gases is characterized by P_m, T_m, and V_m. The entropy change of the mixture is expressed as:

$\Delta S = \Delta S_A + \Delta S_B$

Example:

Calculate ΔS of the system in each case. We mix 600g of oil at 76 °C with 1260 g of oil at 13 °C. We consider it to be an isolated system,

Given :

$C_{poil} = 2.1$ J/K.g

Solution:

$$\sum Q_i = 0 \Longrightarrow Q_1 + Q_2 = 0$$

$$m_1 c_O (T_{eq} - T_1) + m_2 c_O (T_{eq} - T_2) = 0 \Longrightarrow T_{eq} = 306.32K$$

$$\Delta S_{sys} = \Delta S_1 + \Delta S_2 = m_1 c_O \int_{T1}^{Teq} dT + m_2 c_O \int_{T2}^{Teq} dT$$

$$\Delta S_{sys} = m_1 c_O \ln \frac{Teq}{T1} + m_2 c_O \ln \frac{Teq}{T2}$$

$$\Delta S_{sys} = 600.2\, x1x \ln \frac{306.32}{349} + 1260.2\, x1x \ln \frac{306.32}{286} = 17.26\, J/K$$

IV.6 Entropy change during phase transitions

A phase transition in a pure substance is a reversible process that takes place at constant temperature and pressure. During this transformation, the heat exchanged with the surroundings per mole of substance at temperature T is referred to as the latent heat of the phase change, and is denoted by L or by the enthalpy change ΔH.

$$\Delta S = \frac{\Delta H}{T}$$

With:

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

T: Temperature of the phase change.

Phase Changes:

Fusion: Solid → Liquid

Solidification: Liquid →Solid

Sublimation: Solid → Gas

Condensation: Gas →Solid

Vaporization: Liquid →Gas

Liquefaction: Gas → Liquid

Example:

Calculate the entropy change associated with the vaporization of one mole of solid iodine, initially at T_1=25 °C, as it transitions to the gaseous phase at T_2=200 °C, under a pressure of 1 atm.

Data:

$Cp(I_2)s = 54.6\ J.mol^{-1}.K^{-1}$;

$Cp(I_2)l = 81.5\ J.mol^{-1}.K^{-1}$;

$Cp(I_2)g = 93.2\ J.mol^{-1}.K^{-1}$;

$\Delta Hfus$=15.633 kJ/mol ;

$\Delta Hvap$= 25.498 kJ/mol ;

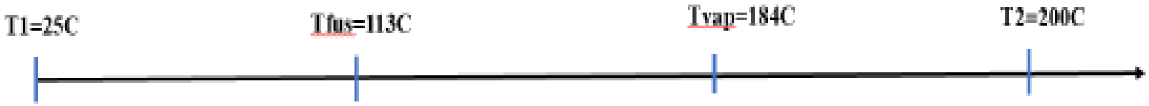
Temperature of iodine fusion T_{fus}=113.6 °C.

Temperature of iodine vaporization T_{vap}=184 °C.

Solution:

According to the exercise statement, iodine changes from the solid state at 25 °C, then it changes to the liquid state at 113.6 °C, and finally, it changes to the gas state at 184 °C.

To better understand these changes, let's draw the temperature scale. The process involves five states based on the diagram provided:



According to this diagram, we observe that there are 5 states. Therefore:

$$S_T = \int_{T1}^{Tfus} nC_{p\,(S)}\frac{dT}{T} + n\frac{\Delta H_{fus}}{T_{fus}} + \int_{Tfus}^{Tvap} nC_{p\,(l)}\frac{dT}{T} + n\frac{\Delta H_{vap}}{T_{vap}} + \int_{Tvap}^{T2} nC_{p\,(g)}\frac{dT}{T}$$

$$S_T = nC_{p\,(I_2,S)}\ln\frac{T_{fus}}{T_1} + n\frac{\Delta H_{fus}}{T_{fus}} + nC_{p\,(I_2,l)}\ln\frac{T_{vap}}{T_{fus}} + n\frac{\Delta H_{vap}}{T_{vap}} + nC_{p\,(I_2,g)}\ln\frac{T_2}{T_{vap}}$$

$$S_T = 54.6\ln\frac{113}{25} + \frac{15633}{113} + 81.5\ln\frac{184}{113} + \frac{25498}{184} + 9302\ln\frac{200}{184} = 406.79\,J/K$$

IV.7 Entropy of a chemical reaction

Consider a chemical reaction taking place under conditions of constant temperature and pressure:

$\upsilon_A A + \upsilon_B B \rightarrow \upsilon_C C + \upsilon_D D$

$$\Delta S_R = \sum v_i S_p - \sum v_i S_r$$

For the previous reaction, we have:

$\Delta S_R = v_C S(C) + v_D S(D) - v_A S(A) - v_B S(B)$.

Under standard conditions at T=298K:

$$\Delta S^{\circ}_{298} = \sum v_i S^{\circ}_{i(298)}\,(P) - \sum v_j S^{\circ}_{j(298)}\,(R)$$

Example:

Calculate the standard entropy change of the following reaction (formation of water) at 298K:

$H_2\,(g) + ½\,O_2\,(g) \rightarrow H_20\,(l)$

Given:

S°_{298} ($H_2$0(l)) = 45.1 cal/K ;

S°_{298} (H_2(g)) = 31.2 cal/K,

S°_{298} (O_2(g)) = 49 cal/K.

Solution:

$$\Delta S^{\circ}_{298} = (\Delta S^{\circ}_{298\,(H2O)}) - \left((\Delta S^{\circ}_{298\,(H2)}) + \frac{1}{2}(\Delta S^{\circ}_{298\,(O2)})\right)$$

$$\Delta S^{\circ}_{298} = 45.1 - \left(31.2 + \frac{1}{2}\,49\right) = -10.6\,cal/K$$

For the formation reaction of a compound AB from its constituent elements A and B, the standard entropy change of formation ΔS$_f$° can be calculated using the following expression:

$$\Delta S^{\circ}_{f,298}(AB) = \Delta S^{\circ}_{f,298}(AB) - \Delta S^{\circ}_{f,298}(A) - \Delta S^{\circ}_{f,298}(B)$$

Entropy Change of a Reaction with Temperature ΔS_R°

Consider a chemical reaction proceeding under constant pressure conditions:

$$\upsilon_A\,A + \upsilon_B\,B \xrightarrow{\Delta S^{\circ}_R} \upsilon_C\,C + \upsilon_D\,D$$

By knowing ΔS_{298}° of this reaction, we can determine Δ S_R° using the Kirchhoff relation:

$$\Delta S^{\circ}_T = S^{\circ}_{298} + \int_{298}^{T} \Delta n\,C_p \frac{dT}{T} \qquad P = cst$$

$$\Delta n\,C_p = \sum n\,C_p\,(P) - \sum n\,C_p\,(R)$$

When the reaction takes place at constant volume, the Kirchhoff equation takes the following form:

$$\Delta S^{\circ}_T = S^{\circ}_{298} + \int_{298}^{T} \Delta n\,C_V \frac{dT}{T} \qquad V = cst$$

$$\Delta n\,C_V = \sum n\,C_V\,(P) - \sum n\,C_V\,(R)$$

Note:

These relations are valid for a temperature change without a phase change.

When the system undergoes a phase transition, the entropies associated with the phase changes must be taken into account.

Example:

Consider the reaction:

$3\ C_2H_2\ (g) \rightarrow C_6H_6\ (g)$

Calculate S°_{298} and S°_{773} for this reaction.

Given at 25 °C:

S°_{298} (C_2H_2 (g)) = 48 cal/mol.K et S°_{298} (C_6H_6 (g)) = 64.4 cal/mol.K.

Cp (C_2H_2 (g)) = 10.5 cal/mol.K et Cp (C_6H_6 (g)) = 19.54 cal/mol.K.

Solution:

$$\Delta S^{\circ}_{298} = \sum \upsilon_i S^{\circ}_{i(298)}\,(P) - \sum \upsilon_j S^{\circ}_{j(298)}\,(R)$$

$$\Delta S^{\circ}_{298} = \Delta S^{\circ}_{298}\,(C_6H_{6\,(g)}) - 3\,\Delta S^{\circ}_{298}(C_6H_{2\,(g)}) = 64.4 - 3x\ 48 = -79.6\ cal/K$$

$$\Delta S^{\circ}_{773} = S^{\circ}_{298} + \int_{298}^{773} \Delta n\ C_p \frac{dT}{T} = S^{\circ}_{298} + \Delta n\ C_p \ln\frac{773}{298}$$

$$\Delta C_p = C_p\big(C_6H_{6\,(g)}\big) - 3\ C_p\big(C_6H_{2\,(g)}\big) = 19.54 - 3x\ 10.51 = -11.99\ cal/K$$

$$\Delta S^{\circ}_{773} = -79.6 - 11.99\ \ln\frac{773}{298} = -91.03\ cal/K$$

IV.8 Carnot Cycle (Ideal Engine)

A Carnot cycle is defined as a reversible diathermal cycle consisting of:

Two isothermal transformations, each carried out in thermal contact with a heat reservoir.

Transformation AB: Isothermal at temperature T_1.

Transformation CD: Isothermal at temperature T_2.

Two Adiabatic Transformations: These allow the system to move from one heat source to another.

Transformation BC: Adiabatic from T_1 to T_2.

Transformation DA: Adiabatic from T_2 to T_1.

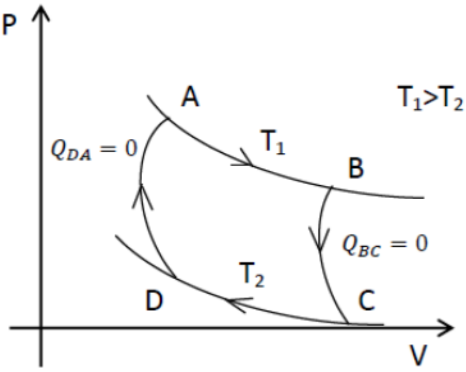


Figure IV.2: Carnot Cycle.

In summary, the Carnot cycle comprises alternating isothermal and adiabatic transformations, involving two heat reservoirs at distinct temperatures T_1 and T_2.

This cycle is diathermal allowing heat exchange and fully reversible, making it an idealized model of a heat engine.

The Carnot cycle serves as a reference standard for assessing the maximum theoretical efficiency of real heat engines.

IV.8.1 Heat Exchange Balance

AB Isothermal Expansion

During this transformation, the change in internal energy is zero, so:

$$Q = -W_{A-B} = nRT \ln \frac{V_B}{V_A}$$

CD Isothermal Compression

Likewise, for this transformation, the variation in internal energy is equal to zero.

$$= -W_{C-D} = nRT \ln \frac{V_D}{V_C}$$

Over the course of the complete cycle, the change in internal energy is zero, in accordance with the first law of thermodynamics. Consequently, the work produced by the cycle is equal in magnitude but opposite in sign to the net heat exchanged during the cycle.

$$W_{Cycle} = -Q_{Cycle} = -(Q_C + Q_h)$$

$$W_{Cycle} = -nRT_h \ln \frac{V_B}{V_A} + nRT_C \ln \frac{V_C}{V_D}$$

To simplify this expression, the property that V_B and V_C are two states of an adiabatic transformation is used. (The same applies to V_A and V_D) For adiabatic transformations, we have:

$$T_{ch}V_B^{\gamma-1} = T_{fr}V_C^{\gamma-1} = cst$$

$$T_{ch}V_A^{\gamma-1} = T_{fr}V_D^{\gamma-1} = cst$$

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

And since these are two adiabatic transformations between the same temperatures, we have:

$$\frac{Q_c}{T_c} + \frac{Q_h}{T} = 0$$

$$\frac{Q_c}{T_c} = \frac{Q_h}{T_h}$$

This is the **Clausius relation** for a reversible bi-thermal cycle. In this cycle, the system undergoes a reversible transformation, exchanging heat Q_h with a hot reservoir at temperature T_h and heat Q_c with a cold reservoir at temperature T_c.
This relation can be generalized to any reversible cycle involving an ideal gas:

$$\sum \frac{Q_i}{T_i}$$

This relation is the differential expression of the second law of thermodynamics.

Note:

The cycle is described in the ABCD direction; it is an engine, and the system provides work. If the cycle is described in the opposite direction, the system receives work, making it a receiver (refrigeration machine or heat pump).

Expression of Efficiencies

The efficiency of a reversible heat engine is given by:

$$\eta_{cycle} = \frac{Energie_{\,P}}{Energie_C} = \frac{W_{cycle}}{Q_R} = 1 - \frac{T_c}{T_h}$$

The efficiency of a reversible heat engine depends solely on the temperatures of the cold and hot reservoirs, T_c and T_h , and is independent of the working substance.
The resulting expression defines the theoretical upper limit of thermal efficiency, commonly referred to as the Carnot efficiency.

In contrast, the efficiency of irreversible (real) engines is always lower than that of a reversible engine operating between the same two temperatures, this fundamental result is known as Carnot's theorem.

Accordingly, for an irreversible diathermal engine:

$$\eta_{irrev} < 1 - \frac{T_c}{T_h}$$

Exercise of application:

1. We consider a steam engine operating between two temperature levels: T_1=550 °C and T_2=250 °C.
2. Recall the definition of the thermal efficiency η of a heat engine.
3. Express η as a function of the heat quantities Q_1 and Q_2, which represent the heat exchanged by the working fluid with the hot and cold reservoirs at temperatures T_1 and T_2, respectively.

4. Give the expression of this efficiency in the case of a reversible two-reservoir (diathermal) cycle, as a function of the given temperatures.

In practice, such an engine will operate at 70% of this maximum efficiency. What is its numerical value?

Solution:

1. Recall the definition of the thermal efficiency η of heat engines

The thermal efficiency η of a heat engine is defined as the ratio of the work produced by the engine to the amount of heat energy Q_1 absorbed from the hot reservoir:

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

Since $W = Q_1 - Q_2$, where Q_2 is the heat rejected to the cold reservoir, we can also write:

$$\eta = \frac{Q_1 - Q_2}{Q1} = 1 - \frac{Q_2}{Q_1}$$

2. Express η as a function of the quantities of heat Q_1 and Q_2 exchanged

As just shown:

$$\eta = 1 - \frac{Q_2}{Q_1}$$

Where:

Q_1 is the heat absorbed from the hot reservoir at temperature T_1

Q_2 is the heat rejected to the cold reservoir at temperature T_2

3. Expression of efficiency in the case of a reversible (Carnot) cycle

For a reversible heat engine, such as the Carnot engine, the thermal efficiency depends solely on the absolute temperatures of the hot and cold reservoirs (in Kelvin) and is given by:

$$\eta_{rev} = 1 - \frac{T_2}{T_1}$$

where T_1 and T_2 must be in Kelvin.

Given:

T_1 = 550= 550 + 273.15 = 823.15 K.

T_2 = 250 = 250 + 273.15 = 523.15 K.

So,

$$\eta rev = 1 - \frac{523.15}{823.15} \approx 1 - 0.6354 \approx 0.3646$$

So the maximum theoretical efficiency is about:

$$\eta_{rev} \approx 36.46\%$$

3. Practical Efficiency (70% of maximum)

Now, if the actual engine works at 70% of the Carnot efficiency:

$$\eta_{actual} = 0.70 \times \eta_{rev} = 0.70 \times 0.3646 \approx 0.2552$$

So the actual efficiency is approximately:

$$\eta_{actual} \approx 25.52\%$$

Practical case studies

- **Refrigeration / Heat pumps (practical Clausius/Kelvin use):** analyze why work must be supplied to move heat from cold to hot and estimate COP vs. Carnot limit.
- **Steam turbine / power-plant case study:** compute Carnot limit between boiler and condenser temperatures and compare to typical plant efficiency (explain irreversibilities: friction, heat losses, non-ideal expansions).
- **Entropy change in mixing gases (industrial separation):** show why spontaneous mixing increases entropy and estimate entropy of mixing for ideal gases.
- **Battery/fuel cell vs. combustion:** contrast chemical reaction spontaneity (ΔG) and entropy changes to explain why combustion releases usable work but the reverse needs energy input.
- **Phase-change thermal storage:** compute entropy and heat flows for charging/discharging a latent-heat storage (e.g., molten salt) at fixed T.

Self-assessment quizzes

1- Multiple Choice

1. For a reversible heat transfer at temperature T, the infinitesimal entropy change is:

   A) $dS=\frac{\delta Q}{T}$ (if δQ is reversible);

   B) $dS=\frac{\delta Q}{T_{env}}$;

   C) $dS=\delta Q$;

   D) $dS=0$.

2. The Clausius statement of the second law says:

   A) Heat cannot flow spontaneously from cold to hot without work;

   B) Energy is conserved;

   C) Entropy always decreases;

   D) All heat can be converted to work.

3. For an isolated system undergoing an irreversible change, the entropy change of the system is:

   A) $=0$;

   B) <0;

   C) >0;

   D) undefined.

2- True / False

A reversible adiabatic process has $\Delta S_{system}=0$.

The Carnot efficiency $1-\frac{T_c}{T_h}$ can be exceeded by clever engineering.

3- Short answer items

Briefly explain why mixing two ideal gases at the same T and P increases entropy.

Write the expression for ΔS for heating n moles of an ideal gas at constant pressure from T_1 to T_2.

In one sentence, state why $\Delta S_{total} \geq 0$ is equivalent to "processes have a preferred direction".

Recap & essential formulas

- Entropy for common ideal-gas processes:

  Isobaric: $\Delta S = nC_p \ln\frac{T_2}{T_1}$;

  Isochoric $\Delta S = nC_v \ln\frac{T_2}{T_1}$;

  Isothermal (ideal gas): $\Delta S = nR \ln\frac{V_2}{V_1}$.
- Entropy of phase change (reversible at Ttrans): $\Delta S=\frac{\Delta H_{trans}}{T_{trans}}$

  (fusion, vaporization, sublimation).
- Carnot efficiency (reversible heat engine between T_h and T_c):

$$\eta_{cycle} = \frac{Energie_{\,P}}{Energie_C} = \frac{W_{cycle}}{Q_R} = 1 - \frac{T_c}{T_h}$$

- For an isolated system: $\Delta S \geq 0$; equality only for reversible processes.
- Reversible processes do not create entropy: $\Delta S_{created}=0$. Irreversible processes create entropy: $\Delta S_{created}>0$.
- Use $dS=\delta Q_{rev}/T$, even if the real process is irreversible, compute ΔS by integrating along any convenient reversible path between the same end states.

Corrected Exercises

Exercise 1:

Consider the decomposition reaction of $CaCO_3$ (s):

$$\mathbf{CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)}$$

1. Calculate the standard enthalpy of this reaction.
2. Determine the thermodynamic nature of this reaction.
3. Can the direction of this reaction's evolution be predicted based on the value of $\Delta H°_{R,298}$?
4. Calculate the standard entropy $\Delta S°_{R,298}$ of this reaction.

	$CaCO_3$ (s)	**CaO (s)**	**CO_2 (g)**
$\Delta H_{f,298}$ (kJ/mol)	-1210.11	-393.14	-634.11
$S_{f,298}$ (J/K.mol)	92.80	213.60	39.71

Exercise 2:

Calculate $S°_R$ at **25 °C** and **187 °C** for the reaction:

$$\mathbf{2\ SO_2\,(g) + O_2\,(g) \longrightarrow 2\ SO_3\,(g)}$$

Species	**C_p ($J.mol^{-1}.K^{-1}$)**	**$S°_{298\,K}$ ($cal.mol^{-1}.K^{-1}$)**
O_2 (g)	29.36	49.00
SO_2 (g)	39.79	59.30
SO_3 (g)	50.63	61.34

Exercise 3:

1. One kilogram of ice at **−5 °C** is taken out of a freezer and placed in a room at **25 °C**, where it reaches thermal equilibrium.

Calculate the **entropy created** during the entire process.

Given: $\Delta H°_{fusion}$ (H_2O, s) = 334 J/g

The specific heat capacities are: Cp (H_2O, l) = 18 J/g.K; Cp (H_2O, s) = 9 J/g.K.

2. a. Two moles of an ideal gas expand isothermally and irreversibly from 30 L to 50 L. Calculate the entropy change of the gas.

b. Calculate the entropy created.

3. Same question as **2-a**, but the expansion is reversible and no longer isothermal, with the temperature changing from 300K to 290K. **Data**: C_v = 5 cal/mol.K.

Exercise 4:

1. Determine the standard molar entropy of water vapor at 127 °C (400 K). Consider the phase transitions and specific heat capacities of water in all phases.

Data:

Specific heat capacities:

C_p (H_2O, s) = 36.4 J/mol.K ;

C_p (H_2O, l) = 75.3 J/K.mol ;

C_p (H_2O, g) = 33.6 J/mol.K;

Enthalpies of phase change:

L_{fus} (H_2O, s) = 6.02 kJ/mol at 0 °C et L_{vap} (H_2O, l) = 40.7 kJ/mol at 100 °C.

2. Calculate the standard entropy change (ΔS°) of the following reaction at 298 K:

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightarrow H_20\,(l)$$

Data:

S^0_{298} ($H_20_{(l)}$) = 45.1 cal/K ;

S^0_{298} ($H_{2(g)}$) = 31.2 cal/K ;

S^0_{298} ($O_{2(g)}$) = 49 cal/K.

Exercise 5:

Consider the reaction:

$3\,C_2H_{2\,(g)} \rightarrow C_6H_{6\,(g)}$

Calculate ΔS^0_{298} et ΔS^0_{773} for this reaction.

Given at 25 °C:

S^0_{298} ($C_2H_{2\,(g)}$) = 48 cal/mol.K et S^0_{298} ($C_6H_{6\,(g)}$) = 64.4 cal/mol.K ;

C_p ($C_2H_{2\,(g)}$) = 10,5 cal/mol.°C et C_p ($C_6H_{6\,(g)}$) = 19.54 cal/mol.°C.

Correction

Exercise 1:

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

1.Calculate the standard enthalpy of reaction $\Delta H°_{r,298}$

$$\Delta H^{\circ}_{R,298} = \Sigma\, n_{ip}\, \Delta H^{\circ}_{f,298}\,(\text{products}) - \Sigma\, n_{iR}\, \Delta H^{\circ}_{f,298}\,(\text{reactants})$$

$$\Delta H^{\circ}_{R,298} = 1\,.\Delta H^{\circ}_{f,298}\, CaO\,(s) + 1\,.\Delta H^{\circ}_{f,298}\, CO_2(s) - 1\,.\Delta H^{\circ}_{f,298}\, CaCO_3\,(s)$$

$$\Delta H^{\circ}_{R,298} = +182.86\, kJ$$

2. Determine the thermodynamic nature of this reaction

Since: $\Delta H^{\circ}_{R,298} > 0 \rightarrow$ the reaction **absorbs heat**, the reaction is endothermic.

3. Can we predict the direction of the reaction based on $\Delta H^{\circ}_{R,298}$?

No, the direction cannot be predicted using only $\Delta H^{\circ}_{R,298}$.

4. Calculate the standard entropy change $\Delta S^{\circ}_{R,298}$

$$\Delta S^{\circ}_{298} = \sum v_i S^{\circ}_{i(298)}\,(P) - \sum v_j S^{\circ}_{j(298)}\,(R)$$

$$\Delta S^{\circ}_{R,298} = 1\,.\Delta S^{\circ}_{f,298}\,CaO\,(s) + 1\,.\Delta S^{\circ}_{f,298}\,CO_2(s) - 1\,.\Delta S^{\circ}_{f,298}\,CaCO_3\,(s)$$

$$\Delta S^{\circ}_{R,298} = 160\,J/K$$

Exercise 2:

2 SO$_2$ (g) + O$_2$ (g) $\longrightarrow$ 2 SO$_3$ (g)

$$\Delta S^{\circ}_{298} = \sum v_i S^{\circ}_{i(298)}\,(P) - \sum v_j S^{\circ}_{j(298)}\,(R)$$

$$\Delta S^{\circ}_{R,298} = 2\,.\Delta S^{\circ}_{f,298}\,SO_3 - 1\,.\Delta S^{\circ}_{f,298}\,O_2 - 2\,.\Delta S^{\circ}_{f,298}\,SO_2 = 2.61.34 - 49 - 2\,.59.3$$

$$\Delta S^{\circ}_{R,298} = -44\,.92\,cal/K$$

$$S^{\circ}_{R}(T) = S^{\circ}_{298} + \int_{298}^{T} \Delta C_p \frac{dT}{T} = S^{\circ}_{298} + \Delta C_p \ln\frac{T}{298}$$

$$\Delta C_p = 2\,.C_p\,SO_3 - 1\,.C_p\,O_2 - 2\,.C_p\,SO_2 = 2\,.50.63 - 29.36 - 2\,.39.79$$

$$\Delta C_p = -7.68\,J/K = -1.83\,cal/K$$

$$S^{\circ}_{R}(460) = S^{\circ}_{298} + \Delta C_p \ln\frac{460}{298} = -44.92 - 1.83\ \ln\frac{460}{298} = -45.71\,cal/k$$

Exercise 3:

1. Entropy created when 1 kg of ice at –5 °C is brought to 25 °C

$$\begin{array}{ccccccc} \mathbf{(H_2O,\,s)} & \xrightarrow[\Delta H_1^{\circ},\,\Delta S_1^{\circ}]{} & \mathbf{(H_2O,\,s)} & \xrightarrow[\Delta H_2^{\circ},\,\Delta S_2^{\circ}]{} & \mathbf{(H_2O,\,l)} & \xrightarrow{\Delta H_3^{\circ},\,\Delta S_3^{\circ}} & \mathbf{(H_2O,\,l)} \\ \mathbf{268\ K} & & \mathbf{273\ K} & & \mathbf{273\ K} & & \mathbf{298\ K} \end{array}$$

The change in the entropy of the system is: ΔS° système = ΔS°$_1$ + ΔS°$_2$ + ΔS°$_3$

$$\Delta S^{\circ}_1 = m\,Cp\,(H_2O,s) \int_{268}^{273} \frac{dT}{T} = 1000\,.9.\ln\frac{273}{268} = 166.36\ J/K$$

$$\Delta S^{\circ}_2 = m\,\frac{\Delta H^{\circ}_{fusion}(H_2O,s)}{T_{fusion}} = 1000\,\left(\frac{334}{273}\right) = 1223.44\,J/K$$

$$\Delta S^{\circ}_3 = m\,Cp\,(H_2O,l) \int_{273}^{298} \frac{dT}{T} = 1000\,.18.\ln\frac{298}{273} = 1577.20\ J/K$$

ΔS° système = ΔS°$_1$ + ΔS°$_2$ + ΔS°$_3$ = 166.36+1223.44+1577.20 = **2967 J/K**

S° exchanged = Q/ T = ∑Qi /T   T = cst = 298K (Room temperature: heat source)

$Q_1 = \Delta H_1^{\circ}$ = mCp (H_2O,s) ΔT = 1000.9. (273 –268) = 45. 10^3 J

$Q_2 = \Delta H_2^{\circ}$ = m ΔH°$_{\text{fusion}}$,273 (H_2O,s) = 1000.334 = 334. 10^3 J

$Q_3 = \Delta H_3^{\circ}$ = m Cp (H_2O,l) ΔT = 1000.18 (298 –273) = 450.10^3 J

∑ Qi =Q_1+ Q_2+ Q_3 = $\Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ}$ = 829.10^3 J

ΔS° exchanged = ∑Qi /T = 829.10^3 /298 = **2782 J/K**

ΔS° created = ΔS system - ΔS exchanged = 2967 – 2782 = **185 J/K**

2-a. Entropy change for 2 mol of ideal gas expanding from 30 to 50 L (T = const)

$$\Delta S = nR\, ln\frac{V_f}{V_i} = 2\,.\,8.314\; ln\frac{50}{30} = 8.5\, J/K$$

2-b. Entropy created (irreversible expansion)

In an irreversible isothermal expansion, entropy change of the gas is as above, and entropy of surroundings does not decrease correspondingly (because no reversible heat transfer occurs).

So: $\Delta S_{\text{created}}$=8.50 J/K

3. Reversible, non-isothermal expansion from 30 to 50 L and T = 300K → 290K

$$\Delta S = nCv\; ln\frac{T_2}{T_1} + nR\; ln\frac{V_2}{1} = 2\,.\,20.92\; ln\frac{290}{300} + \;2\,.\,8.314\; ln\frac{50}{30} = 7.08\, J/K$$

Exercise 4:

1. The standard molar entropy of water at 127 °C.

$$S_{400} = \int_0^{273} \frac{C_p\;(s)dT}{T} + \frac{\Delta H_{fus}}{T_{fus}} + \int_{273}^{373} \frac{C_p\;(l)dT}{T} + \frac{\Delta H_{ebu}}{T_{ebu}} + \int_{373}^{400} \frac{C_p\;(g)dT}{T}$$

$$S_{400} = \; C_p(s)ln273 + \frac{\Delta H_{fus}}{273} + \; C_p\;(l)\ln\frac{373}{273} + \frac{\Delta H_{ebu}}{373} + \; C_p\;(g)\ln\frac{400}{373}$$

$$S_{400} = \; 36.4ln273 + \frac{6.02\;10^3}{273} + \;75.3\ln\frac{373}{273} + \frac{40.7\;10^3}{373} + \;33.6\;\ln\frac{400}{373}$$

$$S_{400} = 361.19\, J/K$$

2. The standard entropy change of the reaction (formation of water) at 298 K:

H_2 (g) + ½ O_2 (g)→ $H_2$0 (l)

$$\Delta S_{298}^{\circ} = \sum v_i S_{i(298)}^{\circ}\,(P) - \sum v_j S_{j(298)}^{\circ}\,(R)$$

$$\Delta S_{R,298}^{\circ} = \; S_{298}^{\circ}\, H_2O - \; S_{298}^{\circ}\, H_2 - \frac{1}{2}\Delta_{298}^{\circ}\, O_2 = 45.1 - 31.2 - \;\frac{1}{2}\;49 = \;-10.6\, cal/K$$

Exercise 5:

3 C_2H_2 $_{(g)}$ → C_6H_6 $_{(g)}$

$$\Delta S_{298}^{\circ} = \sum v_i S_{i(298)}^{\circ}\,(P) - \sum v_j S_{j(298)}^{\circ}\,(R)$$

$$\Delta \overset{\circ}{S}_{R,298} = \overset{\circ}{S}_{298}\, C_6H_6 - \ 3.\overset{\circ}{S}_{298}\, C_2H_2 = 64.4 - 3\,.48 = \ -79.\, cal/K$$

$$\Delta \overset{\circ}{S}_R(773) = \Delta \overset{\circ}{S}_{298} + \int_{298}^{T} \Delta C_p \frac{dT}{T} = \ S\overset{\circ}{\Delta}_{298} + \Delta C_p \ln \frac{773}{298}$$

$$\Delta Cp = \ Cp\ C_6H_6 - 3.\ Cp\ C_2H_2 = 19.54 - 3.10.51 = \ -11.99\ cal/K$$

$$\Delta \overset{\circ}{S}_R(773) = \ -79.6 - 11.99 \ln \frac{773}{298} = \ -91.03\ cal/k$$

Non-corrected problems for personal practice

1. Heating an ideal gas (isobaric): 2 mol of an ideal gas (constant Cp=29.1 $J.mol^{-1}.K^{-1}$) is heated at constant pressure from 300 K to 600 K. Calculate ΔS of the gas.
2. Isothermal compression: 1.50 mol of an ideal gas is isothermally compressed from V1 =10 L to =2 L at 350 K. Compute ΔS.
3. Entropy of mixing: 1.0 mol Ar and 2.0 mol Ne (both ideal) at the same T and P are allowed to mix in one container irreversibly. Calculate the entropy of mixing.
4. Carnot engine exercise (design): A heat engine operates between 800 K and 300 K. (a) Compute the maximum theoretical (Carnot) efficiency. (b) If a real plant attains 40% of that maximum, what is its actual efficiency?
5. Irreversibility and entropy generation: A body at 600 K transfers heat 5.0 kJ to a reservoir at 300 K irreversibly. Compute the entropy change of the hot body, of the reservoir, and of the universe (entropy produced).
6. Phase change entropy: One mole of ice at 0 °C melts reversibly to water at 0 °C. Given ΔH_{fus}=6.01 $k.J.mol^{-1}$, compute ΔS.
7. Entropy of reaction (data look-up required): Using standard molar entropies at 298 K, calculate $\Delta S_{298}°$ for the reaction: C(graphite)+O_2(g)→CO_2(g).
8. Adiabatic irreversible compression: A gas is irreversibly compressed adiabatically so that its temperature rises from 300 K to 450 K and no heat is exchanged. Explain qualitatively and quantitatively what can be said about ΔS_{system} and $\Delta S_{universe}$.

Chapter V:
Third Law of Thermodynamics

V.1 Introduction

Entropy plays a fundamental role in both thermodynamics and statistical mechanics, serving as a measure of the degree of disorder or randomness within a system. On the microscopic scale, a single macroscopic state may correspond to numerous possible microscopic arrangements the larger this number, the greater the entropy. Absolute entropy represents the total entropy of a system, defined relative to a baseline of zero entropy at absolute zero temperature, in accordance with the third law of thermodynamics. A clear understanding of absolute entropy is crucial for analyzing the spontaneity of chemical and physical processes, assessing energy conversion efficiency, and exploring the limits of molecular organization.

V.2 Microscopic interpretation of entropy

Entropy is related to the concept of molecular disorder.

Entropy S = measure of disorder at the molecular level.

A macroscopic state defined by the variables (P, T, n) corresponds to a very large number of microscopic states Ω, in each of which the molecules have determined positions and velocities.

Boltzmann expresses entropy as: $S = K \ln\Omega$

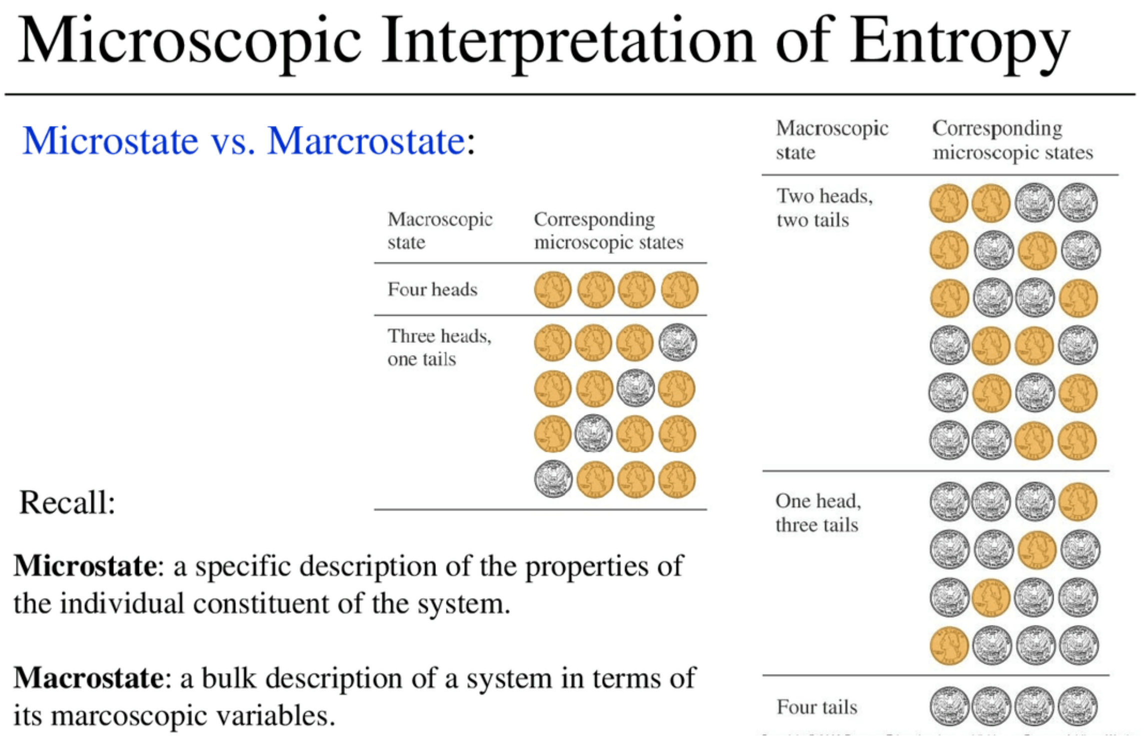
With:

K: Boltzmann constant = $1.38\ 10^{-23}$J/K

Ω: number of microscopic states corresponding to a macroscopic state.

Entropy thus measures molecular disorder.

The second law thus translates as: All isolated systems spontaneously evolve towards a state of maximum molecular disorder.



Microscopic Interpretation of Entropy

Microstate vs. Marcrostate:

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	
Two heads, two tails	
One head, three tails	
Four tails	

Recall:

Microstate: a specific description of the properties of the individual constituent of the system.

Macrostate: a bulk description of a system in terms of its marcoscopic variables.

V.3 Statement of the third principle

At the temperature of absolute zero (T = 0 K), the entropy of any pure substance in the form of a perfect crystal is zero.

$S_0K = 0$ This principle, also called the "Nernst hypothesis," asserts that at 0K, there is perfect order, meaning there is no thermal agitation at this temperature, and the crystal is perfect.

This principle can be justified by the statistical interpretation of entropy.

At absolute zero, every pure substance exists in the solid state in the form of a perfectly ordered crystal without defects. Each atom or molecule forming the crystal lattice is in a perfectly defined and regular position and orientation.

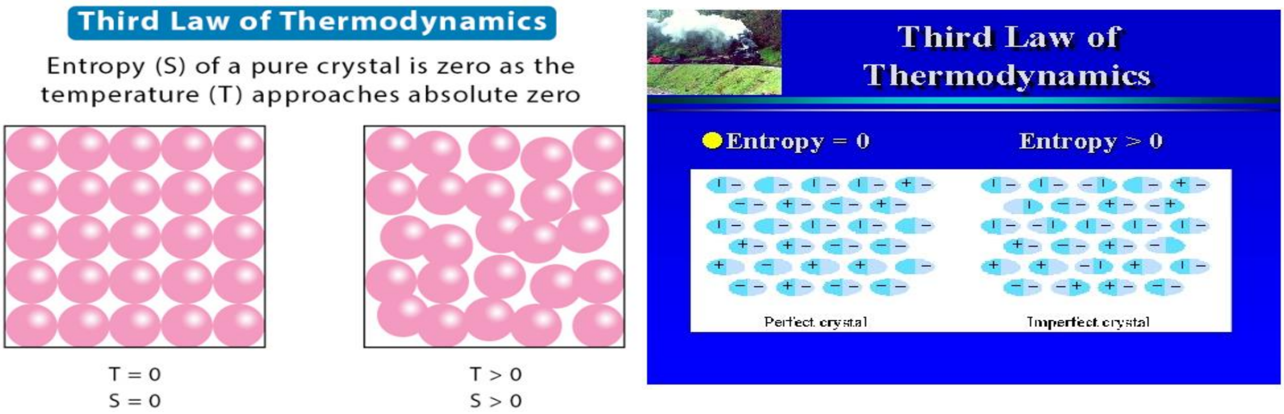


Figure V.1: Third law of thermodynamics.

V.4 Calculation of the absolute molar entropy (standard molar entropy $S°_T$)

We can calculate the entropy of a system at a given temperature, knowing that at the temperature of 0K, the entropy equals zero.

The third principle allows assigning an absolute entropy to any pure substance at temperature T.

At standard conditions, the absolute molar entropy is denoted **$S°_T$.**

The absolute entropy of a pure compound A at temperature T is the variation of its entropy between zero Kelvin and temperature T.

$$0\,K \xrightarrow{\text{solide}} T_f \xrightarrow{\text{liquid}} T_{vap} \xrightarrow{\text{vapor}} T$$

$$\Delta S_{0\to T} = \int_0^T dS = S_T^\circ - S_0 = \int_0^{Tfus} \frac{C_{p\,(S)}dT}{T} + n\,\frac{\Delta H_{fus}}{T_{fus}} + \int_{Tfus}^{Tvap} \frac{C_{p\,(l)}dT}{T} + \frac{\Delta H_{vap}}{T_{vap}} + \int_{Tvap}^{T} \frac{C_{p\,(g)}dT}{T}$$

S_0: Absolute entropy at 0K (S_0=0 by the third principle).

$S°_T$: Absolute entropy at temperature T.

Therefore,

$$S_T^\circ = \int_0^{Tfus} \frac{C_{p\,(S)}dT}{T} + n\,\frac{\Delta H_{fus}}{T_{fus}} + \int_{Tfus}^{Tvap} \frac{C_{p\,(l)}dT}{T} + \frac{\Delta H_{vap}}{T_{vap}} + \int_{Tvap}^{T} \frac{C_{p\,(g)}dT}{T}$$

$S°_T$ can be easily calculated if we know the heat capacities (C_P) and the enthalpies of phase changes. The standard absolute entropies (S°) at T=298 K, P=1 atm, are given in tables.

Example 1:

For water, S°_{liquid} =16.73 cal/mol.K and S°_{solid} =45.1 cal/mol K.

Example 2: with chemical reaction

Calculate the standard entropy of the following reaction (formation of water) at 298 K.

Given:

S°_{298} (H_20) =45.1 *cal /K*

S°_{298} (H_2) =31.2 *cal/K*

S°_{298} (O_2) =49 *cal / K*

Solution:

ΔS°_{298} = (S°_{298} (H_20)) − (S°_{298} (H_2)+12⁄(S°_{298} (O_2)))

ΔS°_{298} = (45.1) − (31.2+12⁄(49))⇒ΔS°_{298} = −10.6 cal/K

Example 3: without chemical reaction

For $CO_2(g)$, calculate S°_{900} :

Given:

Cp = 8.8 cal/mol K and $S^{\circ}_{298} = 51.1$ cal/K.

Solution:

$$dS = n\,\frac{C_p\,dT}{T} \qquad P = cst \;\Rightarrow\; \Delta S = nC_p \ln\frac{T_2}{T_1} \;\Rightarrow\; \Delta S = 1\,x\,1.88\,x \ln\frac{900}{298} = 9.7\;cal/K$$

$$\Delta S = S^{\circ}_{900} - S^{\circ}_{298} \;\Rightarrow S^{\circ}_{900} = \Delta S + S^{\circ}_{298} = 9.7 + 51.1 = 60.8\;cal/K$$

V.5 The standard molar absolute entropy S°_T of a pure substance (solid, liquid, gas)

The standard molar absolute entropy S°_T of a pure substance whether solid, liquid, or gas can be determined as a function of temperature.

It is possible to illustrate this relationship by plotting the variation of entropy with temperature on a diagram.

Since its entropy is zero at zero Kelvin, its absolute value can thus be calculated. Entropy is the only calculable thermodynamic state function.

The third principle, which establishes an origin for entropy, allows assigning an absolute molar entropy to a pure substance at any temperature.

At constant pressure (P=constant):

At 0K, all substances are solids. With an increase in temperature, phase changes occur: melting, vaporization...

These transformations always take place at constant temperature and are accompanied by an increase in entropy.

The absolute molar entropy S°_T of a pure substance at a given temperature T can therefore be calculated by summing all entropy contributions from the reference state at absolute zero (T = 0 K, where S = 0) up to the desired temperature.

V.5.1 Calculation of the absolute entropy of a pure substance in the gaseous state

$S_T = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5$

With:

ΔS_1: change in entropy during the heating of the solid.

ΔS_3: change in entropy during the heating of the liquid.

ΔS_5: change in entropy during the heating of the gas.

$$S_T^{\circ} = \int_{0}^{Tfus} \frac{C_{p\,(S)}dT}{T} + n\,\frac{\Delta H_{fus}}{T_{fus}} + \int_{Tfus}^{Teb} \frac{C_{p\,(l)}dT}{T} + \frac{\Delta H_{eb}}{T_{eb}} + \int_{Teb}^{T} \frac{C_{p\,(g)}dT}{T}$$

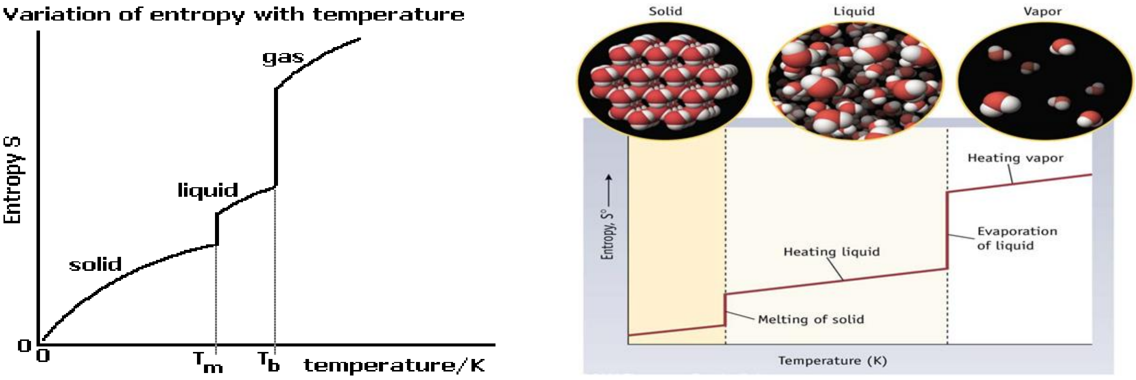


Figure V.2: Entropy vs. Temperature of a Single Substance

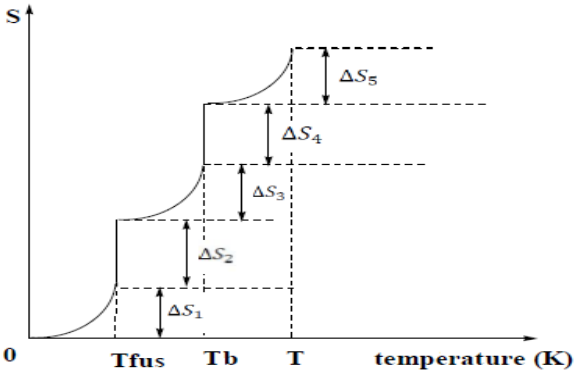


Figure V.3: Variation of entropy with temperature

Exercise of application:

Calculate the standard molar entropy of water at 127 °C.

Given:

Cp (H_2O, s) = 36.4 J/mol.K ;

Cp (H_2O, l) = 75.3 J/mol.K ;

Cp (H_2O, g) = 33.6 J/mol.K.

L_{fus} (H_2O, s) = 6.02 kJ/mol à 0 °C and L_{vap} (H_2O, l) = 40.7 kJ/mol à 100 °C.

$$S_{400}^{\circ} = \int_{0}^{273} \frac{C_{p\,(S)}dT}{T} + n\,\frac{\Delta H_{fus}}{T_{fus}} + \int_{273}^{373} \frac{C_{p\,(l)}dT}{T} + \frac{\Delta H_{eb}}{T_{eb}} + \int_{373}^{400} \frac{C_{p\,(g)}dT}{T}$$

$$S_{400}^{\circ} = C_{p\,(S)} \ln 273 + n\,\frac{\Delta H_{fus}}{273} + C_{p\,(l)} \ln\frac{373}{273} + \frac{\Delta H_{eb}}{373} + C_{p\,(g)} \ln\frac{400}{373}$$

$$S^{\circ}_{400} = C_{p\,(S)} \ln 273 + n\ \frac{5.02\ 10^{3}}{273} + 75.3 \ln \frac{373}{273} + \frac{40.7\ 10^{3}}{373} + 33.6 \ln \frac{400}{373}$$

$$S^{\circ}_{400} = 204.18 + 22.05 + 23.5 + 109.11 + 2.35 = 361.19\, J/K$$

Chapter VI:
Free Energy and Enthalpy - Criteria for System Evolution

Learning Objectives

By the end of this chapter, students should be able to:

- Define Gibbs free energy and explain its thermodynamic significance;
- Apply the Gibbs free energy equation to determine spontaneity of processes;
- Relate Gibbs free energy to enthalpy, entropy, and temperature;
- Interpret ΔG values in chemical and physical transformations;
- Calculate equilibrium constants from Gibbs free energy data.

VI.1 Introduction

The second law of thermodynamics provides a fundamental criterion for determining whether a transformation can occur spontaneously.

$\Delta S > 0$: Spontaneous transformation (irreversible).

$\Delta S = 0$: Reversible transformation.

The relevant entropy is that of the universe, which includes both the entropy change of the system and that of the surroundings (ΔSext).

$$\Delta S = \Delta S_{univ} = \Delta S_{sys} + \Delta S_{ext} \geq 0$$

In the case of isolated systems, $\Delta S_{ext} = 0$, and thus $\Delta S_{univ} = \Delta S_{sys}$.

However, most systems of interest to chemists are non-isolated systems exchanging energy with the surroundings.

The calculation of entropy can then become very complicated, especially when the external environment is composed of multiple subsystems.

It is therefore necessary to find evolution criteria linked only to the system, i.e., independent of the surroundings.

This brings us to the introduction of two fundamental thermodynamic functions: the Helmholtz free energy F and the Gibbs free energy G.

VI.2 Free Energy

For an isothermal process carried out at constant volume V, we define a state function denoted by F, known as the Helmholtz free energy (or simply *free energy*), as follows:

$$dU_{sys} = \partial \mathrm{Q}_{sys} + \partial \mathrm{W}_{sys} = \partial \mathrm{Q}_{sys}$$

$$\partial \mathrm{W}_{sys} = -P_{est} = 0$$

According to the second law:

$$dS_{univ} = dS_{sys} + dS_{ext} \geq 0 \; and \; dS_{ext} = \frac{\partial \mathrm{Q}_{est}}{T}$$

$$dS_{ext} = -\frac{\mathrm{SQ}_{sys}}{T} = -\frac{\mathrm{dU}_{sys}}{T}$$

Therefore:

$$dS_{sys} - \frac{\mathrm{dU}_{sys}}{T} \geq 0$$

$$\mathrm{dU}_{sys} - T\, dS_{sys} \leq 0$$

$$\mathrm{d(U - TS)}_{sys} \leq 0$$

We define a new thermodynamic function, known as free energy or the Helmholtz function, by the expression F=U−TS.

Since it is derived from two state functions (U and S) and one state variable (T), F itself is a state function. It serves as a criterion for spontaneous processes occurring at constant temperature and volume, independently of the surroundings.

For such transformations, the differential form satisfies dF≤0, which implies that ΔF≤0 for any finite process.

However, because chemical reactions typically take place at constant pressure, the Helmholtz free energy is less commonly used in chemistry than the Gibbs free energy, which provides a more appropriate criterion for spontaneity under constant-pressure conditions.

VI.3 Gibbs Free Energy

The Gibbs free energy, denoted G (also called Gibbs energy), is a state function that combines enthalpy and entropy, introduced by Josiah Willard Gibbs.

It serves as a key criterion for determining the spontaneity of a process.

At constant temperature and pressure, G provides a reliable condition for spontaneous change.

For a system undergoing a transformation under constant pressure, performing only pressure volume work, the heat exchanged with the surroundings is equal to ΔH_{sys}.

Therefore, the infinitesimal amount of heat received or released by the surroundings is:

$$\partial Q_{est} = dH_{ext} = -dH_{sys}$$

The spontaneity condition is written as:

$$dS_{univ} = dS_{sys} + dS_{ext} = dS_{sys} + \frac{dH_{ext}}{T}$$

$$dS_{univ} = dS_{sys} - \frac{dH_{sys}}{T} \geq 0$$

$$dH_{sys} - T\,dS_{sys} \leq 0$$

$$\mathrm{d(H - TS)}_{sys} \leq 0$$

By defining: G = H - TS

We obtain a new state function defining a condition of spontaneous evolution linked only to the characteristics of the studied system:

$$dG_{sys} \leq 0$$

G: Gibbs free energy or Gibbs function For a finite transformation:

$$G\Delta = H\Delta - T\Delta S$$

A system undergoing a transformation at constant pressure and temperature will evolve spontaneously if its Gibbs free energy decreases.

The process continues until this decrease reaches a minimum, at which point the system attains a state of thermodynamic equilibrium.

Irreversible transformation ⟹ spontaneous evolution ⟹ $\Delta G < 0$

Reversible transformation ⟹system in equilibrium ⟹ $\Delta G = 0$

Impossible transformation ⟹ no evolution ⟹ $\Delta G > 0$

VI.4 Calculation of ΔG_R of the reaction at constant pressure and temperature

A chemical reaction involves the transformation of matter from an initial state to a final state, typically assumed to occur under constant temperature and pressure.
The Gibbs free energy change ΔG associated with the reaction is calculated as the difference between the Gibbs energies of formation of the products and those of the reactants.
To predict the direction in which the reaction will proceed, it is sufficient to examine the sign of ΔG.

Consider the reaction:

$$A \underset{2}{\overset{1}{\Leftrightarrow}} B \qquad\qquad \Delta G = G_B - G_A$$

The ΔG° of the reaction is given by the following relation: $\Delta G° = \Delta H° - T\Delta S°$.

VI.5 Determination of ΔG_R from the standard Gibbs free energy of formation, ΔG_R°

Because enthalpy is a state function, its change during a chemical reaction can be determined using Hess's law.

In a similar way to enthalpy and entropy, a standard Gibbs free energy of reaction, denoted $\Delta G°_R$, is defined for each substance.

The standard values of Gibbs free energy are typically listed in reference tables at 298 K.
By convention, the standard Gibbs free energy of pure elements in their most stable form is taken to be zero under standard conditions.

ΔG_R° is calculated using the following expression:

$$\Delta G_{298}^\circ = \sum v_i \, \Delta G_{298}^\circ \, (P) - \sum v_i \, \Delta G_{298}^\circ \, (R)$$

ΔG_R°: Standardized free energy change.

Example:

$$CO\,(g) + \frac{1}{2}\,O_2\,(g) \rightarrow CO_2\,(g)$$

$\Delta G_f^\circ\,(CO) = -32.81\,Kcal/mol$

$\Delta G_f^\circ\,(CO_2\,) = -94.26\,Kcal/mol$

$\Delta G_{298}^\circ = \Delta G_f^\circ\,(CO_2\,) - \Delta G_f^\circ\,(CO) = -94.26 + 32.81 = -61.35\,Kcal$

VI.6 Variation of ΔG$_R$ with temperature

If the reaction occurs at a temperature 'T' different from the data temperature (298K), ΔG_T is calculated using the following relation:

$$\Delta G_{RT} = \Delta H_{RT} - T\Delta S_{RT}$$

ΔH_T and ΔS_T are calculated by applying Kirchoff's law:

$$\Delta H_R^\circ(T) = \Delta H_R^\circ(298K) + \Delta C_p(T - 298)$$

$$\Delta S_R^\circ(T) = \Delta S_R^\circ(298K) + \Delta C_p \ln\frac{T}{298}$$

- $\Delta G_R < 0 \Rightarrow$ The reaction is possible in direction 1
- $\Delta G_R = 0 \Rightarrow$ The system does not evolve $\Rightarrow$ it is in equilibrium
- $\Delta G_R > 0 \Rightarrow$ The reaction does not evolve in direction 1, so it evolves in direction 2.
- The function G thus expresses the spontaneity criterion for the evolution processes of systems.

Example:

Calculate ΔG° at 298K and 773K.

$$3C_2H_2\,(g) \rightarrow C_6H_6(g)$$

$\Delta G_f^\circ\left(C_2H_2\,(g)\right) = 54.2\,Kcal/mol$

$\Delta G_f^\circ\,(C_6H_6(g)) = 19.84\,Kcal/mol$

$S^\circ\left(C_2H_2\,(g)\right) = 48\,cal/mol.K$

$S^\circ(C_6H_6(g)) = 64.4\,cal/mol.K$

$Cp\,\left(C_2H_2\,(g)\right) = 10.51\,cal/mol.K$

$Cp(C_6H_6(g)) = 19.54\,cal/mol.K$

Solution:

$\Delta G_{298}^\circ = \Delta G_f^\circ(C_6H_6(g)) - 3\,\Delta G_f^\circ\left(C_2H_2\,(g)\right) = 19.84 - 3x\,54.2 = -142.76\,kcal/mol$

$\Delta S^{\circ}_{298} = S^{\circ}(C_6H_6(g)) - 3\,S^{\circ}\big(C_2H_2\,(g)\big) = 64.4 - 3x\,48 = -79.6\ cal/mol.K$

$\Delta G^{\circ}_{298} = \Delta H^{\circ}_{298} - T\,\Delta S^{\circ}_{298} = -142.76 + 298\ 79.6\ 10^{-3} = -119.03\ kcal/mol$

$\Delta H^{\circ}_{R}\,(T) = \Delta H^{\circ}_{R}\,(298K) + \Delta Cp\,(T - 298)$

$\Delta H^{\circ}_{R}\,(773) = -142.76 + (19.54 - 3\,x\,10.51)\,(773 - 298)10^{-3} = -148.45\ kcal/mol$

$$\Delta S^{\circ}_{R}(T) = \Delta S^{\circ}_{R}(298K) + \Delta C_p \ln\frac{T}{298}$$

$$\Delta S^{\circ}_{R}(773) = -79.6 + (19.54 - 3\,x\,10.51)\ln\frac{773}{298} = -91.02\ cal/mol.K$$

$\Delta G^{\circ}_{R}(773K) = \Delta H^{\circ}_{R}(773K) - T\,\Delta S^{\circ}_{R}(773K) = -148.45 + 773x\,91.02\,x\,10^{-3}$

$\Delta G^{\circ}_{R}(773K) = -78.08\ kcal/\text{mol}$

VI.7 Calculation of the Gibbs free energy G of a gaseous component

VI.7.1 Variation with pressure at constant temperature

Consider a system evolving isothermally and reversibly with n moles of ideal gas, the function G is expressed as follows:

$G = H - TS = U + PV - TS = (Q + W) + PV - TS$

$dG = \partial Q + \partial W + PdV + VdP - TdS - SdT$

$dG = \partial Q - PdV + PdV + VdP - TdS - SdT$

$dG = \partial Q + VdP - TdS - SdT$

$\partial Q = \partial Q_{rev} = TdS$

At constant temperature:

$$dG = VdP \text{ and } (\frac{\partial G}{\partial P})_T = V$$

$$\int_{Ei}^{Ef} dG = \int_{P_1}^{P_2} VdP \quad with\ V = \frac{nRT}{P}$$

$$\Delta G_T = G_{Ei} - G_{Ef} = G_{T,P2} - G_{T,P1} = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Delta G_T = nRT \ln\frac{P_2}{P_1}$$

When the initial state (EI) is a standard state, we have:

$P_1 = P^{\circ} = 1\ bar$

$G_{Ei,T} = G^{\circ}_T$

$\Delta G_T = G_{T,P} - G_T^{\circ} = nRT \ln P$

$G_{T,P} = G_T^{\circ} + nRT \ln P$

- $G_{T,P}$: the Gibbs free energy of n moles of ideal gas at temperature T under pressure P.
- G_T°: the Gibbs free energy of n moles of ideal gas under standard conditions at temperature T.

VI.7.2 Variation with temperature at constant pressure

$$G = H - TS \Longrightarrow S = \frac{H - G}{T}$$

$$dG = VdP - SdT$$

At constant pressure:

$dG = -SdT$

$(\frac{\partial G}{\partial T})_P = -S \; and \; \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{S}{T} + \frac{G - H}{T^2}$

$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{1}{T}\frac{\partial G}{\partial T} - \frac{\Delta G}{T^2}$

$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2} \; Gibbs - Helmoltz \; Relation$

Example 1:

For the synthesis reaction of ammonia:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$$

Calculate the value of ΔG_R at 350 K, knowing that:

$\Delta G_R^{\circ}(298K) = -16.64 \; kJ/mol$and the change in enthalpy can be considered constant and equal to −46.19 kJ/mol.

Solution:

$\frac{\Delta G_R^{\circ}(T_2)}{T_2} - \frac{\Delta G_R^{\circ}(T_1)}{T_1} = \Delta H_R^{\circ} \; (\frac{1}{T_2} - \frac{1}{T_1})$

$\Delta G_R^{\circ}(350\,K) = T_2\left[\frac{\Delta G_R^{\circ}(298K)}{T_1} + \Delta H_R^{\circ}\;\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = 350\left[\frac{-16.64}{298} - 46.19\;(\frac{1}{350} - \frac{1}{298})\right]$

$\Delta G_R^{\circ}(350\,K) = -11.47\;kJ$

Example 2:

A sample of one mole of an ideal gas undergoes a reversible isothermal expansion at 27 °C, with its pressure decreasing from 100 atm to 1 atm.
Calculate the following thermodynamic quantities in joules: ΔU, ΔH, ΔS, ΔF, and ΔG.

Solution:

$$\Delta U = 0 \; and \; \Delta H = 0$$

$$W = -nRT \, ln\frac{V2}{V1} = -nRT \, ln\frac{P1}{P2} = -8.31 \times 300 \, ln\frac{100}{1} = -11.48 \, kJ$$

$$Q = -W = 11{,}48 \, kJ$$

$$\Delta S = nR \, ln\frac{V2}{V1} = nR \, ln\frac{P1}{P2} = 8.31 \, ln\frac{100}{1} = 38.27 J/K$$

$$F = U - TS \Rightarrow dF = dU - TdS - SdT = -TdS$$

$$\Delta F = -T\Delta S = -300 \times 38.27 = -11.48 \, kJ$$

$$G = H - TS \Rightarrow dG = dH - TdS - SdT = -TdS$$

$$\Delta G = -T\Delta S = -300 \times 38.27 = -11.48 \, kJ$$

VI.8 Chemical Equilibria

VI.8.1 Definition

Thermodynamics allows us to predict if a chemical reaction will occur ($\Delta G°_R<0$) and in other words, if the reactants (initial state) will spontaneously transform into products (final state).
Consider the following reaction:

$$aA + bB \Leftrightarrow cC + dD \qquad \Delta G^{\circ}_{R,T}$$

A chemical equilibrium is a state of no net change in a system resulting from a chemical reaction limited in both directions. It is reversible (it occurs in both directions (1) and (2)), and it can be shifted in one direction or the other by modifying one of its variables (T, P, C). When equilibrium is reached ⇒ $\Delta G^{\circ}_{R,T} = 0J$.

VI.8.2 Nature of the equilibrium

Homogeneous equilibrium: equilibrium is achieved between components in the same phase (gas, liquid, solid).

Example:

the formation of ammonia reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Heterogeneous equilibrium: if the components are in different phases.

Example:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(l)$$

VI.8.3 Law of Mass Action

The law of mass action (or Guldberg and Waage law (1864)) allows the study of chemical equilibria at a given temperature.

It applies rigorously to equilibria in homogeneous phases or ideal solutions, for equilibria in heterogeneous phases, the application is only approximate.

When the chemical reaction reaches equilibrium, the composition of the mixture no longer changes.

At equilibrium, the reaction quotient takes a very important particular value called the equilibrium constant, generally denoted as K, given by the law of mass action.

Let's consider the chemical reaction at temperature T.

$$aA + bB \Leftrightarrow cC + dD \qquad \Delta G^{\circ}_{R,T} = 0J$$

$$K(T) = \frac{a^c(C)xa^d(D)}{a^a(A)xa^b(B)}$$

With:

a(x): Activity of the component (x) at equilibrium (concentration, pressure, mole fraction).

K(T): Equilibrium constant at temperature T.

The equilibrium constant K(T) is dimensionless and depends only on the reaction temperature.

a. The law of mass action relative to concentrations

Let [A], [B], [C], and [D] be the respective molar concentrations of the reactants and products in the aqueous state.

$$K(T) = K_c = \frac{[C]^c x[D]^d}{[A]^a\, x[B]^b} = f(T)$$

Example:

$$Mg(OH)_2\,(S) \Leftrightarrow Mg^{2+} + 2OH^-\,(aq)$$

$$K_c = \frac{[Mg^{2+}]^1 x[OH^-]^2}{[Mg(OH)_2]}$$

$$[Mg(OH)_2] = 1$$

$$K_c = [Mg^{2+}]^1 x[OH^-]^2$$

b. Law of mass action in terms of partial pressures (Pi)

Let P_A, P_B, P_C, and P_D represent the partial pressures of the gaseous reactants and products. The law of mass action expressed in terms of partial pressures is written as follows:

$$K(T) = K_p = \frac{P_C^c x P_D^d}{P_A^a x P_B^b} = f(T)$$

Example:

$$NO(g) + \frac{1}{2}\, O_2(g) \Leftrightarrow NO_2(g)$$

$$K(T) = K_p = \frac{P_{NO_2}^1}{P_{NO}^1 x P_{O_2}^{1/2}}$$

c. Law of mass action using mole fractions (xi)

Let X_A, X_B, X_C, and X_D denote the mole fractions of the reactants and products. The law of mass action in terms of mole fractions is given as follows:

$$K(T) = K_X = \frac{X_C^c x X_D^d}{X_A^a x X_B^b} = f(T)$$

d. Relationship between K_C, K_P, and K_X

According to the ideal gas law:

$$P_i = \frac{n_i}{V} RT \Rightarrow P_i = C_i RT$$

Let's replace the partial pressures by their values in terms of concentrations:

$$K_p = \frac{P_C^c x P_D^d}{P_A^a x P_B^b} = \frac{C_C^c\,(RT)^c x C_D^d (RT)^d}{C_A^a (RT)^a x C_B^b (RT)^b}$$

$$K_p = \frac{C_C^c x C_D^d}{C_A^a x C_B^b}\, x\, \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$K_c = \frac{C_C^c x C_D^d}{C_A^a x C_B^b} \Rightarrow K_p = K_c\,(RT)^{(c+d)-(a+b)}$$

$$\Delta n = c + d - (a + b) \Rightarrow K_p = K_c\,(RT)^{\Delta n}$$

$$\Delta n = \sum_{i=1}^{n} n_i(P)_g - \sum_{i=1}^{n} n_i(R)_g$$

On the other hand, we know that according to the ideal gas law for gas mixtures, there is a relationship between total pressure and partial pressure:

$$P_i = X_i \, x \, P_t \qquad\qquad X_i = \frac{n_i}{n_t}$$

By replacing the partial pressures by their values in terms of mole fractions in the expression for KP, we obtain:

$$K_p = \frac{P_C^c x P_D^d}{P_A^a x P_B^b} = \frac{X_C^c \, P_t^c x X_D^d \, P_t^d}{X_A^a P_t^a x X_B^b P_t^b} = \frac{X_C^c x X_D^d}{X_A^a x X_B^b} \, x \, \frac{P_t^{c+d}}{P_t^{a+b}}$$

$$K_X = = \frac{X_C^c x X_D^d}{X_A^a x X_B^b} \Longrightarrow K_p = K_X \, P_t^{(c+d)-(a+b)}$$

$$\Delta n = c + d - (a + b) \Longrightarrow \; K_p = K_X \, P_t^{\Delta n} \Longrightarrow$$

Note:

If the system is in the gas phase, all three constants are applicable.

However, when the system is in the liquid phase, only the expressions involving mole fractions (K_X) and concentrations (K_C) are applicable.

VI.9 Law of mass action and Gibbs free energy

Consider the gaseous equilibrium:

$$a\,A(g) \; + \; b\,B(g) \; \rightleftharpoons \; c\,C(g) \; + \; d\,D\,(g)$$

The equilibrium constant is determined from the variation in Gibbs free energy (ΔG°) for a reaction occurring in a homogeneous gaseous phase.

We know that: $G = H - T\,S \Rightarrow dG = dH - TdS - SdT$

$$dH = dU + d(PV) = dU + PdV + VdP \; dU = \delta Q + \delta W$$

With $\delta W = -PdV \; and \; \delta Q = TdS \; dU = TdS - PdV \; dH = TdS - PdV + PdV + VdP$

$$\Rightarrow dH = TdS + VdPdG = TdS + VdP - TdS - SdT \; dG = VdP - SdT$$

At constant temperature ⇒ isothermal evolution: (dT=0)

dG = VdP by the ideal gas law

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

$$dG = nRT\frac{dP}{P}$$

By integrating over the interval [$P_i = P_0$ = 1 atm, P_f= P], we obtain:

$$\int_i^f dG = \int_{P_0}^{P} nRT\frac{dP}{P}$$

$$G_T^P - G_T^0 = nRT\,(\ln P - \ln P_0\,) \; with \; lnP_0 = 0$$

$$G_T^P = G_T^0 + nRT \; \ln P$$

This relation can be applied to a chemical reaction, where the **Gibbs free energy change** at given pressure and temperature $\Delta G_{P,R,T}$ is expressed as:

$$\Delta G^{\circ}_{R,T} = c\,\Delta G^{\circ}_{f,T}\,(C) + d\,\Delta G^{\circ}_{f,T}\,(D) - \left[a\,\Delta G^{\circ}_{f,T}\,(A) + b\,\Delta G^{\circ}_{f,T}\,(B)\right] + RT\,[c\ln P_C + d\ln P_D - a\ln P_A - b\ln P_B]$$

$$\Delta G^{P}_{R,T} = \Delta G^{\circ}_{R,T} + RT\ln\frac{P_C^c x P_D^d}{P_A^a x P_B^b}$$

$$\Delta G^{P}_{R,T} = \Delta G^{\circ}_{R,T} + RT\ln K_p$$

In equilibrium: $\Delta G^{P}_{R,T} = 0$ Joul

$$\Delta G^{\circ}_{R,T} + RT\ln K_p = 0$$

$$\Delta G^{\circ}_{R,T} = -RT\ln K_p$$

$$\ln K_p = -\frac{\Delta G^{\circ}_{R,T}}{RT}$$

$$K_p = e^{-\frac{\Delta G^{\circ}_{R,T}}{RT}}$$

This relationship allows the calculation of Kp knowing $\Delta G^{\circ}_{R,T}$.

$\Delta G^{\circ}_{R,T}$Standard change in Gibbs free energy of the reaction.

If $\Delta G^{\circ}_{R,T} < 0 \Rightarrow K_p\,(T) > 1$

If $\Delta G^{\circ}_{R,T} > 0 \Rightarrow K_p\,(T) < 1$

The forward reaction is favored (reactants →products)

The reverse reaction is more favored (reactants ← products)

Application:

When a gaseous stream, considered an ideal gas mixture of CO, CO_2, and H_2, is introduced into a furnace at 900 °C under a total pressure of 1 atm, the system reaches the following equilibrium:

$$CO\,(g) + H_2O\,(g) \underset{2}{\overset{1}{\Leftrightarrow}} H_2(g) + CO_2\,(g)$$

1. Provide the enthalpy (ΔH°_R, 298) and entropy (ΔS°_R, 298) changes for the reaction at standard conditions.
2. Determine the equilibrium constant K_p at 900 °C.
3. Calculate the equilibrium composition (in moles of each species) at 900 °C, for an initial mixture containing 20 moles of CO, 15 moles of CO_2, and 25 moles of H_2.
4. Determine the equilibrium inversion temperature at which the reaction shifts to favor the formation of water.

Given data:

	$CO\ (g)$	$H_2O\ (g)$	H_2 (g)	CO_2 (g)
S°_{298} (J/mol.K)	197.7	188.7	130.6	213.4
ΔH°_{298} (kJ/mol)	-110.4	-241.6	0	-393.1

Solution:

1.

$$\Delta H^\circ_{R,298} = \Delta H^\circ_{f,298}\,(H_2,g) + \Delta H^\circ_{f,298}\,(CO_2,g) - \Delta H^\circ_{f,298}\,(CO,g) - \Delta H^\circ_{f,298}\,(H_2O,g)$$

$$\Delta H^\circ_{R,298} = 0 + (-393.1) - (-110.4) - (-241.6) = -41.10\,kJ$$

$$\Delta S^\circ_{R,298} = S^\circ_{298}\,(H_2,g) + S^\circ_{298}\,(CO_2,g) - S^\circ_{298}\,(CO,g) - S^\circ_{298}\,(H_2O,g)$$

$$\Delta S^\circ_{R,298} = 130.6 + 213.4 - 197.7 - 188.7 = -42.4\,J.K^{-1}$$

2.

$$\Delta G^\circ_T = \Delta G°T + RT\ lnKp = 0$$

$$\Delta G^\circ_T = -RT\ln Kp = \Delta H^\circ_T - T\Delta S^\circ_T = -41100 - 1173\,.(-42.4) = 8635.2J$$

$$\ln Kp = -\Delta G^\circ_T RT = -8635.2\ 8{,}31\ (273 + 900) = -0.8859$$

$$Kp = 0.412\ \ at\ temperature = 1173\ K$$

3.

$$CO\ (g) + H_2O\ (g) \overset{1}{\underset{2}{\Leftrightarrow}} H_2(g) + CO_2\ (g)$$

	$CO\ (g)$	$H_2O\ (g)$	$H_2(g)$	$CO_2\ (g)$
t=0	20	0	25	15
teq	20-X	0-X	25+X	15+X

$$Kp = \frac{P_{H_2}P_{CO_2}}{P_{CO}P_{H_2O}}$$

$$Kp = \frac{n_{H_2}n_{CO_2}}{n_{CO}n_{H_2O}}$$

$$Kp = \frac{(25+X)(15+X)}{(20-X)(-X)} = 0.412$$

$$\Rightarrow 0.6\,X^2 + 32\,X + 375 = 0$$

$$\Rightarrow X = -8.7\,mol$$

$$n_{CO} = 28.7\,mols;\ n_{H_2} = 16.3\,mols$$

$$n_{CO_2} = 6.3\,mols;\ n_{H_2O} = 8.7\,mols$$

4.

$\Delta G^{\circ} = 0, Kp = 1$

$$T_i = \frac{\Delta H}{\Delta S}$$

$$T_i = \frac{-41.10\ 10^3}{-42.4} = 969.3\ K$$

VI.10 Influence of temperature on the equilibrium constant, Van't Hoff equation

We know that:

$$\Delta G^{\circ}_{R,T} = -RT \ln K_p \qquad\qquad \ln K_p = -\frac{\Delta G^{\circ}_{R,T}}{RT}$$

Let us determine how the equilibrium constant Kp varies with temperature:

$$\ln K_p = -\frac{\Delta G^{\circ}_{R,T}}{RT} \Rightarrow \frac{\delta}{\delta T}\,(\ln K_p) = -\,\frac{\delta}{\delta T}\left(\frac{\Delta G^{\circ}_{R,T}}{RT}\right) = -\,\frac{1}{R}\frac{\delta}{\delta T}\,(\frac{\Delta G^{\circ}_{R,T}}{T})$$

$$\frac{\delta}{\delta T}\left(\frac{1}{T}\,\Delta G^{\circ}_{R,T}\right) = -\,\frac{\Delta G^{\circ}_{R,T}}{T^2} + \frac{1}{T}\,\frac{\delta}{\delta T}\,[\Delta G^{\circ}_{R,T}]$$

$$\Delta G^{\circ}_{R,T} = \Delta H^{\circ}_{R,T} - T\,\Delta S^{\circ}_{R}$$

$$\frac{\delta}{\delta T}\,[\Delta G^{\circ}_{R,T}] = \frac{\delta}{\delta T}\,[\Delta H^{\circ}_{R,T} - T\,\Delta S^{\circ}_{R}] \qquad\qquad \Delta H^{\circ}_{R,T} = cst\ and\ \Delta S^{\circ}_{R} = cst$$

$$\Rightarrow \frac{\delta}{\delta T}\,[\Delta G^{\circ}_{R,T}] = -\,\Delta S^{\circ}_{R}$$

$$\frac{\delta}{\delta T}\left[\frac{1}{T}\,\Delta G^{\circ}_{R,T}\right] = -\,\frac{\Delta H^{\circ}_{R,T}}{T^2} + \frac{\Delta S^{\circ}_{R}}{T} + \frac{1}{T}\,(-\Delta S^{\circ}_{R})$$

$$\Rightarrow \frac{\delta}{\delta T}\left[\frac{1}{T}\,\Delta G^{\circ}_{R,T}\right] = -\,\frac{\Delta H^{\circ}_{R,T}}{T^2}$$

$$\frac{\delta}{\delta T}\,[\ln Kp] = -\,\frac{1}{R}\frac{\delta}{\delta T}\left(\frac{\Delta G^{\circ}_{R,T}}{T}\right) = -\,\frac{1}{R}\left[-\frac{\Delta H^{\circ}_{R,T}}{T^2}\right] = \frac{\Delta H^{\circ}_{R,T}}{RT^2}$$

$$\frac{\delta}{\delta T}\,[\ln Kp] = \frac{\Delta H^{\circ}_{R,T}}{RT^2} \qquad\qquad Van't\ Hoff$$

$$\Delta H^{\circ}_{R,T} = cst \qquad\qquad [T_1 - T_2]$$

$$\int_{T_1}^{T_2} d\ln Kp = \int_{T_1}^{T_2} \frac{\Delta H^{\circ}_{R,T}}{R}\,\frac{dT}{T^2}$$

$$\ln Kp\ (T_2) - \ln Kp\ (T_1) = -\frac{\Delta H^{\circ}_{R,T}}{R}\,\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln\frac{K_p(T_2)}{K_p(T_1)} = \frac{\Delta H^{\circ}_{R,T}}{R}\,\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

VI.11 Le Chatelier's Principle

Le Chatelier's Principle, also known as the general law of moderation, was formulated by Henry Le Chatelier in 1884 based on experimental observations.

This principle applies within the framework of an equilibrium shift, not an equilibrium breakdown.

Statement:

When a physicochemical system at equilibrium is subjected to an external disturbance, it responds by shifting toward a new equilibrium state in a direction that opposes the imposed change and reduces its impact.

VI.11.1 Effect of Temperature (Van't Hoff's Law)

An increase in temperature applied to a closed system in equilibrium and maintained at constant pressure or volume causes a shift or even a breakdown of equilibrium in the direction of the reaction which, at constant temperature and pressure or volume, is endothermic.

(T ↗⇒ $\Delta H^{\circ}_{R} > 0$) (T ↘⇒ $\Delta H^{\circ}_{R} < 0$)

In practice, for a closed system at equilibrium, an increase in temperature will shift the equilibrium:

toward the forward reaction if the process is endothermic,

and toward the reverse reaction if the process is exothermic.

Examples:

Consider the chemical equation for the synthesis of methanol:

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH\,(g)$ $\qquad \Delta H^{\circ}_{R,298} = -90.7$ kJ

$\Delta H^{\circ}_{R,298} = -90.7$ kJ < 0 ⇒ exothermic reaction

T↗ ⟹ The equilibrium shifts in the endothermic direction, meaning toward the reverse reaction, which leads to the formation of CO(g) and H_2(g).

Consider the chemical equation for the dissociation of $PCl_5(g)$:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)$ $\Delta H^{\circ}_{R,298} = 92.3$ kJ

$\Delta H^{\circ}_{R,298} = 92.3$ kJ > 0 ⇒ endothermic reaction

T↗ ⟹equilibrium shift in the endothermic direction, i.e., in the forward direction (production of PCl_3 (g) and Cl_2 (g))

VI.11.2 Effect of pressure

An increase in pressure causes the system to shift toward the side of the reaction that contains fewer moles of gas.

For gaseous systems, we apply the ideal gas law equation:

$$PV = nRT$$

At constant temperature, a change in pressure ΔP results in a corresponding change in volume ΔV and in the number of moles of gas Δn.

$$\Delta(PV) = \Delta(nRT) \Rightarrow P\Delta V + V\Delta P = RT\Delta n$$

(P ↗, V ↘, and n ↘) (P ↗⇒Δn (g) < 0) (P ↘⇒ Δn(g) > 0)

Example:

Let us consider the chemical reaction involved in the synthesis of methanol:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH\,(g)$$

$$\Delta H^{\circ}_{R,298} = -90.7\,kJoul$$

$$\Delta n\,(g) = 1 - (1 + 2) = -2\,mols < 0$$

P ↗⇒ equilibrium shift in the direction of decreasing the number of gaseous moles, meaning in the direction of CH_3OH (g) production (direct direction).

VI.11.3 Effect of concentration

The system evolves in the direction that consumes the added reactant.

Examples:

$$PbSO_4(S) + 2I^-(aq) \rightleftharpoons PbI_2(S) + {SO_4}^{2-}(aq)$$

If we increase the concentration of I^-, the system decreases the concentration of I^- by favoring the direct reaction, and Kc becomes larger.

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$$

If we add Fe^{3+}, the system reacts by favoring the formation of FeSCN (to maintain its concentration constant).

If we add FeSCN, the system reacts by favoring the formation of Fe^{3+} and SCN^-

Consider the chemical equation for the dissociation of PCl_5(g):

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g) \quad \Delta H^{\circ}_{R,298} = 92.3\,kJ$$

$$\Delta n\,(g) = (1 + 1) - 1 = 1mol > 0$$

P ↘⇒ The equilibrium shifts toward the side with fewer gaseous moles, that is, toward the formation of PCl_5(g) corresponding to the reverse reaction.

VI.12 Description of the equilibrium state

VI.12.1 Dissociation coefficient α

In a chemical reaction, the formation of products is inherently associated with the consumption of reactants.

We then define a quantity called the dissociation coefficient, denoted by α:

$$\alpha = \frac{n_d}{n_0} \Rightarrow n_d = \alpha\, n_0 \qquad\qquad 0 \leq \alpha \leq 1$$

	AB ⇔	A +	B	n_{tot}
t=0	n_0	0	0	n_0
teq	$n_0 - \alpha n_0$	αn_0	αn_0	$n_0 + \alpha n_0$

Example:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)$

	$PCl_5(g)$	PCl_3	Cl_2	n_{tot}
t=0	n_0	0	0	n_0
teq	$n_0 - \alpha n_0$	αn_0	αn_0	$n_0 + \alpha n_0$

$$n_{tpt} = n_0 - \alpha n_0 + \alpha n_0 + \alpha n_0 = n_0\,(1+\alpha)$$

$$K_p = \frac{P^1_{Cl_2} P^1_{PCl_3}}{P^1_{PCl_5}}$$

$$P_{PCl_3} = P_t\, X_{PCl_3} = P_t\, \frac{\alpha n_0}{n_0\,(1+\alpha)} = P_t \frac{\alpha}{1+\alpha}$$

$$P_{PCl_5} = P_t\, X_{PCl_5} = P_t\, \frac{n_0 - \alpha n_0}{n_0\,(1+\alpha)} = P_t \frac{1-\alpha}{1+\alpha}$$

$$P_{Cl_2} = P_t\, X_{Cl_2} = P_t\, \frac{\alpha n_0}{n_0\,(1+\alpha)} = P_t \frac{\alpha}{1+\alpha}$$

$$K_p = P_t\, \frac{\alpha^2}{1-\alpha^2}$$

VI.12.2 Degree of advancement

The advancement of a reaction is characterized by the variable ξ such that:

$$n = n_0 + \nu_i \xi$$

with νi> 0 for the products and νi< 0 for the reactants.

Example:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2\ (g)$

	$PCl_5(g)$	PCl_3	Cl_2	n_{tot}
t=0	n_0	0	0	n_0
Teq	$n_0 - 1\xi$	$0+1\xi$	$0+1\xi$	$n_0 + \xi$

$$n_{tot} = n_0 - 1\xi + 1\xi + 1\xi = n_0 + \xi$$

$$K_p = \frac{P_{Cl_2}^1 P_{PCl_3}^1}{P_{PCl_5}^1}$$

$$P_{PCl_5} = P_t\, X_{PCl_5} = P_t \frac{n_0 - \xi}{n_0 + \xi}$$

$$P_{PCl_3} = P_t\, X_{PCl_3} = P_t \frac{\xi}{n_0 + \xi}$$

$$P_{Cl_2} = P_t\, X_{Cl_2} = P_t \frac{\xi}{n_0 + \xi}$$

$$K_p = P_t \frac{\xi^2}{n_0^2 - \xi^2}$$

Contextual Real-World Examples

- **Battery Operation**: Explain how the Gibbs free energy determines whether a battery will deliver electrical energy spontaneously, with ΔG linked to cell potential $\Delta G = -nFE_{cell}$.
- **Metabolism and ATP Hydrolysis**: Show how biochemical reactions such as ATP → ADP + Pi have a negative ΔG, providing energy for muscle contraction and nerve impulses.
- **Ammonia Synthesis (Haber Process)**: Analyze ΔG at different temperatures to explain why high temperatures favor reaction rate but not spontaneity.
- **Lithium-Ion Charging**: Discuss how a positive ΔG during charging means external work (electricity) is needed.

Self-Assessment Quiz

1- MCQs

If $\Delta G < 0$ for a reaction at constant T and P, the reaction is:

a) Non-spontaneous;

b) Spontaneous;

c) At equilibrium;

d) Endothermic.

For a reaction where $\Delta H = -200$ kJ and $\Delta S = -0.5$ kJ/K, at which temperature will it be non-spontaneous?

a) Below 400 K;

b) Above 400 K;

c) At 400 K;

d) Never

2- True/False

$\Delta G = 0$ indicates a reaction is at equilibrium. (T/F)

A reaction with $\Delta H > 0$ and $\Delta S > 0$ is spontaneous at all temperatures. (T/F)

3- Short Question

Explain why ice melts spontaneously at room temperature but not in a freezer using ΔG.

Recap & Key Formulas

- Gibbs free energy combines enthalpy and entropy effects into a single criterion for spontaneity.
- $\Delta G < 0$ → spontaneous process ; $\Delta G = 0$ → equilibrium ; $\Delta G > 0$ → non-spontaneous process.
- Temperature can shift spontaneity when enthalpy and entropy effects compete.
- Gibbs free energy links thermodynamics to equilibrium via $\Delta G^\circ = -RT\ln K$.

Essential Formulas :

1. $G = H - TS$;
2. $\Delta G = \Delta H - T\Delta S$;
3. $\Delta G^\circ = -RT\ln K$;
4. $\Delta G = \Delta G^\circ + RT\ln Q$.

Corrected Exercises

Exercise 1:

Consider the following reaction (synthesis of nitrosyl)

$$N_2 + O_2 \rightleftharpoons 2\,NO$$

Performed under a constant pressure equal to 1 atm. The enthalpies of formation and entropies in the standard state are given:

$S°_{298}(NO) = 50.34$ cal/mol.K; $S°_{298}(N_2) = 45.77$ cal/mol.K; $S°298(O_2) = 49$ cal/mol.K; $\Delta Hf°_{298}(NO) = 21.6$ kcal/mol.

1. Does this reaction require heat or not, and why?
2. Is it thermodynamically possible at 1 atm and 298 K?
3. Assuming that the effects of temperature on enthalpy and entropy are negligible, calculate the Gibbs free energy change ΔG at 2000 K, and provide a brief interpretation of the result.
4. Determine the value of the equilibrium constant at this temperature (2000 K).

What is the temperature required for the reversal of the equilibrium to favor the formation of nitrogen at 1 atm?

Exercise 2:

Determine the standard Gibbs free energy of formation of ozone (O_3) at 298 K, based on the following data:

$\Delta H°_f(O_3)$ g = 34 K cal/ mol ; S° O_2 (g) = 49 cal/ K. mol; S° O_3 (g) = 56.8 cal/ K. mol.

Exercise 3:

Calcium carbonate $CaCO_3$ (s) undergoes decomposition according to the reaction:

$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

1. Is this reaction thermodynamically possible under standard conditions?
2. At what temperature does it become possible? It is assumed that enthalpy and entropy remain constant with respect to temperature.

Data:

Substance	$\Delta H°_f$ (kJ/mol)	$S°_f$ ($J \cdot mol^{-1} \cdot K^{-1}$)
$CaCO_3$ (s)	−1210.11	92.80
CaO (s)	−634.11	39.71
CO_2 (g)	−393.10	213.40

Exercise 4:

Calculate the Gibbs free energy change for the spontaneous transformation of 1 mole of water occurring at atmospheric pressure:

$$H_2O \text{ (liquid)} \rightarrow H_2O \text{ (ace)}$$

25 °C ***-5 °C***

Given:

$C_p(H_2O, l) = 18$ cal/K;

$C_p(H_2O, s) = 9$ cal/K.

$\Delta H°_{solidifi}(H_2O, l) = -1438$ cal.

Exercise 5:

100 L of nitrogen gas at T = 0 °C (gas assumed to be ideal) undergoes a **reversible adiabatic compression** from 1 atm to 20 atm.

Calculate: ΔU, ΔH, ΔS, ΔF, and ΔG.

Given: $C_p(N_2) = 6.97$ cal/mol·K, $S° = 45.2$ cal/mol·K at T_1, and $\gamma = 1.4$.

Exercise 6:

Determine the standard Gibbs free energy change $\Delta G°_R$ for the following reactions at 25 °C:

Rac → Prod	**$\Delta H°_R$ (kJ)**	**$\Delta S°_R$ (J.K^{-1})**
$2O_3$ (g) → $3O_2$ (g)	-285.4	137.55
$2NO_2$ (g) → N_2O_4 (g)	-57.20	-175.83
2NO (g) → N_2 (g) + O_2 (g)	-180.74	-24.87
N_2O_5 (g) → $2NO_2$ (g) + ½ O_2 (g)	216.48	938.23
$2SO_2$ (g) + O_2 (g) → $2SO_3$ (g)	-198.24	-189.63

Exercise 7:

Calculate $\Delta G°_R$ for the reduction reactions of iron and copper oxides by graphite carbon:

- 2 Fe_2O_3 (s) + 3 C (graphite) → 4 Fe (s) + 3 CO_2 (g)
- 2 CuO (s) + C (graphite) → 2 Cu (s) + CO_2 (g)

These conditions are favorable for the reduction of oxides at 298 K and 1 atm.

Given:

$\Delta G°_f$ (CuO, s) = -130 kJ/mol.

$\Delta G°_f$ (CO_2, g) = -395 kJ/mol.

$\Delta G°_f$ (Fe_2O_3, s) = 742.2 kJ/mol.

Correction

Exercise 1:

1. Does this reaction require heat or not, and why?

We compute the enthalpy change for the reaction:

$$\Delta H^{\circ}_{R;298} = \sum \Delta H^{\circ}_f(products) - \sum \Delta H^{\circ}_f(reactants)$$

$$\Delta H^{\circ}_{R;298} = 2\Delta H^{\circ}_{f,298}\,(NO) - \Delta H^{\circ}_{f,298}\,(O_2) - \Delta H^{\circ}_{f,298}\,(N_2)$$

$$\Delta H^{\circ}_{R;298} = 2 \times 21.6 - (0 + 0) = 43.2\,kcal/mol$$

The reaction requires heat; it is endothermic because the enthalpy change is positive.

2. Is it thermodynamically possible at 1 atm and 298 K?

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

$$\Delta S^{\circ}_{R,298} = 2\Delta H^{\circ}_{f,298}\,(NO) - \Delta S^{\circ}_{f,298}\,(O_2) - \Delta S^{\circ}_{f,298}\,(N_2)$$

$$\Delta S^{\circ}_{R,298} = 2 \times 50.34 - 45.77 - 49.00 = 5.91 cal/mol$$

$$\Delta G^{\circ}_{R,298} = \Delta H^{\circ}_{R,298} - T\Delta S^{\circ}_{R,298} = 43200 - 298 \times 5.91 = 41.439\,kcal.$$

$\Delta G^{\circ}_{R,298} > 0$ ⇒ the reaction is not spontaneous at 298 K and 1 atm. It is not thermodynamically favorable under these conditions.

3. Calculate ΔG at 2000 K and comment on the result:

$$\Delta G^{\circ}_{R,2000} = \Delta H^{\circ}_{R,298} - T\Delta S^{\circ}_{R,298} = 43200 - 2000 \times 5.91 = 31380 cal = 31.38\,kcal$$

Even at 2000 K, the reaction still has a positive Gibbs energy, the reaction at 2000 K is still impossible in this direction.

4. Calculate the equilibrium constant K at 2000 Kp

$$\Delta G^{\circ}_T = -RT lnKp$$

$$lnKp = -\frac{\Delta G^{\circ} T}{RT}$$

$$Kp = e^{-\frac{\Delta G^{\circ} T}{RT}} = e^{-\frac{31380}{2 . 2000}} = 3.7 \times 10^{-4}$$

5. What is the temperature required for the equilibrium to reverse and favor nitrogen formation?

$$\Delta G^{\circ} T = 0 \; or \; Kp = 1$$

$$\Delta G^{\circ}_{R,T} = \Delta H^{\circ}_{R,298} - T\Delta S^{\circ}_{R,298} = 0 \Longrightarrow T = \frac{\Delta H^{\circ}_{R,298}}{\Delta S^{\circ}_{R,298}} = \frac{43200}{5.91} = 7310K$$

The equilibrium starts to favor the formation of N_2 and O_2 (reverse reaction) below approximately 7310 K.

Exercise 2:

The formation reaction is:

$$\boldsymbol{\frac{3}{2}O_2 \longrightarrow O_3}$$

$$\Delta S^{\circ}_{R,298} = \sum \Delta S^{\circ}_f(products) - \sum \Delta S^{\circ}_f(reactants) = \Delta S^{\circ}_f\, O_3 - \frac{3}{2}\ \Delta S^{\circ}_f\, O_2$$

$$\Delta S^{\circ}_{R,298} = 56.8 - \frac{3}{2}\ \times 49 = 16.7\, cal/K.mol$$

$$\Delta G^{\circ}_{R,298} = \Delta H^{\circ}_{R,298} - T\Delta S^{\circ}_{R,298} = 34000 - 298 \times (-16.7)$$

$$\Delta G^{\circ}_{R,298} = 38976.6\, cal/mol = 38.98\, kcal/mol$$

Exercise 3:

1. Is this reaction thermodynamically possible under standard conditions (298 K)?

We calculate the standard Gibbs free energy change

$$\Delta G^{\circ}_R = \Delta H^{\circ}_R - T\Delta S^{\circ}_R$$

$$\Delta H^{\circ}_R = \sum \Delta H^{\circ}_f(products) - \sum \Delta H^{\circ}_f(reactants)$$

$$\Delta H^{\circ}_R = \Delta H^{\circ}_f\,(CO_2) + \Delta H^{\circ}_f\,(CaO) - \Delta H^{\circ}_f\,(CaCO_3)$$

$$\Delta H^{\circ}_R = -634.11 - 393.14 + 1210.11 = 182.86\, KJ$$

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

$$\Delta S^{\circ}_R = \Delta S^{\circ}_f\,(CO_2) + \Delta S^{\circ}_f\,(CaO) - \Delta S^{\circ}_f\,(CaCO_3)$$

$$\Delta S^{\circ}_R = 39.71 + 213.4 - 92.8 = 160.31\, J/K$$

$$\Delta G^{\circ}_R = 182.86 - 298\, x\, 160.31\ 10^{-3}\,)\ 135.08\, Kj$$

0ΔGo>0, the decomposition of calcium carbonate is not thermodynamically spontaneous (impossible) under standard conditions (298 K).

2. At what temperature does the reaction become thermodynamically possible?

$$\Delta G^{\circ}_{R,T} = \Delta H^{\circ}_{R,298} - T\Delta S^{\circ}_{R,298} = 0 \Rightarrow T = \frac{\Delta H^{\circ}_{R,298}}{\Delta S^{\circ}_{R,298}} = \frac{182.86}{160.31\ 10^{-3}} = 1139.24$$

Exercise 4:

$$\Delta G^{\circ} = \Delta H^{\circ} - T_{final}\Delta S^{\circ}$$

Cooling the liquid from 25 °C to 0 °C

$$\Delta H_1 = n\ C_p\ (l) \cdot (T_{final} - T_{initial}) = 1 \cdot 18 \cdot (273.15 - 298.15) = -451.8 \text{cal}$$

$$\Delta S_1 = n\ C_p\ (l) \cdot ln\left(\frac{T_{final}}{T_{initial}}\right) = 18 \cdot \ln\left(\frac{273.15}{298.15}\right) = 18 \cdot (-0.0889) = -1.6\ cal/K$$

Solidification at 0 °C

$$\Delta H_2 = 1438 \text{cal}$$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{-1438}{273.15} = -5.26 cal/K$$

Cooling the ice from 0 °C to –5 °C

$$\Delta H_3 = n\ C_p\ (s) \cdot (T_{final} - T_{initial}) = \ 1 \cdot 9 \cdot (-5) = -45 cal$$

$$\Delta S_3 = n\ C_p\ (s) \cdot ln\left(\frac{T_{final}}{T_{initial}}\right) = 9 \cdot \ln\left(\frac{268.15}{273.15}\right) = 9 \cdot (-0.0185) = -0.17\ cal/K$$

Total ΔH and ΔS

$$\Delta H_{total} = \Delta H_1 + \Delta H_2 + \Delta H_3 = -451.8 - 1438 - 45 = -1934.8 \text{ cal}$$

$$\Delta S_{total} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -1.6 - 5.26 - 0.17 = -7.03 \text{ cal/K}$$

Compute ΔG at –5 °C (268.15 K)

$$\Delta G^{\circ} = \Delta H^{\circ} - T_{final}\Delta S^{\circ} = \ -1934.8 - 268.15 \times (-7.03) = \ -50.6 \text{ cal/mol}$$

The **Gibbs free energy change** for the spontaneous freezing of 1 mol of water from 25 °C to –5 °C is: $\Delta G° = -50.6$ cal/mol

Exercise 5:

$$PV = nRT \Rightarrow n = \frac{P_1 V_1}{RT_1} = \frac{1\,.\,100}{0.082\,.\,273} = 4.46\ mol$$

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = 273.15 \times \left(\frac{20}{1}\right)^{\frac{0.4}{1.4}} = 805.6\ K$$

Calculate ΔU (Change in Internal Energy)

$$\gamma = \frac{Cp}{Cv} = 1.4 \Rightarrow Cv = \frac{Cp}{\gamma} = \frac{6.97}{1.4} = 4.9786\ cal/molK$$

$$\Delta U = nCv(T_2 - T_1) = 4.46\,.\,4.9786\ (805.6 - 273) = 11818.7\ cal = 11.82\ kcal$$

Calculate ΔH (Change in Enthalpy)

$$\Delta H = nCvp(T_2 - T_1) = \ 4.46\,.\,6.97\ (805.6 - 273) = 16557.1\ cal = \ 16.56\ kcal$$

Calculate ΔS (Entropy change)

$\Delta S=0$ (no heat exchange, reversible)

Calculate ΔF (Change in Helmholtz Free Energy)

$$\Delta F = \Delta U - T_2 \Delta S = \Delta U - 805.6 \times 0 = 11.82 \text{ kcal}$$

Calculate ΔG (Change in Gibbs Free Energy)

$$\Delta G = \Delta H - T_2 \Delta S = \Delta H - 805.6 \times 0 = 16.56\, kcal$$

Exercise 6:

T=25 °C = 298 K.

$$\Delta G_R^\circ = \Delta H_{R,298}^\circ - T\Delta S_{R,298}^\circ$$

Rac → Prod	ΔH°_R (kJ)	ΔS°_R (J/K)	ΔG_R°
$2O_3$ (g) → $3O_2$ (g)	-285.4	137.55	$\Delta G_R^\circ = -285.4 - 298x137x10^{-3} = -326.39$ kJ
$2NO_2$ (g) → N_2O_4 (g)	-57.20	-175.83	$\Delta G_R^\circ = -57.2 + 298x\, 175.83x10^{-3} = -4.82$ kJ
2NO (g) → N_2 (g) + O_2 (g)	-180.74	-24.87	$\Delta G_R^\circ = -180.74 + 298\, x24.87x10^{-3} = -173.33$ kJ
N_2O_5 (g) → $2NO_2$ (g) + ½ O_2 (g)	216.48	938.23	$\Delta G_R^\circ = 216.48 - 298x938.23x10^{-3} = -63.12$ kJ
$2SO_2$ (g) + O_2 (g) → $2SO_3$ (g)	-198.24	-189.63	$\Delta G_R^\circ = -198.24 + 298x189.63x10^{-3} = -141.75$ kJ

Exercise 7:

$$\Delta G_R^\circ = \sum \Delta G_f^\circ(products) - \sum \Delta G_f^\circ(reactants)$$

2 Fe_2O_3 (s) + 3 C (graphite) → 4 Fe (s) + 3 CO_2 (g)

$$\Delta G_R^\circ = 4.\Delta G_f^\circ(Fe,s) + 3.\Delta G_f^\circ(CO_2,g) - 3.\Delta G_f^\circ(C,\text{graphite}) - 2\,.\Delta G_f^\circ(Fe_2O_3,s)$$

$$\Delta G_R^\circ = 4x0 + 3x\,(-395) - 2x742.2 - 3x0 = -2669.4\, kJ$$

$$\Delta G_f^\circ(Fe_2O_3,s) = 0$$

$$\Delta G_f^\circ(C,\text{graphite}) = 0$$

2 CuO (s) + C (graphite) → 2 Cu (s) + CO_2 (g)

$$\Delta G_R^\circ = 2.\Delta G_f^\circ(Cu,s) + \Delta G_f^\circ(CO_2,g) - \Delta G_f^\circ(C,\text{graphite}) - 2\,.\Delta G_f^\circ(CuO,s)$$

$$\Delta G_R^\circ = 2x0 + (-395) - 2\,(-130) - 0 = -135\, kJ$$

$$\Delta G_f^\circ(Cu,s) = 0$$

$$\Delta G_f^\circ(C,\text{graphite}) = 0$$

Non-Corrected Problems for Practice

1. Calculate the temperature at which the following reaction becomes spontaneous: $\Delta H = 50$ kJ/mol, $\Delta S = 100$ J/mol.K.
2. The standard Gibbs free energy change for a reaction is -45 kJ/mol. Determine the equilibrium constant K at 298 K.
3. Using the equation $\Delta G = \Delta H - T\Delta S$, explain under what conditions an endothermic reaction can still be spontaneous.
4. For the Haber process at 298 K, given $\Delta H° = -92.4$ kJ/mol and $\Delta S° = -198$ J/mol.K, determine if the reaction is spontaneous.

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Glossary of Symbols and Thermodynamic Terms

This glossary provides definitions of the main symbols and thermodynamic terms used throughout the course. Units are provided where applicable.

Glossary of Symbols and Units

Symbol	Meaning	Unit
ΔG	Gibbs free energy change	$J \cdot mol^{-1}$ or $kJ \cdot mol^{-1}$
ΔH	Enthalpy change	$J \cdot mol^{-1}$ or $kJ \cdot mol^{-1}$
ΔS	Entropy change	$J \cdot mol^{-1} \cdot K^{-1}$
T	Absolute temperature	K (Kelvin)
P	Pressure	Pa ($N \cdot m^{-2}$), atm, or bar
V	Volume	m^3 or L
n	Amount of substance	mol
R	Universal gas constant	8.314 $J \cdot mol^{-1} \cdot K^{-1}$
H	Enthalpy	J or kJ
U	Internal energy	J or kJ
S	Entropy	$J \cdot mol^{-1} \cdot K^{-1}$
G	Gibbs free energy	J or kJ
A	Helmholtz free energy	J or kJ
C_p	Heat capacity at constant pressure	$J \cdot mol^{-1} \cdot K^{-1}$
C_v	Heat capacity at constant volume	$J \cdot mol^{-1} \cdot K^{-1}$
Δ	Change in a property	—
k	Rate constant or Boltzmann constant	s^{-1} or $J \cdot K^{-1}$ (Boltzmann: 1.380649×10^{-23} $J \cdot K^{-1}$)
μ	Chemical potential	$J \cdot mol^{-1}$
Q	Heat exchanged	J or kJ
W	Work done	J or kJ
K	Equilibrium constant	Dimensionless
ΔU	Internal energy change	J or kJ
ΔE	Energy change (general)	J or kJ

Glossary of Thermodynamic Terms

Term	Definition
Gibbs Free Energy (G)	Thermodynamic potential that indicates the maximum reversible work obtainable from a process at constant temperature and pressure, defined as $G=H-TS$. Predicts spontaneity: process is spontaneous if $\Delta G < 0$.
Spontaneous Process	A process that can occur without external work ($\Delta G<0$).
Enthalpy (H)	Total heat content of a system at constant pressure, defined as $H=U+pV$.
Entropy (S)	Measure of disorder or dispersal of energy in a system.
Standard State	Reference state at 1 bar (or 1 atm) and a specified temperature (usually 298 K).
Equilibrium Constant (K)	Ratio of product activities to reactant activities at equilibrium.
Endothermic Process	Process that absorbs heat from surroundings ($\Delta H>0$).
Exothermic Process	Process that releases heat to surroundings ($\Delta H<0$).
Helmholtz Free Energy (F)	Thermodynamic potential used for systems at constant temperature and volume, defined as $F=U-TS$.
Internal Energy (U)	Total energy contained within a system due to the motion and position of its particles.
Heat Capacity	Amount of heat required to raise the temperature of a system by one degree.
Isothermal Process	Process occurring at constant temperature.
Adiabatic Process	Process with no heat exchange between the system and its surroundings.
Reversible Process	Ideal process that can be reversed without leaving any net change in the system or surroundings.
Irreversible Process	Real process that cannot be reversed without changes in the system or surroundings.
Phase Transition	Transformation of a substance from one state of matter to another (e.g., solid → liquid).

Chemical Potential (μ)	Change in Gibbs free energy when an additional mole of substance is introduced into the system at constant temperature and pressure.
Calorie (cal)	Energy unit; 1 cal=4.184 J.
Kilocalorie (kcal)	1 kcal=1000 cal=4184 J (scientific notation uses lowercase “k”).