Ministère de l’Enseignement Supérieur et de la Recherche Scientifique
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Département de Génie des Procédés

HANDOUT ON THERMODYNAMICS
Lectures and Exercises

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DEPARTEMENT OF PROCESS ENGINEERING

HANDOUT ON THERMODYNAMICS
Lectures and Exercises

For first-year common core programs in Science and Technology, Material Sciences, Engineering, and Life Sciences

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Preamble

The study of thermodynamics transcends mere scientific curiosity; it holds fundamental importance in understanding and shaping our world. This cornerstone module equips you with the knowledge to unlock the mysteries of energy and its transformations, offering a profound perspective on the very dynamics that govern our physical universe.

Thermodynamics delves into the intricate dance of energy transfer and conversion. By unraveling the principles of heat, work, and energy flow, it empowers scientists and researchers to gain deep insights into natural phenomena, from the behavior of substances under varying conditions to the intricate workings of mechanical systems. This knowledge forms the very bedrock of engineering and physics, driving advancements in diverse fields like energy production, environmental science, and mechanical engineering.

But the power of thermodynamics extends far beyond mere comprehension. It serves as a springboard for innovation, fueling the development of sustainable energy technologies and groundbreaking engineering solutions. By harnessing the principles of energy conservation and entropy, we can design efficient and sustainable systems and processes. This empowers us to create a better future, from developing renewable energy sources to optimizing industrial processes for minimal environmental impact.

This tutorial booklet serves as your trusted companion on your journey into the fascinating world of thermodynamics. It's specifically designed for students embarking on their first years in science and technology programs, mechanical engineering, or environmental science and chemical engineering. Additionally, it proves valuable for preparatory school students and those seeking a solid foundation in energy principles.

The exercises and problems meticulously chosen from various universities in Western Algeria and renowned textbooks provide a practical learning experience. The manual, meticulously structured around the curriculum established by the Algerian Ministry of Higher Education and Scientific Research, ensures a comprehensive and consistent learning journey.

Each chapter is thoughtfully crafted to begin with a concise review of key concepts, ensuring a strong foundation for tackling the problems that follow. The appendix provides all necessary data and constants, arming you with the tools you need to succeed. The selection and quantity of exercises are carefully balanced, employing both objective-based and competency-based approaches to cater to diverse learning styles and maximize your understanding.

Contents

Introduction

Studying thermodynamics is of significant importance for engineers across various disciplines. Here are several reasons why the study of thermodynamics is crucial for engineers:

1. Understanding Energy Conversion: Thermodynamics is the study of energy and its transformations. Engineers often work with systems that involve the conversion of energy from one form to another. Whether it's designing engines, power plants, or electronic devices, a solid understanding of thermodynamics is essential for optimizing energy conversion processes.

2. Efficiency Improvement: Engineers aim to design systems and processes that are efficient. Thermodynamics provides the principles and tools to analyze and optimize the efficiency of various engineering systems. This is critical in fields such as mechanical engineering, chemical engineering, and electrical engineering.

3. Heat Transfer Applications: Many engineering systems involve heat transfer, whether it's for heating or cooling purposes. Thermodynamics provides the foundation for understanding heat transfer mechanisms and designing systems to manage heat effectively. This is crucial in fields like HVAC (heating, ventilation, and air conditioning) systems, thermal management in electronics, and more.

4. Combustion and Propulsion Systems: For engineers working in aerospace, automotive, or marine industries, a deep understanding of thermodynamics is necessary. It's crucial for designing combustion engines, jet propulsion systems, and other forms of propulsion where the conversion of chemical energy to mechanical work is involved.

5. Material Selection and Behavior: Thermodynamics is also relevant in materials engineering. Engineers need to understand how materials behave under different temperature and pressure conditions. This knowledge is vital for selecting appropriate materials for specific applications and ensuring the reliability and safety of structures.

6. Environmental Considerations: As sustainability becomes a more significant concern, thermodynamics plays a role in understanding and minimizing the environmental impact of engineering processes. This includes considerations related to energy efficiency, waste heat recovery, and the overall ecological footprint of engineering systems.

7. Problem-Solving Skills: Thermodynamics involves complex mathematical and conceptual challenges. Studying thermodynamics helps engineers develop strong problem-solving skills that can be applied across various engineering disciplines. The ability to analyze and solve thermodynamic problems is a valuable skill for engineers in their professional careers.

In summary, thermodynamics provides the fundamental principles and tools necessary for engineers to analyze, design, and optimize a wide range of systems, making it a cornerstone of engineering education.

Chapter 1

Generalities on Thermodynamics

Thermodynamics is a fascinating branch of physics that studies the relationships between heat, work, temperature, and energy. It governs how energy flows and transforms, dictating the possibilities and limitations of everything from steam engines to refrigerators to the stars themselves.

Here's a brief overview of some key concepts in thermodynamics:

1. Systems and surroundings:

○ **System:** Any part of the universe we choose to focus on for our study. It can be a simple gas confined in a piston-cylinder, a complex chemical reaction, or even an entire galaxy. (Image of a piston-cylinder system)

○ **Surroundings:** Everything outside the system. It can exchange energy with the system in the form of heat, work, or matter. (Image of heat transfer between a system and its surroundings)

2. Energy and its forms:

○ **Energy:** The ability to do work. It exists in various forms, including:

- **Thermal energy:** Associated with the temperature of a system. (Image of thermal energy transfer)
- **Mechanical energy:** Associated with the motion of an object. (Image of mechanical energy transfer)
- **Chemical energy:** Stored in the bonds of molecules. (Image of chemical energy transfer)
- **Electromagnetic energy:** Carried by light and other waves. (Image of electromagnetic energy transfer)

3. Laws of thermodynamics:

○ **First law:** Energy cannot be created or destroyed, only transferred or transformed. In simpler terms, the total energy of a closed system remains constant. (Image of the first law of thermodynamics)

○ **Second law:** Entropy, a measure of disorder, always increases in a closed system over time. This means that processes tend to move towards greater randomness and less usable energy. (Image of the second law of thermodynamics)

○ **Zeroth law:** Two systems in thermal equilibrium with a third system are in thermal equilibrium with each other. This allows us to define and measure temperature. (Image of the zeroth law of thermodynamics)

4. Applications:

Thermodynamics has countless applications in various fields, including:

○ **Engineering:** Design of efficient engines, power plants, and refrigeration systems. (Image of a power plant)

○ **Chemistry:** Understanding chemical reactions and predicting their feasibility. (Image of a chemical reaction)

○ **Cosmology**: Studying the evolution of stars and galaxies. (Image of a galaxy)

○ **Biology:** Understanding energy flow in living organisms. (Image of energy flow in a cell)

This is just a glimpse into the vast and fascinating world of thermodynamics. I encourage you to explore further and delve deeper into this fundamental science that governs the universe around us.

Remember, these are just some basic concepts. As you delve deeper into thermodynamics, you'll encounter more complex ideas and applications. But hopefully, this brief overview has given you a starting point for your exploration!

1.1 Introduction

Thermodynamics (from the Greek "Thermos" meaning heat and "Dunamis" meaning power) is a science that focuses on the study of energy transformations in various forms (chemical, nuclear, mechanical, thermal, etc.), especially the conversion of heat into work and vice versa.

The emergence of thermodynamics is attributed to the development of steam engines in the 2nd century, marking the transformation of heat into usable work. It plays a crucial role in numerous fields such as chemistry, chemical engineering, biology, physics, biochemistry, and thermal machines (engines, heat pumps, etc.). In chemistry, it holds significance as it explores the energy balance of chemical reactions and addresses topics central to modern chemistry, such as the study of reactions at equilibrium.

The system evolves through changes in easily measurable parameters such as temperature, pressure, volume, and chemical composition. Thermodynamics investigates the exchange of matter and energy between a material medium known as the "system" and its surrounding environment referred to as the "external."

Classical thermodynamics only involves macroscopic, experimentally measurable quantities such as temperature, pressure, volume, and composition. The principles of thermodynamics facilitate the integration of this science with mathematics, incorporating mathematical concepts like differentials.

1.2 Mathematical Concepts

1.2.1 Differential of a function with one variable

Let f be a function with a single variable x ($f(x)$), the differential of this function is:

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

1.2.2 Function with several variables. Partial derivatives

The partial derivative of the function f with respect to x is: $\left(\frac{\partial f}{\partial x}\right)_y$

It is the ordinary derivative of f with respect to x, assuming that y is constant.

The partial derivative of the function f with respect to x is: $\left(\frac{\partial f}{\partial x}\right)_x$

1.2.3 Function with several variables. Total derivatives

Let f be a function of several variables. For three variables, it is denoted by $f(x, y, z)$; the total differential of f is defined as:

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz$$

The functions denoted as $\frac{\partial f}{\partial x}$, $\frac{\partial f}{\partial y}$, and $\frac{\partial f}{\partial z}$ are the partial derivatives of f with respect to x, y, and z, respectively.

1.2.4 Differential of a state function (Second cross partial derivative)

As the second derivatives of state functions are continuous, when calculating a second cross partial derivative, the result is independent of the order in which the derivative is taken. Let f be a state function with two variables:

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

1.3 Definitions of Thermodynamic Systems and the External Environment:

Concept of a System:

In thermodynamics, the object under study is referred to as a "system." By definition, a system Ω is a part of the universe with a specified mass, delimited by a closed surface. It is composed of a large number of constituents or elements (atoms, molecules, ions, etc.). The rest of the universe constitutes the external environment.

The combination of the system and the external environment forms the entirety of the Universe.

A system can undergo exchanges with the external environment in the form of energy (thermal or heat Q and work W) or matter. The energies exchanged with the external environment will be positive when received by the system and negative otherwise. A system can be open, closed, or isolated.

1.3.1 Open System

An open system is a system in which both matter and energy can be exchanged with the external environment.

Examples:

- Boiling water in a beaker.
- Living organisms are open systems.

1.3.2 Closed System

A closed system is a system that exchanges only energy with the external environment and does not exchange matter.

Example:

- The gas contained in a cylinder closed by a piston is a closed system.

1.3.3 Isolated System

An isolated system is a system that cannot exchange either matter or energy with the external environment.

Examples:
- The universe is an isolated system.
- Thermos
- Calorimeter

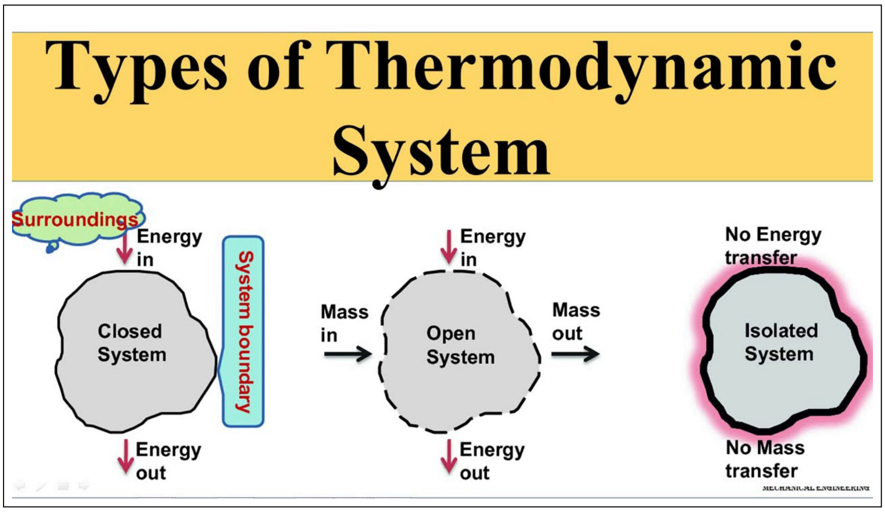

Figure 1.1: Types of Thermodynamic System

1.4 Description of a Thermodynamic System

1.4.1 State of a Thermodynamic System

A system, before undergoing a transformation, exists in a certain state. The state of a system at a given moment is described by a set of macroscopic properties, such as temperature, volume, pressure, density, viscosity, thermal and electrical conductivity, mass, concentration, density, molar quantity, partial pressure, etc. All these properties are referred to as state variables.

1.4.2 State Variables (Parameters or Quantities)

The state of a system at a given moment is defined by a set of macroscopic variables known as "state variables." The state variables characterizing a system include temperature (T), pressure (P), volume (V), mass (m), concentration, density, molar quantity (n), and partial pressure. In thermodynamics, the state variables are T, P, and V. They are divided into two types:

1.4.2.1 Extensive Variables

Extensive variables are proportional to the quantity of matter.

Example: Mass, volume, etc.

1.4.2.2 Intensive Variables

Intensive variables are independent of the quantity of matter.

Example: Temperature, pressure, density, etc.

1.4.3 State Function

State variables are not always independent; some of them may be related by equations known as equations of state or state functions of the form: $f(p, V, T) = 0$. These are mathematical relationships. The most well-known examples include:

- The equation of state for an ideal gas: $pV = nRT$;
- The Van der Waals equation for n moles of gas.

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

The variation of a state function depends only on the initial and final states of the system and not on how the modification is carried out.

1.4.4 Equilibrium State

A system is said to be in a thermodynamic equilibrium state if all its state variables remain constant over time, and there is no transfer of matter and energy (isolated system).

1.4.4.1 Mechanical Equilibrium

The resultant forces acting on the system are zero ($P = P_e$).

1.4.4.2 Thermal Equilibrium

The temperature of the system is uniform (the temperature is the same at every point and does not change over time, i.e., $T = T_e$).

1.4.4.3 Chemical Equilibrium

No variation in the composition of the system.

1.5 Transformations of the state of a system

A transformation of a thermodynamic system is the transition from an initial equilibrium state 1 to another final equilibrium state 2. This transformation involves changes in one or more state variables, leading to an exchange of energy in the form of heat (Q) and work (W) with the external environment. Various types of transformations are distinguished :

1.5.1 Isothermal Transformation

The transformation of a system that occurs at a constant temperature $T_1 = T_2$ (the temperature of the final state T_2 is equal to the temperature of the initial state T_1 is called an isothermal transformation. Isothermal transformations can occur through compression or expansion.

1.5.2 Isobaric Transformation

This is a transformation that occurs at a constant pressure $P_1 = P_2$ (the pressure of the final state P_2 is equal to the pressure of the initial state P_1).

1.5.3 Isochoric Transformation

The transformation of a system is isochoric if it is carried out at constant volume $V_1 = V_2$ (the volume of the final state V_2 is equal to the volume of the initial state V_1).

1.5.4 Adiabatic Transformation

The transformation is adiabatic if it occurs without the exchange of heat with the external environment (Q = 0). Therefore, the system is said to be thermally isolated.

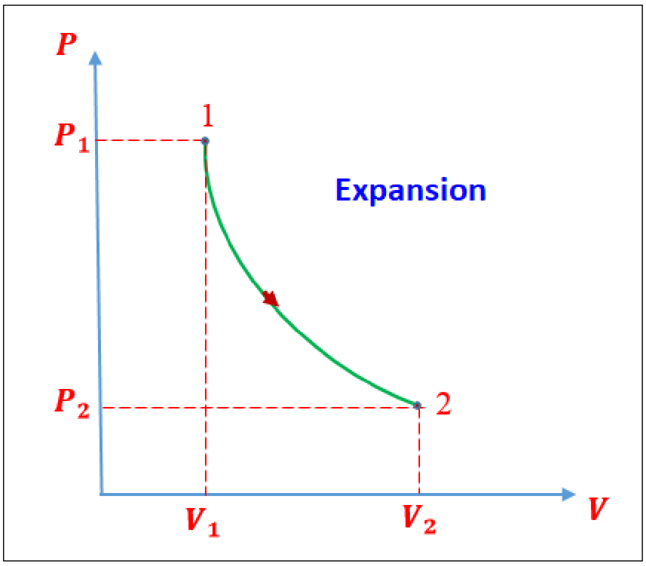

Figure 1.2: Adiabatic expansion

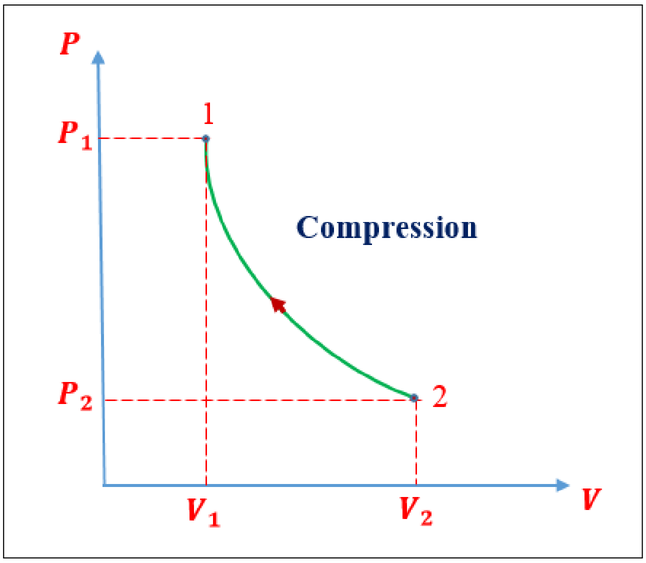

Figure 1.3: Adiabatic compression

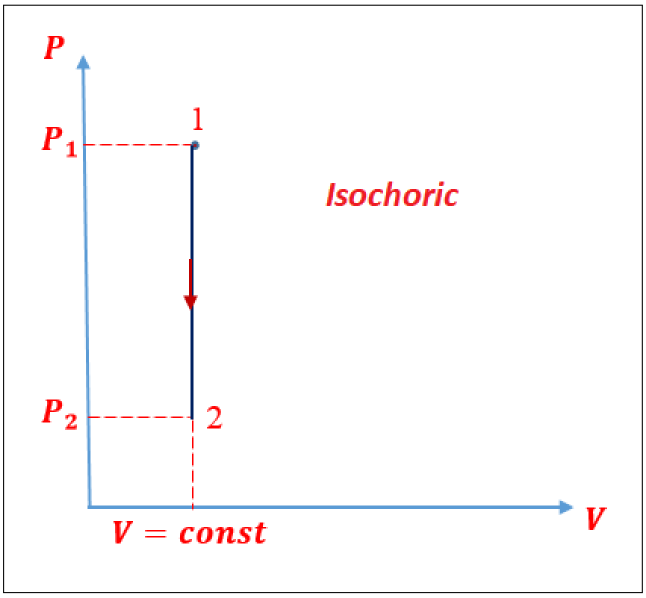

Figure 1.4: Isochoric transformation

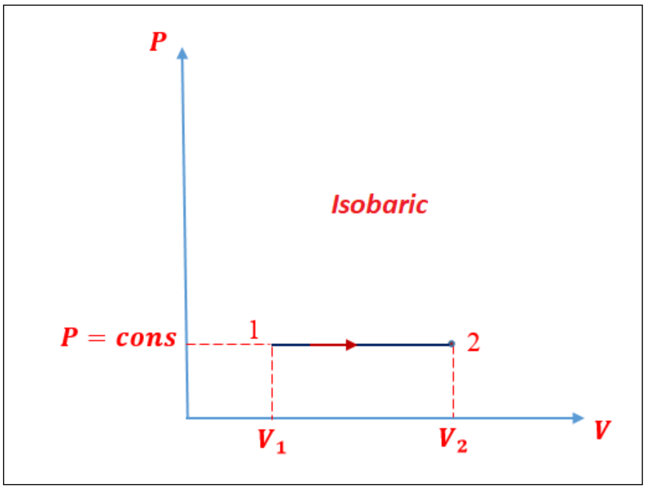

Figure 1.5: Isobaric transformation

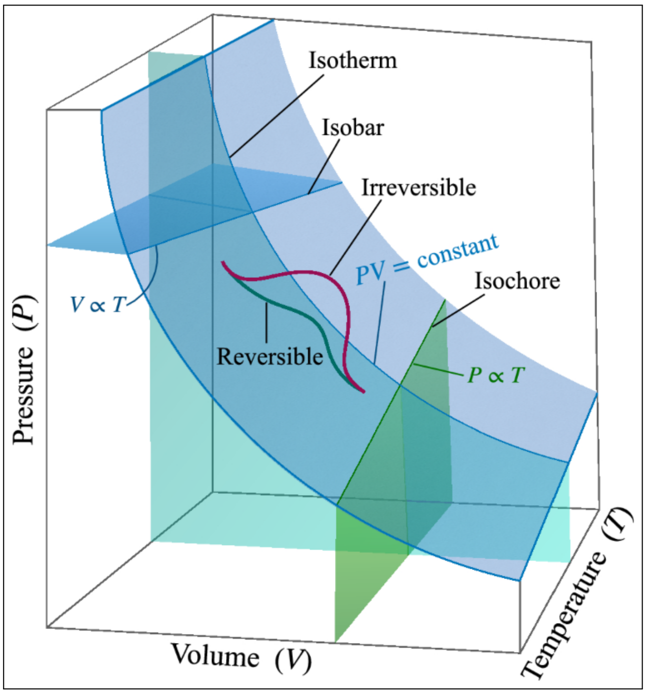

Figure 1.6: Transformation States Diagram

1.5.5 Open Transformation

An open transformation is a transformation where the final state of the system is different from the initial state.

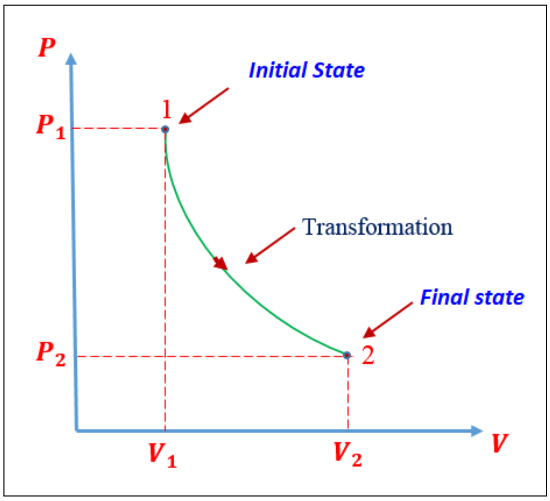

Figure 1.7: Open Transformation Diagram

1.5.6 Closed (Cyclic) Transformation

A closed transformation is a transformation where the final state of the system is identical to the initial state.

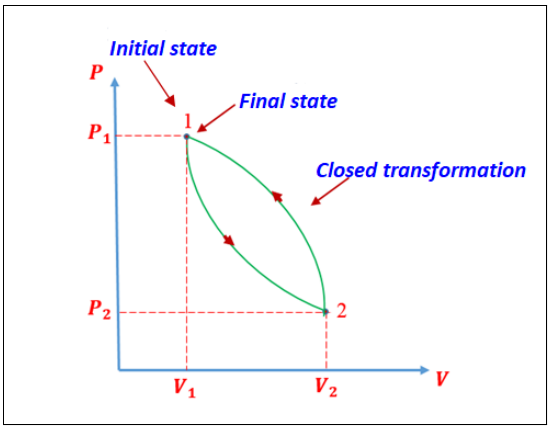

Figure 1.8: Closed (Cyclic) Transformation Diagram

1.5.7 Spontaneous Transformation

It is a transformation that does not require energy from the external environment to occur.

Example: acid-base reaction

1.5.8 Non-Spontaneous Transformation

It is a transformation that requires energy from the external environment.

Example: water vaporization

1.5.9 Mono-thermal Transformations

The system is in contact with only one heat source, which enforces equality between the initial and final temperatures of the system.

1.5.10 Infinitesimal Transformation

A transformation is called infinitesimal when the initial and final equilibrium states are infinitely close.

1.5.11 Quasi-Static Transformation

A transformation of a system is quasi-static if the system is at every instant infinitely close to an internal equilibrium state.

1.5.12 Reversible Transformation

A transformation is called reversible (or ideal) if it satisfies two conditions:

- It must be infinitely slow.
- It must be reversible, i.e., it occurs in both directions (from A $\longrightarrow$ B and similarly in the opposite direction, B $\longrightarrow$ A). In a reversible transformation, the system evolves through a series of closely spaced equilibrium states. This assumes the absence of friction, diffusion (mass transfer), and system inhomogeneity (heat transfer). These phenomena are the causes of the irreversibility of the system.

For example, a gradual heating or cooling of a system by coming into contact with an infinite number of heat sources ($T = T + dT$, etc.).

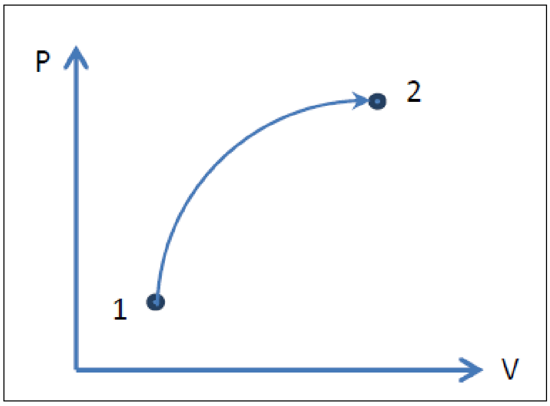

Figure 1.9: Reversible Transformation Diagram

1.5.13 Irreversible Transformation

An irreversible transformation is a real transformation that does not go through a series of equilibrium states; hence, it cannot be described in both directions. It is a rapid (abrupt) transformation.

Example: life processes, explosive reactions.

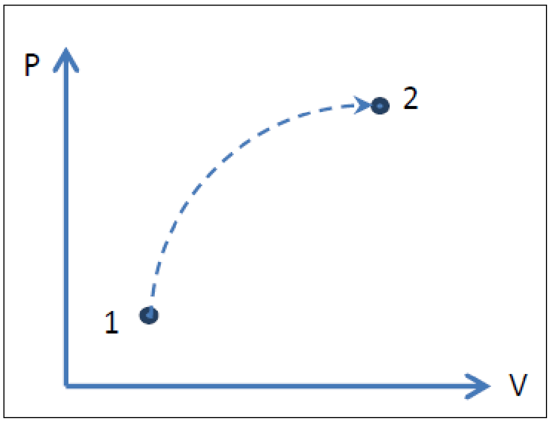

Figure 1.10: Irreversible Transformation Diagram

1.6 Graphical Representation of Ideal Gas Transformations

1.6.1 Ideal Gases

A gas is considered ideal if it is subjected to low pressure at room temperature. At low pressure, the Van der Waals forces are negligible, suggesting that the shape of atoms and molecules is spherical.

The ideal gas is a theoretical model based on the following assumptions:

- There is no interaction between molecules (molecules are far apart).
- Molecules are treated as point masses.
- Collisions between molecules or with the walls of the container are perfectly elastic.

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

- P: pressure of the gas
- V: volume occupied by the gas
- n: number of moles of gas
- T: temperature in Kelvin

R: constant $= 0.082$ L.atm.mol^{-1} K^{-1} $= 8.314$ J.mol^{-1} K^{-1} $= 1.987$ cal.mol^{-1} K^{-1}.

1.6.2 Clapeyron Diagram: $P = f(V)$ in the (P, V) plane

The Clapeyron diagram is a graph representing the evolution of transformations at constant temperature. In this diagram, pressure (P) is plotted on the ordinate axis, and volume (V) is plotted on the abscissa axis.

1.6.3 Amagat's Diagram: $pV = f(p)$ in the (pV, p) plane

Amagat's diagram is a thermodynamic graph that represents, at constant temperature, the variation of the product of pressure (P) and volume (V) as a function of pressure. It can also depict the evolution of the compressibility factor as a function of pressure. This diagram is named after the French physicist Émile Amagat. Amagat's diagram is used to graphically represent the deviation in behavior of a real gas compared to an ideal gas.

1.7 Review of the Laws of Ideal Gases

1.7.1 Boyle's Law (Mariotte's Law)

In 1662, Robert Boyle and Edme Mariotte demonstrated that the product of the pressure P of a gas by its volume V depends only on the temperature. It was stated that at constant temperature ($T =$ Constant), the pressure P of a given mass m of gas is inversely proportional to its volume V ($P = \frac{nRT}{V}$). The product $P \cdot V$ remains constant. When the gas is taken between two states, the equation is expressed in the form:

$$P_1V_1 = P_2V_2 = nRT = \text{Constant}$$

1.7.1.1 Gay-Lussac's Law

In 1800, Louis Joseph Gay-Lussac demonstrated that at constant pressure ($P =$ Constant), the volume occupied by a specific quantity of an ideal gas is proportional to the absolute temperature.

$$\frac{V}{T} = nRT \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2} = nRT = \text{Constant}$$

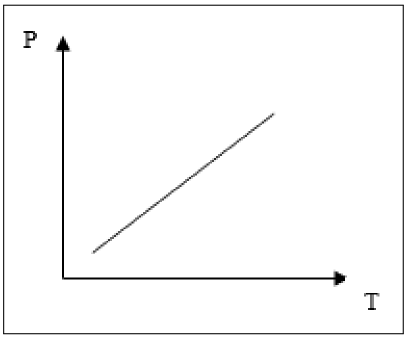

Figure 1.11: Gay-Lussac's Law Diagram

1.7.2 Charles's Law

For a given mass of gas at constant volume ($V = \text{Constant}$), the pressure P of the gas is directly proportional to its absolute temperature T ($P = \frac{nRT}{V}$).

$$\frac{P}{T} = nRT \Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2} = nRT = \text{Constant}$$

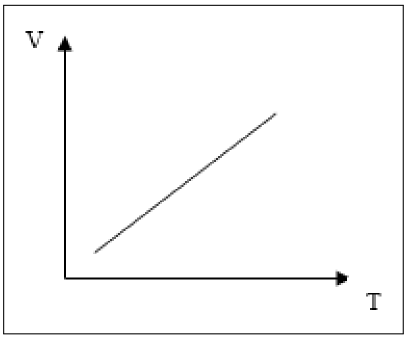

Figure 1.12: Charles's Law Diagram

1.7.3 Dalton's Law

Dalton's Law, or the law of partial pressures, is a thermodynamic law formulated by John Dalton in 1801. This law states that the pressure of a mixture of ideal gases is equal to the sum of the partial pressures of its components. It is named in honor of John Dalton.

For a mixture of gases assumed to be ideal with the total number of moles n where:

$$n = \sum_i n_i \Rightarrow n = n_1 + n_2 + n_3 + ... + n_k$$

The law of ideal gases applied to this mixture is expressed in the form:

$$PV = nRT \Rightarrow P = \frac{nRT}{V} \Rightarrow P = \frac{n_1 + n_2 + n_3 + ...n_k}{V}$$

This equation is thus presented in the following form:

$$P = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + ... + \frac{n_kRT}{V}$$

The terms that make up this pressure are merely forms of pressure known as partial pressures of the gas, with:

$$P_i = \frac{n_iRT}{V}$$

The total pressure is therefore: $P = \sum_i P_i$

The ratio between partial pressure and total pressure represents the molar fraction of the gas.

$$\frac{P_i}{P} = \frac{\frac{n_iRT}{V}}{\frac{\sum n_iRT}{V}} = \frac{n}{\sum n_i} \Rightarrow \frac{P_i}{P} = \chi_i$$

$$P_i = P\chi_i$$

This is Dalton's law with χ_i representing the molar fraction.

Exercise 1:

The following figure represents the three main temperature scales:

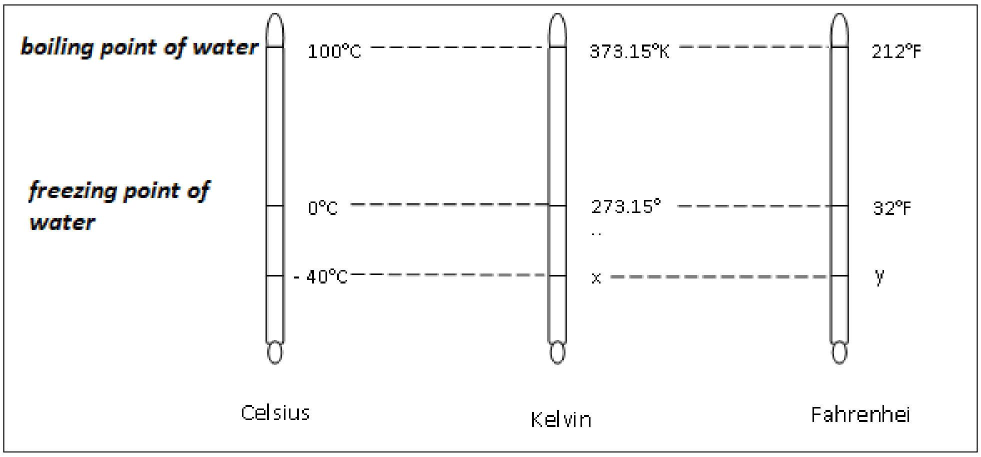

Figure 1.13: The three main temperature scales

1- Complete this figure. Explain, knowing that the transformation from one scale to another is linear.

2- What is the temperature in °C of a healthy person with 98.6°F?

3- At what temperature will the thermometer graduated in °F and the thermometer graduated in degrees Celsius indicate the same value? What is this temperature in Kelvin?

Solution:

We have the linear relationship :$\theta = ax + b$

The relationship between the Kelvin sclae and the Celsius sclae:

$$T(K) = a \cdot T(°C) + b \Rightarrow \begin{cases} 273.15 = a \cdot 0 + b; \\ 373.15 = a \cdot 100 + b. \end{cases}$$

We solve the system of two equations and find :

$T(K) = T(°C) + 273.15$ or $T(°C) = T(K) - 273.15$

The relationship between the Celsius scale and the Fahrenheit scale :

$$T(°C) = a \cdot T(°F) + b \Rightarrow \begin{cases} 0 = a \cdot 32 + b; \\ 100 = a \cdot 212 + b. \end{cases}$$

After solving the two equations, we find that :

$T(°C) = \frac{10}{18} T(°F) - \frac{320}{18}$ or $T(°F) = 1.8 T(°C) + 32$

The relationship between the Fahrenheit scale and the Kelvin scale :

$$T(°F) = a \cdot T(°K) + b \Rightarrow \begin{cases} 32 = a \cdot 273.15 + b; \\ 212 = a \cdot 373.15 + b. \end{cases}$$

After solving the two equations, we find that :

$T(°F) = 1.8 T(K) - 459.67$ or $T(K) = \frac{10}{18} T(°F) + 255.37$

Calculating the temperature in °C corresponding to T = 98.6 °F

$T(°C) = \frac{10}{18} T(°F) - \frac{320}{18} \Rightarrow T(°C) = \frac{10}{18} \cdot 98.6 - \frac{320}{18} \Rightarrow T(°C) = 37°C$

Calculating the temperature when $T(°C) = T(°F)$

We use the relationship :

$T(°C) = \frac{10}{18}T(°F) - \frac{320}{18}$

$\Rightarrow T(°C) = \frac{10}{18}T(°C) - \frac{320}{18}$

$\Rightarrow T = -40°C = -40°F$

$T(K) = T(°C) + 273.15$

$\Rightarrow T(K) = -40 + 273.15$

$\Rightarrow T(K) = 233.15K$

Exercise 02:

Provide the dimensions of the ideal gas constant (R) and determine its value when expressed in:

1. $\mathrm{L \cdot atm\,mol^{-1} \cdot K^{-1}}$
2. $\mathrm{J/mol^{-1} \cdot K^{-1}}$
3. $\mathrm{L \cdot mmHg\,mol^{-1} \cdot K^{-1}}$
4. $\mathrm{Cal/mol^{-1} \cdot K^{-1}}$

Solution:

Provide the dimensions of the ideal gas constant (R) and determine its value when expressed in:

1. $\mathrm{L \cdot atm\,mol^{-1} \cdot K^{-1}}$

The ideal gas constant R has the dimensions of volume pressure divided by temperature times the amount of substance. Its value when expressed in liters, atmospheres, moles, and kelvin ($\mathrm{L \cdot atm\,mol^{-1} \cdot K^{-1}}$) is approximately 0.0821.

2. $\mathrm{J/mol^{-1} \cdot K^{-1}}$

To convert from $\mathrm{L \cdot atm\,mol^{-1} \cdot K^{-1}}$ to $\mathrm{J/mol^{-1} \cdot K^{-1}}$, we use the conversion factor $1\,\mathrm{atm} = 101.325\,\mathrm{kPa}$ and $1\,\mathrm{L} = 0.001\,\mathrm{m^3}$. Thus, $R = 8.314\,\mathrm{J/mol^{-1} \cdot K^{-1}}$.

3. $\mathrm{L \cdot mmHg\,mol^{-1} \cdot K^{-1}}$

To convert from $\mathrm{L \cdot atm\,mol^{-1} \cdot K^{-1}}$ to $\mathrm{L \cdot mmHg\,mol^{-1} \cdot K^{-1}}$, we use the conversion factor $1\,\mathrm{atm} = 760\,\mathrm{mmHg}$. Thus, $R = 62.36\,\mathrm{L \cdot mmHg\,mol^{-1} \cdot K^{-1}}$.

4. $\mathrm{Cal/mol^{-1} \cdot K^{-1}}$

To convert from $\mathrm{L \cdot atm\,mol^{-1} \cdot K^{-1}}$ to $\mathrm{Cal/mol^{-1} \cdot K^{-1}}$, we use the conversion factor $1\,\mathrm{J} = 0.239\,\mathrm{cal}$. Thus, $R = 1.987\,\mathrm{Cal/mol^{-1} \cdot K^{-1}}$.

Exercise 03:

It is found that a mass of 0.896 g of a gaseous compound containing only nitrogen and oxygen occupies a volume of 524 $\mathrm{cm^3}$ at a pressure of 730 mm Hg and a temperature of 28°C. What is the molar mass and chemical formula of this compound?

Solution :

Given: Mass of the compound N_xO_y, $m = 0.896$ g Volume of the compound, $V = 524$ $\mathrm{cm^3}$ Pressure, $P = 730$ mm Hg Temperature, $T = 28°C = 28 + 273.15$ K

The molar mass of the compound : $M = \dfrac{m}{n}$

We assume that this compound is an ideal gas; we apply the ideal gas law : $PV = nRT \Rightarrow n = \dfrac{PV}{RT}$

We substitute the number of moles (n) into the molar mass relation, and we find :

$M = \dfrac{mRT}{PV} = \dfrac{0.869 \cdot 63.36}{730 \cdot 524 \cdot 10^{-3}} = 43.97 g/mol$

The molar mass of the compound $N_xO_y$is M = 14x + 16y = 43.97 g/mol

With x and y being integers, the suitable pair is x = 2 and y = 1.

Therefore, the chemical formula is: N_2O

Exercise 04:

A gas mixture consists of 0.2 g of H_2, 0.21 g of N_2, and 0.51 g of NH_3 at a pressure of one atmosphere and a temperature of 27°C. Calculate:

1. The mole fractions.
2. The partial pressure of each gas.
3. The total volume.

Data: M(H) = 1 g·mol^{-1} and M(N) = 14 g·mol^{-1}.

Solution :

Given:

- Mass of hydrogen (H_2), $m_{H_2} = 0.2$ g
- Mass of nitrogen (N_2), $m_{N_2} = 0.21$ g
- Mass of ammonia (NH_3), $m_{NH_3} = 0.51$ g
- Pressure, $P = 1$ atm
- Temperature, $T = 27°C = 27 + 273.15$ K
- Molar mass of hydrogen, $M(H) = 1$ g/mol
- Molar mass of nitrogen, $M(N) = 14$ g/mol

To find:

1. Mole fractions of each gas.
2. Partial pressure of each gas.
3. Total volume of the gas mixture.

1. Mole fractions:

The number of moles of each gas can be calculated using the formula:

$$n_i = \frac{m_i}{M_i}$$

where m_i is the mass of gas i and M_i is its molar mass.

For hydrogen:

$$n_{H_2} = \frac{0.2\,\mathrm{g}}{1\,\mathrm{g/mol}} = 0.1\,\mathrm{mol}$$

For nitrogen:

$$n_{N_2} = \frac{0.21\,\mathrm{g}}{28\,\mathrm{g/mol}} \approx 0.0075\,\mathrm{mol}$$

For ammonia:

$$n_{NH_3} = \frac{0.51\,\mathrm{g}}{17\,\mathrm{g/mol}} \approx 0.03\,\mathrm{mol}$$

The total number of moles, n_{total}, is the sum of the moles of each gas:

$$n_{\text{total}} = n_{H_2} + n_{N_2} + n_{NH_3} = 0.1375 mol$$

Mole fraction (X_i) of each gas is given by:

$$X_i = \frac{n_i}{n_{\text{total}}}$$

The mole fraction of H_2 is $X_{H_2} = \dfrac{0.1}{0.1375} = 0.727$

The mole fraction of N_2 is $X_{N_2} = \dfrac{0.0075}{0.1375} = 0.055$

The mole fraction of NH_3 is $X_{NH_3} = \dfrac{0.03}{0.1375} = 0.218$

Calculate X_i for each gas using the calculated moles.

2. Partial pressures:

Partial pressure (P_i) of each gas is given by the formula:

$$P_i = X_i \cdot P_{\text{total}}$$

where P_{total} is the total pressure of the gas mixture.

Calculate P_i for each gas using the calculated mole fractions and the given total pressure ($P_{\text{total}} = 1$ atm).

3. Total volume:

The ideal gas law states:

$$PV = nRT$$

We rearrange it to find the total volume (V) of the gas mixture:

$$V = \frac{n_{\text{total}} RT}{P_{\text{total}}}$$

Substitute the values of n_{total}, R, T, and P_{total} to calculate V.

Perform the calculations for each part to find the answers.

Exercise 05:

Consider a mass of 80 g of a gaseous mixture of nitrogen and methane, consisting of 31.14% by weight of nitrogen and occupying a volume of 0.995 liters at 150°C.

1. Calculate the total pressure of the gas mixture.
2. Calculate the partial pressures of each gas.

Solution :

Given:

- Mass of the gaseous mixture, $m = 80$ g
- Nitrogen content by weight, $w_{N_2} = 31.14\%$
- Volume of the gas mixture, $V = 0.995$ L
- Temperature, $T = 150°C = 150 + 273.15$ K

We are asked to:

1. Calculate the total pressure of the gas mixture.
2. Calculate the partial pressures of each gas.

1. Total pressure of the gas mixture:

We'll first calculate the number of moles of nitrogen (n_{N_2}) and methane (n_{CH_4}) in the mixture.

Given that the mixture is 31.14% nitrogen by weight, we can calculate the mass of nitrogen (m_{N_2}) as:

$$m_{N_2} = 0.3114 \times 80\,\text{g} = 24.912\,\text{g}$$

To find the number of moles of nitrogen, we use its molar mass $M_{N_2} = 28\,\text{g/mol}$:

$$n_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{24.912\,\text{g}}{28\,\text{g/mol}} \approx 0.889\,\text{mol}$$

The mass of methane (m_{CH_4}) can be calculated as the difference between the total mass and the mass of nitrogen:

$$m_{CH_4} = 80\,\text{g} - 24.912\,\text{g} = 55.088\,\text{g}$$

To find the number of moles of methane, we use its molar mass $M_{CH_4} = 16\,\text{g/mol}$:

$$n_{CH_4} = \frac{m_{CH_4}}{M_{CH_4}} = \frac{55.088\,\text{g}}{16\,\text{g/mol}} \approx 3.443\,\text{mol}$$

The total number of moles of the gas mixture is the sum of the moles of nitrogen and methane:

$$n_{\text{total}} = n_{N_2} + n_{CH_4}$$

Now, we can use the ideal gas law to find the total pressure (P_{total}) of the gas mixture:

$$PV = nRT$$

$$P_{\text{total}}V = n_{\text{total}}RT$$

$$P_{\text{total}} = \frac{n_{\text{total}}RT}{V}$$

Substitute the given values for V, T, and the gas constant $R = 0.0821\,\mathrm{L} \cdot \mathrm{atm/mol} \cdot \mathrm{K}$ to calculate P_{total}.

$$P_{\text{total}} = 151.049 \ atm$$

2. Partial pressures of each gas:

Once we have the total pressure (P_{total}), we can use the mole fractions of nitrogen and methane to calculate their partial pressures.

The mole fraction of nitrogen (X_{N_2}) is given by:

$$X_{N_2} = \frac{n_{N_2}}{n_{\text{total}}}$$

Similarly, the mole fraction of methane (X_{CH_4}) is given by:

$$X_{CH_4} = \frac{n_{CH_4}}{n_{\text{total}}}$$

Now, the partial pressure (P_i) of each gas is given by:

$$P_i = X_i \cdot P_{\text{total}}$$

Calculate P_{N_2} and P_{CH_4} using their respective mole fractions and the total pressure.

Perform the calculations to find the answers for each part.

Chapter 2

Exchanged Energies (Heat and Work) and Calorimetry

Exchanged Energies: Heat and Work

Energy is never lost or created, it only transforms! Understanding how energy changes form is crucial in various fields, from physics and chemistry to biology and engineering. We encounter two main forms of energy exchange: heat and work. Heat is transferred between objects at different temperatures. Imagine a hot cup of coffee next to a cold ice cube. Heat flows from the coffee (higher temperature) to the ice cube (lower temperature) until they reach thermal equilibrium (same temperature). This flow of thermal energy is what we call heat.

Work involves a force acting through a distance. For example, lifting a book against gravity requires work. The energy used to do this work can be converted into other forms, like heat. Imagine rubbing your hands together. The friction generates heat due to the work done by the force of your rubbing against each other.

Calorimetry is the science of measuring heat. Calorimeters are instruments designed to isolate a system and measure the heat exchanged during a process. They often involve containers with good thermal insulation to minimize heat loss to the surroundings. By measuring the temperature changes and masses of the substances involved, we can calculate the amount of heat transferred.

2.1 Notion of temperature

2.1.1 Thermometry

Thermometry is the field of measuring temperature using instruments called thermometers. If the thermometer is in thermal equilibrium with the body whose temperature we want to measure, the temperature measured by the thermometer is that of the considered body. The temperature, denoted as T, is a macroscopic quantity that measures the degree of heat in a system. From a microscopic point of view, it represents the "motion" or agitation of molecules and atoms within the considered system.

2.1.2 The zeroth law of thermodynamics

The zeroth law states that two bodies A and B, when brought into contact, tend towards a state of thermal equilibrium. They are thus characterized by the same temperature. Two bodies in thermal equilibrium with a third are in thermal equilibrium with each other.

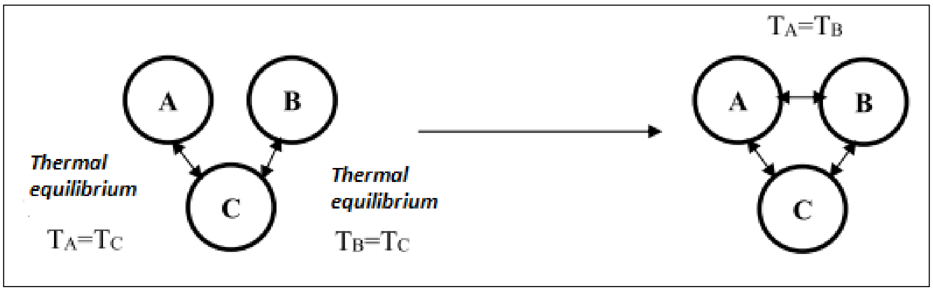

Figure 2.1: Thermal equilibrium

2.1.3 Centesimal Scale

The centesimal scale is a linear scale defined by the thermodynamic function:

$$t = aX + b \tag{2.1}$$

Where a and b are determined by two fixed points, defined as follows:

- When the thermometer is in melting ice under normal atmospheric pressure (1 atm), the temperature is t = 0,

- When the thermometer is in boiling water vapor under normal atmospheric pressure, the temperature is t = 100.

If we designate by: t, t_0, and t_{100} the thermometric values corresponding to temperatures t, 0, and 100, respectively, the relation 2.1 is then written as follows :

$$0 = aX_0 + b \tag{2.2}$$

$$100 = aX_100 + b \tag{2.3}$$

Then we deduce :

$a = \dfrac{100}{X_{100} - X_0}$ *and* $b = 100\dfrac{-X_0}{X_{100} - X_0}$

When we substitute a and b into relation 2.1, it follows that :

$t = \dfrac{100(X - X_0)}{X_{100} - X_0} \Rightarrow t = \dfrac{100}{X_{100} - X_0}X + \dfrac{100}{X_0 - X_{100}}X_0$

Celsius Scale

The Celsius scale, denoted as °C, with reference points 0 and 100 corresponding respectively to the melting point and boiling point of water under atmospheric pressure. This scale was developed by the Swedish astronomer Anders Celsius (1701–1744).

2.1.4 Kelvin Absolute Scale

This is the universal scale also known as the Kelvin degree, denoted as K, the "SI unit of temperature." This scale was proposed by Lord Kelvin (1824-1907), where the lower temperature corresponds to absolute zero, which is -273.15 °C.

The relationship between the Kelvin scale and the Celsius scale is given by the relation:

The relation defines the absolute temperature scale (K) in kelvin in terms of Celsius as follows :$T(K) = T(°C) + 273.15$.

Denoted as °F, on this scale, the temperature of the melting and boiling points of water under atmospheric pressure are 32 °F and 212 °F, respectively. The relationship between the Celsius and Fahrenheit scales is given by the expression: $T(°F) = 1.8T(°C) + 32$.

However, the relationship between the Kelvin and Fahrenheit scales is: $T(°F) = 1.8T(K) - 460.3$

2.1.5 Operating Principle of a Thermometer

When thermal equilibrium is established following temperature variations between two bodies, several physical phenomena related to the functioning mode of the used thermometer can occur, namely:

- Expansion of a liquid (volume change): alcohol thermometers, mercury thermometers

- Change in electrical resistance (R): Resistance thermometer, thermistor (Platinum resistors usable between 200 to 630 °C and semiconductor resistors in Germanium (Ge) for T $<$ 77 K)

- Emission of radiation (radiated energy E): optical pyrometers (Optical pyrometers above 1063 °C)

◆ Variation in potential difference between two metals: Thermocouple, example: Pt–Pt rhodium (Thermocouples based on the Seebeck effect from 600 to 1300 °C)

For each thermometric quantity x, there is an associated temperature change ΔT.

2.2 Pressure

Pressure, denoted as P, is defined as the pressing force dF exerted by a fluid in equilibrium on a surface element dS : $P = \frac{dF}{dS}$

dF is normal to the surface element dS.

From a microscopic perspective, pressure is solely due to the collisions of molecules or atoms on the system's walls. The unit of pressure in the International System of Units (SI) is the Pascal (Pa).

$$Pa = \frac{N}{m^-3}$$

$1\ atm = 1.013 \cdot 10^5 Pa = 1.013\ bar = 760\ mmHg = 760 Torr$

2.3 Concept of Heat and Work

During a transformation, a system can exchange energy with the external environment in the form of heat and mechanical work.

2.3.1 Work of Pressure Forces (W)

Work is another form of energy (mechanical energy) required to move or deform a body.

On a microscopic scale, it is an energy exchanged in an orderly manner (thanks to displacement, for example, of a piston that imparts a certain direction to the atoms).

Mechanical work results from a change in the volume of the deformable (non-rigid) system due to the pressure forces acting on that system.

Work is not a state function; it depends on the path taken.

Consider a system contained in a cylinder closed by a piston. Apply a pressure force to the piston.

The work done on a piston (2.2 is the force (F) multiplied by the displacement (dy):

$$\mathrm{d}W = F_{\text{ext}}\,\mathrm{d}y$$

Pressure is :

$$P = \frac{F}{S} \implies F = P \cdot S$$
$$\mathrm{d}W = P_{\text{ext}} \cdot S\,\mathrm{d}y$$

The volume of the cylinder is (S: Surface) :

$$V = S \cdot y \implies \mathrm{d}V = S \cdot \mathrm{d}y$$
$$\mathrm{d}W = P_{\text{ext}} \cdot \mathrm{d}V$$

By convention, the received work dW is greater than 0, and for a compression dV less than 0; therefore :

$$\mathrm{d}W = -P_{\text{ext}}\,\mathrm{d}V$$

After integration, we find : $W = -\int_1^2 P_{ext} dV$

[W] = Pa.m^3 = Joules

[W] = l. atm 1 l.atm = 101.325 J

[W] = Cal 1 Cal = 4.185 J

If the volume increases (expansion dV > 0): W < 0 (the system does work on the external surroundings).

If the volume decreases (compression dV < 0): W > 0 (the system receives work from the external surroundings).

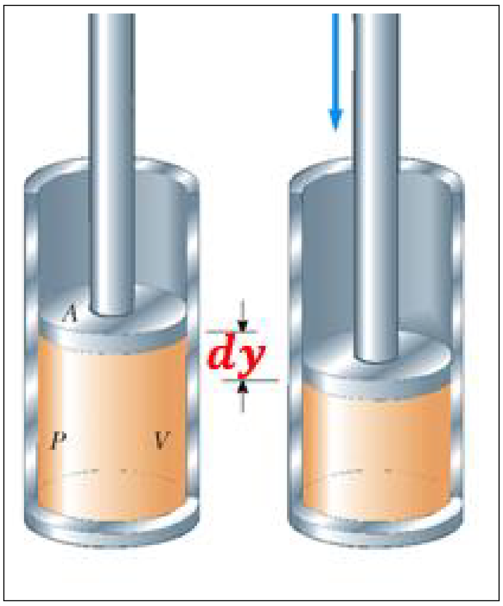

Figure 2.2: Work done on a piston

2.3.1.1 Reversible Transformation Work:

For a reversible transformation (during which all intermediate states are defined): the pressure of the gas P is equal to the external pressure.

We have: P = P_{ext}

As a result,: $W_{rev} = -\int_1^2 PdV \Rightarrow W_{rev} = -P\int_{V_1}^{V_2} dV$

2.3.1.2 Irreversible Transformation Work

For irreversible transformations that are rapid and spontaneous: P ≠Pext, the work is given by the equation

$$W_{irrev} = -\int_1^2 PdV \Rightarrow W_{irrev} = -P\int_{V_1}^{V_2} dV$$

2.3.1.3 Pressure work of an ideal gas

In the case of an ideal gas, several types of transformations can be distinguished, where the work received or released by the system can be calculated each time during these transformations :

a Isothermal transformation (T = Constant)

For an isothermal transformation of an ideal gas from the initial state (1) to a final state (2), only the variables P and V change. If the pressure P increases, the volume V decreases, and vice versa.

$The\,initial\,state\,(1) : V_1, P_1, and\,T_1$

$$The\,final\,state(2) : V_2, P_2, and\,T_2 \begin{cases} P_1V_1 = nRT_1 \\ P_2V_2 = nRT_2 \\ T_1 = T_2 = T \end{cases} \Rightarrow \begin{cases} P_1V_1 = nRT \\ P_2V_2 = nRT \end{cases}$$

$$\{\ P_1V_1 = P_2V_2 = PV = nRT = constant\ \ \{\ P_1V_1 = P_2V_2 = PV = nRT = constant$$

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

Reversible case :

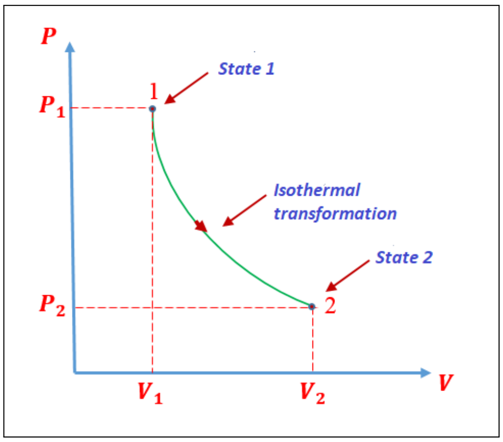

Figure 2.3: Reversible case diagram

$$\mathrm{d}W_{\text{rev}} = -P\,\mathrm{d}V \quad , \quad PV = nRT \implies P = \frac{nRT}{V}$$

$$\mathrm{d}W_{\text{rev}} = -nRT\frac{\mathrm{d}V}{V} \quad , \quad W_{\text{rev}} = \int_{V_1}^{V_2} -nRT\frac{\mathrm{d}V}{V}$$

$$W_{\text{rev}} = -nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} \quad , \quad W_{\text{rev}} = -nRT\,[\ln V]_{V_1}^{V_2}$$

$$W_{\text{rev}} = -nRT\,[\ln V_2 - \ln V_1] \quad , \quad W_{\text{rev}} = -nRT\left[\ln\frac{V_2}{V_1}\right]$$

$$W_{\text{rev}} = -nRT\ln\frac{V_2}{V_1} \quad , \quad W_{\text{rev}} = nRT\ln\frac{V_1}{V_2} \quad , \quad W_{\text{rev}} = nRT\ln\frac{P_2}{P_1}$$

Irreversible case:

$$\mathrm{d}W_{\text{irrev}} = -P_{\text{ext}}\,\mathrm{d}V \quad , \quad \delta W_{\text{irrev}} = \int_{V_1}^{V_2} -P_{\text{ext}}\,\mathrm{d}V \quad , \quad W_{\text{irrev}} = -P_{\text{ext}}[V]_{V_1}^{V_2} \quad , \quad W_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1)$$

$$PV = nRT \to V = \frac{nRT}{P} \quad , \quad W_{\text{irrev}} = -P_{\text{ext}}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right) \quad , \quad W_{\text{irrev}} = -P_{\text{ext}}\cdot nRT\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$$

b Isochoric transformation (V = Constant)

In the isochoric transformation of an ideal gas from the initial state (1) to a final state (2), only the variables P and T change. The pressure P is proportional to the temperature T.

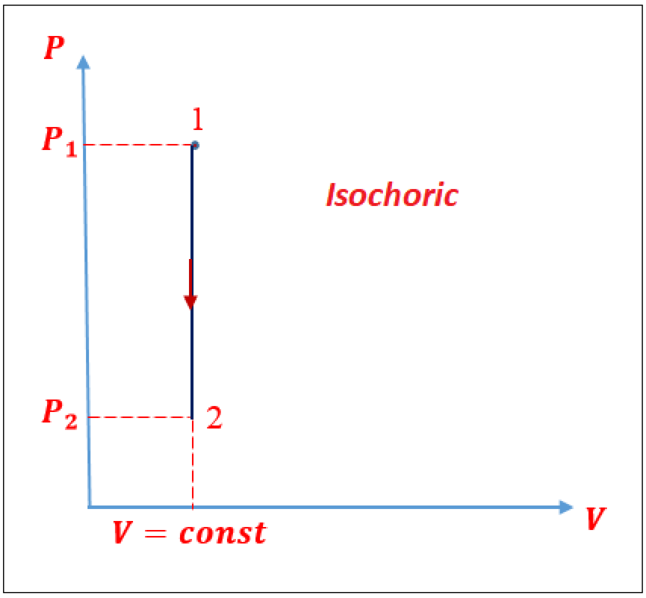

Figure 2.4: Isochoric transformation

$$dW = -PdV \to W = \int_{V_1}^{V_2} -PdV = constant \to dV = 0 \Rightarrow W = 0$$

b Isobaric transformation (P = Constant)

In the isobaric transformation of an ideal gas from the initial state (1) to a final state (2), only the variables V and T change. The volume V is proportional to the temperature T.

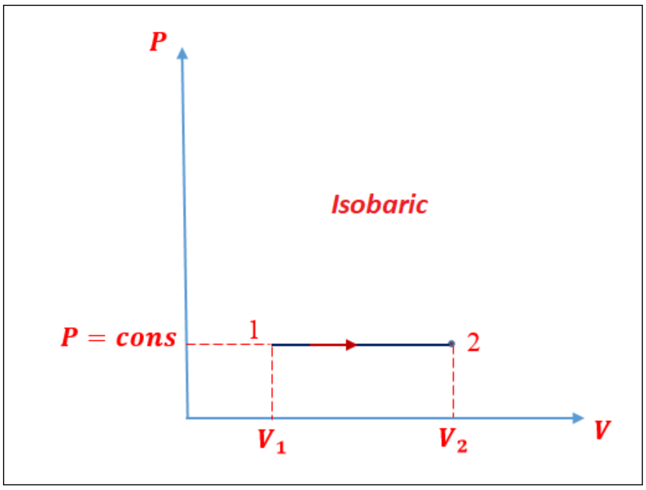

Figure 2.5: Isobaric transformation

The system evolving from the initial state (1) to the final state (2) leads to: $P_1 = P_2 = P_{ext}$ (The pressure at state 1 equals the pressure at state 2 equals the external pressure).

$$dW = -PdV \implies W = \int_{V_1}^{V_2} -PdV \quad ,W = -P(V_2 - V_1) \implies W = -PV_2 + PV_1 \quad ,W = -nRT_2 + nRT_1 \implies W = nR(T_2 - T_1)$$

2.3.2 Heat or Heat Quantity (Q)

Heat, denoted as Q, is the amount of energy transferred from a hot medium to a cold medium (at a lower temperature). Therefore, the quantity of heat Q is proportional to the temperature difference between the hotter medium and the medium with the lowest temperature. It is expressed in joules [J] or [kcal].

On a microscopic scale, heat reflects the variation in the kinetic energy of molecules (energy exchanged due to molecular agitation). Heat is not a state function.

The exchange of heat between the system and the external environment is characterized by either:

- A change in the temperature of the system
- A change in the physical state of the matter constituting the system.

2.3.2.1 Temperature Change

The quantity of exchanged (or transferred) heat is proportional to the amount of matter (mass or number of moles) and the temperature difference of the system. It is a specific form of energy expressed in joules (J) or calories (cal).

This results in a proportional relationship between the elementary heat received (δQ) and the elementary temperature change (dT) for a transformation.

For n moles we have: $\delta Q = nc\,dT$

With: n is the number of moles, dT is the temperature change, c is the molar heat (molar heat capacity) in $J \cdot mol^{-1} \cdot K^{-1}$.

The total quantity of heat is:

$$Q = \int_{T_1}^{T_2} nc\,dT$$

If c is constant, $\Rightarrow Q = nc(T2 - T1)$

For a mass m we have: $\delta Q = mc_m\,dT$

With: m is the mass, dT is the temperature change, c_m is the specific heat (specific heat capacity) in $J \cdot kg^{-1} \cdot K^{-1}$.

The total quantity of heat is:

$$Q = \int_{T_1}^{T_2} nc_m \, dT$$

If c_m is constant: $\Rightarrow Q = mc_m(T2 - T1)$.

a Specific heat or molar heat of a pure substance

Specific heat, denoted as c or cm, is a physical property of pure substances. It is defined as the amount of heat energy required to raise the temperature of one unit of mass (1 kg or 1 g) or one mole of a pure substance by 1 degree Kelvin (or 1 degree Celsius).

$[c]$: $\mathrm{cal\,g^{-1}\,{}^{\circ}C^{-1}}$ or $\mathrm{cal\,mol^{-1}\,{}^{\circ}C^{-1}}$

Example:

$$c\,(\text{liquid water}) = 1\,\text{cal g}^{-1}\,{}^{\circ}\text{C}^{-1} = 18\,\text{cal mol}^{-1}\,{}^{\circ}\text{C}^{-1}$$

$$c\,(\text{solid water}) = 0.45\,\text{cal g}^{-1}\,{}^{\circ}\text{C}^{-1} = 8.1\,\text{cal mol}^{-1}\,{}^{\circ}\text{C}^{-1}$$

Case of pure substances in the gaseous state

For pure substances in the gaseous state, we define the specific heat or molar heat at constant pressure denoted as c_p, and the specific heat or molar heat at constant volume denoted as c_v : $c_p \neq c_v$

The values of specific heat (or molar heat) at constant pressure and constant volume for monoatomic and diatomic gases are represented in the following table

Gas	c_v	c_p
Monoatomic	(3/2)R	(5/2) R
Diatomic	(5 /2)R	(7/2) R

- Case of pure substances in the liquid or solid state:
  For pure substances in the solid and liquid state, we define the specific heat or molar heat: $c_p = c_v = c$.

b Thermal heat capacity

The heat capacity or thermal capacity, denoted as C, of a pure substance is defined as the product of its specific heat or molar heat and its mass or number of moles, respectively: $C = n \cdot c = m \cdot c_m$. The thermal heat capacity is expressed in $J \cdot K^{-1}$, $J \cdot K^{-1}$, or $cal \cdot^{\circ} C^{-1}$.

Calculation of the heat quantity for the various transformations of an ideal gas :

Isochoric transformation For an isochoric transformation of a gas, we have dV = 0 (V = constant), consequently, the amount of heat involved is :
$\delta Q_v = nc_v dT \implies Q = \int_{T_1}^{T_2} nc_v \, dT$
If c_v is constant between T_1 and T_2, then :
$Q_v = C_v \int_{T_1}^{T_2} dT = nc_v \int_{T_1}^{T_2} dT = mc'_v \int_{T_1}^{T_2} dT$
Then
$Q_v = C_v(T_2 - T_1) = nc_v(T_2 - T_1) = mc'_v(T_2 - T_1)$

Isobaric transformation For an isobaric transformation of a gas, we have d$P = 0$ (P constant), consequently, the amount of heat involved is:

$$\delta Q_P = nc_P \mathrm{d}T \implies Q = \int_{T_1}^{T_2} nc_P \, \mathrm{d}T$$

If c_P is constant between T_1 and T_2 then:

$$Q_P = C_P \int_{T_1}^{T_2} \mathrm{d}T = nc_P \int_{T_1}^{T_2} \mathrm{d}T = mc'_P \int_{T_1}^{T_2} \mathrm{d}T$$

Then:

$$Q_P = C_P(T_2 - T_1) = nc_P(T_2 - T_1) = mc'_P(T_2 - T_1)$$

2.3.2.2 Change of the physical state of matter

When the exchanged heat does not cause a variation in temperature but rather a change of state (phase transition), which corresponds to modifications in the particulate structure of matter (solidification, fusion, boiling). A change of state occurs at constant temperature. The diagram below illustrates the various state changes.
In this case, we refer to the latent heat of the phase change L, which corresponds to the amount of heat required to transform one mole (or 1 kg) of the substance. Thus, Q is expressed as: $Q = n \times L$

L: Molar latent heat ($J \cdot kg^{-1}$).

Or: $Q = m \times L'$

L': Specific latent heat ($J \cdot mol^{-1}$).

There are three types of latent heats related to the six physical state changes (L_{sub}, L_{vap}, and L_f), for each type of substance.

Where L_{sub}, L_{vap}, or L_{f}: are the molar or specific latent heats associated respectively with sublimation, vaporization, and fusion.

$S \longrightarrow L :$ Latent heat of fusion; $L_f > 0$

$L \longrightarrow S :$ Latent heat of solidification; $L_s = -L_f < 0$

$L \longrightarrow G :$ Latent heat of vaporization; $L_{\text{vap}} > 0$

$G \longrightarrow L :$ Latent heat of liquefaction; $L_{\text{liq}} = -L_{\text{vap}} < 0$

$S \longrightarrow G :$ Latent heat of sublimation; $L_{\text{sub}} > 0$

$G \longrightarrow S :$ Latent heat of condensation; $L_{\text{cond}} = -L_{\text{sub}} < 0$

Example:

The latent heat of fusion of water (at 0 °C under 1 atm) = 80.4 cal/g

The latent heat of vaporization of water (at 100 °C under 1 atm) = 535 cal/g)

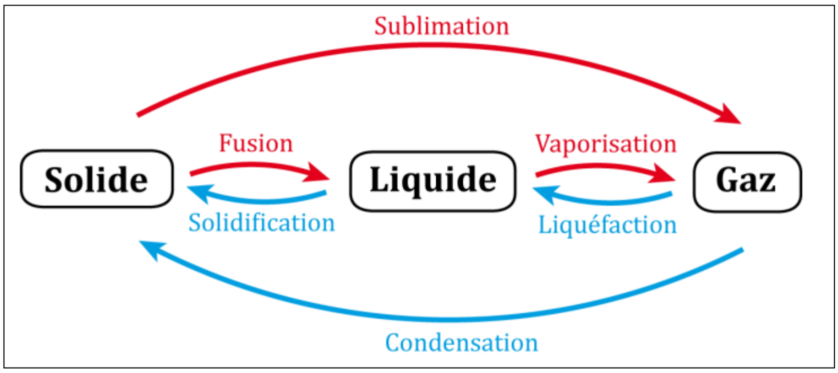

Figure 2.6: The various state changes

2.4 Heat Balance Concept

2.4.1 Heating of a Pure Substance

Consider a pure substance with mass m in the solid state at temperature T_1. This substance receives a quantity of heat Q, leading it to the gaseous state at temperature T_2. We have recorded the temperature evolution over time. The result of calculating the heat quantities during the heating of a solid is represented in the graph below.

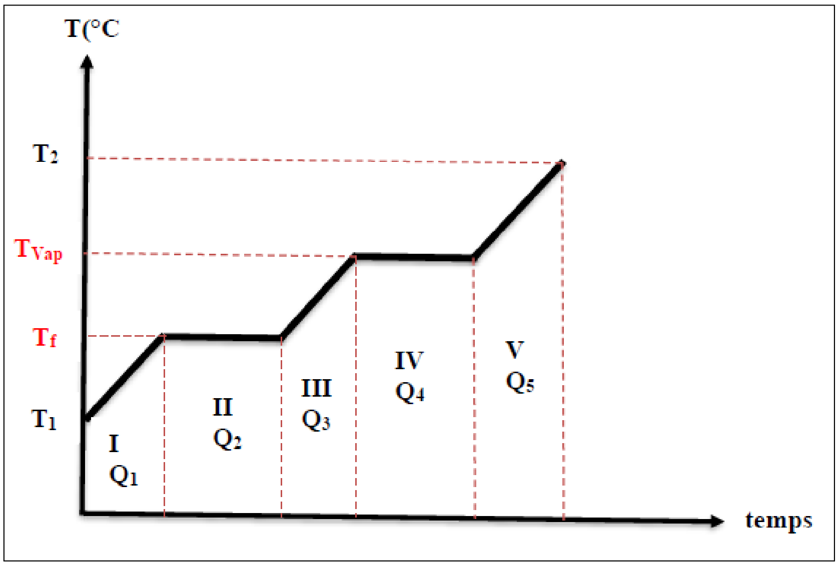

Figure 2.7: Heat quantities during the heating of a solid

In this graph, we observe the existence of five domains.

Domain I: From T_1 to T_f, the temperature increases; this is the heating of the solid phase.

Domain II: Presence of a temperature plateau at T_f, indicating the phase change from solid to liquid; this is fusion (a phase change occurs at constant temperature).

Domain III: From the melting temperature (T_f) to the vaporization temperature (T_{Vap}), the temperature increases again; this is the heating of the liquid phase.

Domain IV: Presence of a vaporization temperature plateau. Phase change from the liquid state to the gaseous state; this is vaporization (a phase change occurs at constant temperature).

Domain V: From T_{Vap} to T_2, again, the temperature increases; this is the heating of the gaseous phase.

The amount of heat required for this mass to go from T_i to T_f is :

$$
\begin{aligned}
Q &= Q_1 + Q_2 + Q_3 + Q_4 + Q_5 \\
Q_1 &= \int_{T_1}^{T_f} mc_{P,\text{Solid}}\, dT + mc_{P,\text{Solid}}(T_f - T_1) \\
Q_2 &= mL_f \\
Q_3 &= \int_{T_f}^{T_\text{Vap}} mc_{P,\text{Liquid}}\, dT + mc_{P,\text{Liquid}}(T_\text{Vap} - T_f) \\
Q_4 &= mL_\text{Vap} \\
Q_5 &= \int_{T_\text{Vap}}^{T_2} mc_{P,\text{Gas}}\, dT + mc_{P,\text{Gas}}(T_2 - T_\text{Vap})
\end{aligned}
$$

2.4.2 Mixing of Pure Substances

Consider a body A with mass m_A at temperature T_A and a body B with mass m_B at temperature T_B, where $T_A > T_B$. Let's bring body A into contact with body B. After a certain time, both bodies will reach the same temperature T_eq (equilibrium temperature).

Heat Balance:

Body A cools down by giving heat to body B and reaches temperature T_eq.

Body B heats up by receiving heat from body A and reaches temperature T_eq.

The heat given by body A = The heat received by body B.

$$
\begin{aligned}
-Q_A &= Q_B \\
-m_A c_A(T_\text{eq} - T_A) &= m_B c_B(T_\text{eq} - T_B) \\
m_A c_A(T_\text{eq} - T_A) + m_B c_B(T_\text{eq} - T_B) &= 0 \\
T_\text{eq} &= \frac{m_A c_A T_A + m_B c_B T_B}{m_A c_A + m_B c_B}
\end{aligned}
$$

If n bodies are put in contact, we have:

$$
\begin{aligned}
Q_1 + Q_2 + Q_3 + \ldots + Q_N &= 0 \\
m_1 c_1(T_\text{eq} - T_1) + m_2 c_2(T_\text{eq} - T_2) + m_3 c_A(T_\text{eq} - T_A) + \ldots + m_N c_N(T_\text{eq} - T_N) &= 0 \\
\sum_{i=1}^{N} m_i c_{P_i}(T_\text{eq} - T_i) &= 0
\end{aligned}
$$

$$
\implies T_\text{eq} = \frac{\sum_{i=1}^{N} m_i c_{P_i} T_i}{\sum_{i=1}^{N} m_i c_{P_i}}
$$

2.4.3 Calorimetry

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (all other matter, including components of the measurement apparatus, that serve to either provide heat to the system or absorb heat from the system).

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature. The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

$$Q_e + Q_c + Q_s = 0$$

Q_e: Heat received by the water in the calorimeter

Q_c: Heat received by the accessories of the calorimeter (the vessel, the stirrer, and the thermometer)

Q_s: Heat released by the solid body

$$m_e c_e(T_{\text{eq}} - T_e) + m_c c_c(T_{\text{eq}} - T_c) + m_s c_s(T_{\text{eq}} - T_s) = 0$$

$$T_e = T_c, \quad c_c = c_e,$$

$$m_e c_e(T_{\text{eq}} - T_e) + m_c c_c(T_{\text{eq}} - T_e) + m_s c_s(T_{\text{eq}} - T_s) = 0$$

$$(m_e c_e + m_c c_e)(T_{\text{eq}} - T_e) + m_s c_s(T_{\text{eq}} - T_s) = 0$$

$$m_c c_e = C_{\text{cal}},$$

$$(m_e c_e + C_{\text{cal}})(T_{\text{eq}} - T_e) + m_s c_s(T_{\text{eq}} - T_s) = 0$$

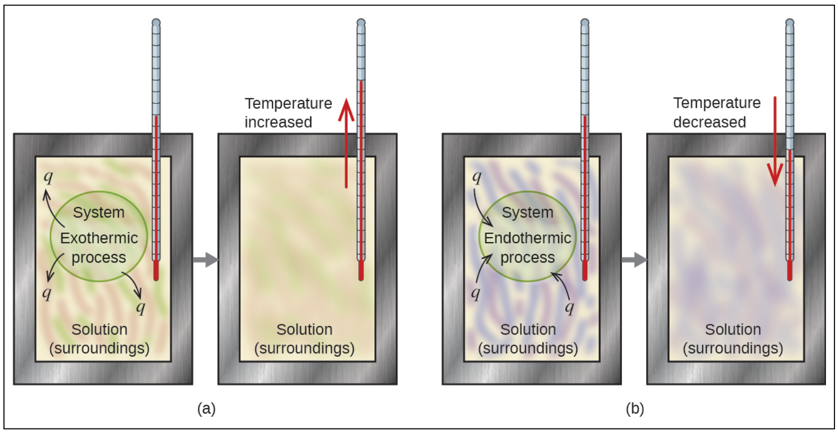

Figure 2.8: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Calorimetry measurements are important in understanding the heat transferred in reactions involving everything from microscopic proteins to massive machines. During her time at the National Bureau of Standards, research chemist Reatha Clark King performed calorimetric experiments to understand the precise heats of various fluorine compounds. Her work was important to NASA in their quest for better rocket fuels.

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment, which effectively limits the "surroundings" to the nonsystem components with the calorimeter (and the calorimeter itself). This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure 2.8). These easy-to-use "coffee cup" calorimeters allow more heat exchange with the outside environment, and therefore produce less accurate energy values.

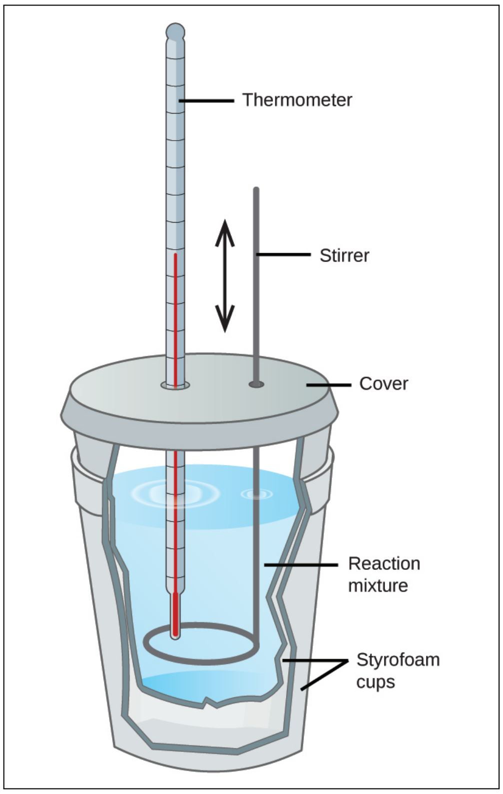

Figure 2.9: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture..

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure 2.10).

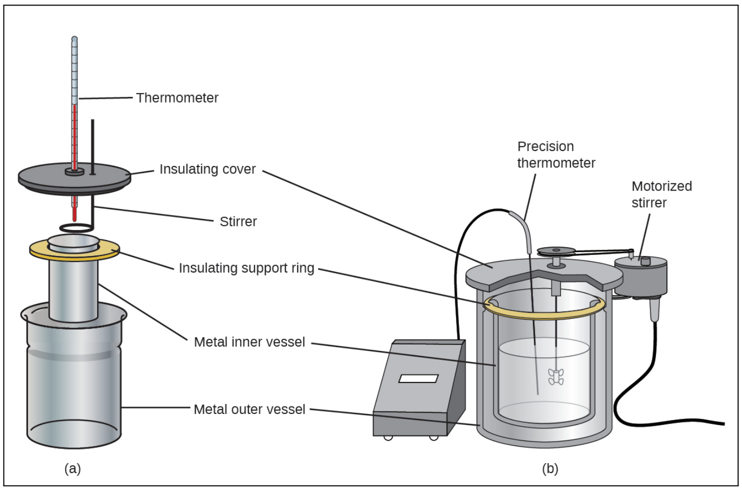

Figure 2.10: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research..

Before discussing the calorimetry of chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 2.11). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either its external environment. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance}}M + q_{\text{substance}}W = 0$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance}}M = -q_{\text{substance}}W$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{\text{substance}}$ M and qsubstance W are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{\text{substance}}$ M is a negative value and $q_{\text{substance}}$ W is positive, since heat is transferred from M to W.

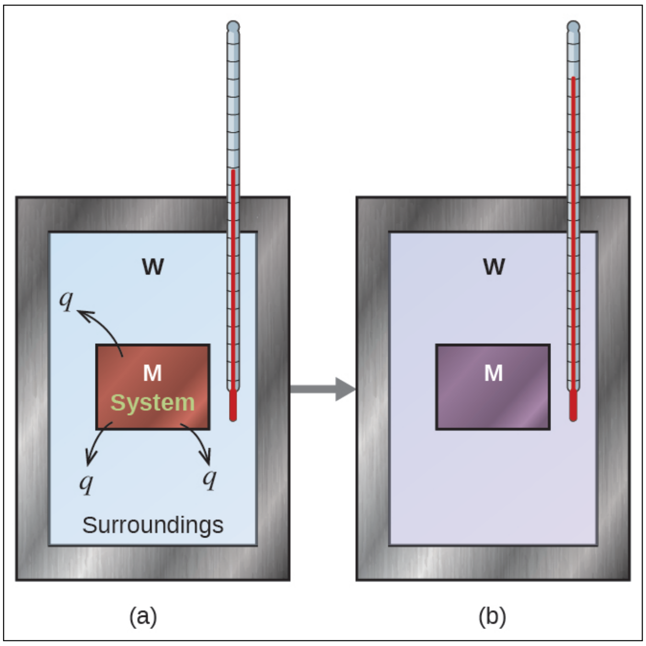

Figure 2.11: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the outside environment. Because energy is neither created nor destroyed during a chemical reaction, the heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

This concept lies at the heart of all calorimetry problems and calculations.

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure 2.12). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is absorbed by the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.

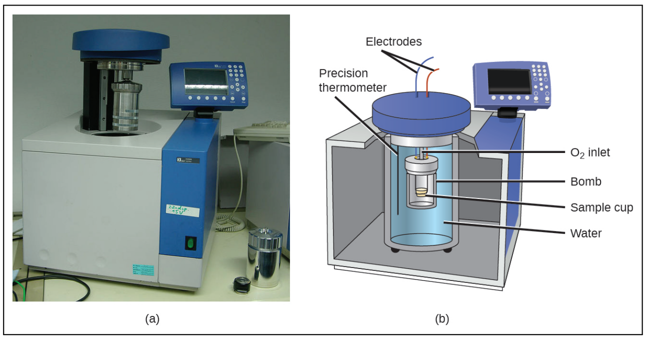

Figure 2.12: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.2 These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes.

For example Carla Prado's team at University of Alberta undertook whole-body calorimetry to understand the energy expenditures of women who had recently given birth. Studies like this help develop better recommendations and regimens for nutrition, exercise, and general wellbeing during this period of significant physiological change. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Exercise 01

A calorimeter contains $m_1 = 95\,\mathrm{g}$ of water at $T_1 = 20°\mathrm{C}$. We add $m_2 = 71\,\mathrm{g}$ of water at $T_2 = 50°\mathrm{C}$.

a- What would be the equilibrium temperature T_{eq} if we could neglect the thermal capacity of the vessel and its accessories?

b- The actual equilibrium temperature is $T_{\mathrm{eq}} = 31.3°\mathrm{C}$, deduce the value of the water m_e of the vessel and its accessories.

c- The same calorimeter now contains $m'_1 = 100\,\mathrm{g}$ of water at $T'_1 = 15°\mathrm{C}$. We immerse a metallic sample of mass $m = 25\,\mathrm{g}$ coming out of an oven at $T'_2 = 95°\mathrm{C}$. The equilibrium temperature is $T'_{\mathrm{eq}} = 16.7°\mathrm{C}$. Calculate the specific heat capacity of the metal, with the specific heat capacity of water being $c_{\mathrm{w}} = 4.185\,\mathrm{J}\cdot\mathrm{g}^{-1}\cdot^{\circ}\mathrm{C}^{-1}$.

Solution: a) To find the equilibrium temperature T_{eq} when neglecting the thermal capacity of the vessel and its accessories, we use the principle of conservation of energy:

$$m_1 c_{\mathrm{w}}(T_{\mathrm{eq}} - T_1) + m_2 c_{\mathrm{w}}(T_{\mathrm{eq}} - T_2) = 0$$

Substituting the given values:

$$95 \times 4.185(T_{\mathrm{eq}} - 20) + 71 \times 4.185(T_{\mathrm{eq}} - 50) = 0$$

Expanding, simplifying and Combining like terms:

$$T_{\mathrm{eq}} = \approx 32.83°\mathrm{C}$$

b) Given $T_{\mathrm{eq}} = 31.3°\mathrm{C}$, we deduce the value of m_e using the equation:

$$m_1 c_{\mathrm{w}}(T_{\mathrm{eq}} - T_1) + m_2 c_{\mathrm{w}}(T_{\mathrm{eq}} - T_2) + m_e c_{\mathrm{w}}(T_{\mathrm{eq}} - T_1)$$

Substituting the given values and solving for m_e:

$$m_e \approx 22.5\ \mathrm{g}$$

c) To calculate the specific heat capacity of the metal, we can use the principle of conservation of energy again. The equation for this case would be similar to part (b).

Exercise 02:

What is the final temperature obtained by mixing 1 kg of ice at 0°C with 9 kg of water at 50°C?

We add 5 kg of steam at 100°C to 250 kg of water at 4°C. Find the final temperature of the mixture.

Data:

- Heat of fusion of ice (L_f at 0°C) = $3.3 \times 10^5\,\mathrm{J/kg}$

- Heat of vaporization of water (L_{vap} at 100°C) $= 2.25 \times 10^3\,\mathrm{J/kg}$
- Specific heat capacity of liquid water $c_{\mathrm{w}} = 4.185 \times 10^3\,\mathrm{J/kg^\circ C}$

Solution :

I. The liquid water ($m_1 = 9\,\mathrm{Kg}$) with $T_1 = 50°\mathrm{C}$ + The ice ($m_2 = 1\,\mathrm{Kg}$) with $T_2 = 0°\mathrm{C}$ (water in solid state).

After thermal equilibrium, the liquid mixture with T_{eq}.

$Ice(S, 0°) \xrightarrow{Fusion\ \ Liquide} (0°, C) \xrightarrow{Heating\ \ Mixture} (Liq, T_eq) \xleftarrow{Cooling} 9\ kg\ water$

We have :

$$Q_1 = m_1 C_w (T_{eq} - T_1) \quad \text{Cooling of hot water}$$

$$Q_2 = m_2 L_f \quad \text{Ice fusion}$$

$$Q_3 = m_2 C_w (T_{eq} - T_2)$$

$$\sum Q_i = 0 \implies Q_1 + Q_2 + Q_3 = 0$$

W find that T$_{eq}$ = 37.12 ° C

II. Liquid water ($m_1 = 250\,\mathrm{Kg}$) with $T_1 = 4°\mathrm{C}$ + Water vapor ($m_2 = 5\,\mathrm{Kg}$) with $T_2 = 100°\mathrm{C}$ (water in solid state).

After thermal equilibrium, liquid mixture with T_{eq}.

$Vapor(g, 100°C) \xrightarrow{Liquefaction} (100°, C) \xrightarrow{Mixture} (Liq, T_eq) \leftarrow 250\ kg\ water$

$Q_1 = m_1 C_w (T_{\mathrm{eq}} - T_1)$

Liquefaction of vapor ($L_{\mathrm{liq}} = -L_{\mathrm{vap}}$) : $Q_2 = m_2 L_{\mathrm{liq}}$

$Q_3 = m_2 C_w (T_{\mathrm{eq}} - T_2)$

$\sum Q_i = 0$; we found that $T_{eq} = 5.89°C$

Exercise 03:

A calorimeter contains a mass $m_1 = 250\,\mathrm{g}$ of water, the initial temperature of the system is $T_1 = 18°\mathrm{C}$. We add a mass $m_2 = 300\,\mathrm{g}$ of water at the temperature $T_2 = 80°\mathrm{C}$.

1- What would be the thermal equilibrium temperature T_{eq} of the system if the thermal capacity C of the calorimeter and its accessories were negligible?

2- We actually measure a thermal equilibrium temperature $T_{\mathrm{eq}} = 50°\mathrm{C}$, determine the thermal capacity C of the calorimeter and its accessories.

Data: Specific heat capacity of liquid water: $c_{\mathrm{w}} = 4185\,\mathrm{J/kg^\circ C}$.

Solution :

Since the thermal capacity of the calorimeter and its accessories are negligible, the heat gained by the cooler water (Q_1) will be equal to the heat lost by the hotter water (Q_2) when they reach thermal equilibrium.

Using the principle of conservation of energy:

$$m_1 c_{\mathrm{w}}(T_{\mathrm{eq}} - T_1) = -m_2 c_{\mathrm{w}}(T_{\mathrm{eq}} - T_2)$$

Solving for T_{eq}:

$$250 \times 4185 \times (T_{\mathrm{eq}} - 18) = -300 \times 4185 \times (T_{\mathrm{eq}} - 80)$$

$$250 \times 4185 \times T_{\mathrm{eq}} - 250 \times 4185 \times 18 = -300 \times 4185 \times T_{\mathrm{eq}} + 300 \times 4185 \times 80$$

$$250 \times 4185 \times T_{\mathrm{eq}} + 300 \times 4185 \times T_{\mathrm{eq}} = 300 \times 4185 \times 80 + 250 \times 4185 \times 18$$

$$T_{\mathrm{eq}} = \frac{300 \times 4185 \times 80 + 250 \times 4185 \times 18}{250 \times 4185 + 300 \times 4185}$$

$$T_{\mathrm{eq}} = \frac{300 \times 80 + 250 \times 18}{250 + 300}$$

$$T_{\mathrm{eq}} = \frac{24000 + 4500}{550}$$

$$T_{\mathrm{eq}} = \frac{28500}{550}$$

$$T_{\mathrm{eq}} \approx 51.82^\circ\mathrm{C}$$

So, the thermal equilibrium temperature $T_{\mathrm{eq}} \approx 51.82^\circ\mathrm{C}$.

2- We actually measure a thermal equilibrium temperature $T_{\mathrm{eq}} = 50^\circ\mathrm{C}$, determine the thermal capacity C of the calorimeter and its accessories.

Now, considering the measured thermal equilibrium temperature $T_{\mathrm{eq}} = 50^\circ\mathrm{C}$, we can determine the thermal capacity C of the calorimeter and its accessories.

Using the equation derived in part 1, but rearranging it to solve for C:

So, the thermal capacity $C \approx 130.78\,\mathrm{J/^\circ C}$.

Exercise 04:

A brass calorimeter with a mass $M_1 = 200\,\mathrm{g}$ contains a mass of water $M_0 = 280\,\mathrm{g}$ at the temperature $T_0 = 20^\circ\mathrm{C}$. We introduce a mass $M_g = 100\,\mathrm{g}$ of ice at the temperature $T_g = -5^\circ\mathrm{C}$. When thermal equilibrium is reached, we notice that there is still some ice remaining.

Give the equilibrium temperature T_f and determine the mass of the unfrozen ice.

Given:

- The respective specific heats of brass $C_1 = 0.09\,\mathrm{cal/g^\circ C}$, of ice $C_g = 0.5\,\mathrm{cal/g^\circ C}$, and of water $C_0 = 1\,\mathrm{cal/g^\circ C}$.

- The latent heat of fusion of ice: $L = 80\,\mathrm{cal/g}$.

Solution:

To solve this exercise, we will use the principle of conservation of energy, which states that the total energy lost by the hot objects (brass calorimeter and initial water) must be equal to the total energy gained by the cold object (ice) and the energy required for melting a portion of the ice.

Let T_f be the final equilibrium temperature, and M_w be the mass of the melted ice (water).

When thermal equilibrium is reached, there is still some ice remaining, which implies that there is an equilibrium between the ice and the liquid water. Therefore, the equilibrium temperature T_{eq} must be equal to 0°C, which implies $T_f = 0^\circ C$.

The energy lost by the brass calorimeter and the initial water is given by: $Q_{\mathrm{lost}} = M_1 C_1 (T_f - T_1) + M_0 C_0 (T_f - T_1)$

The energy gained by the ice and the energy required for melting a portion of the ice is given by: $Q_{\mathrm{gained}} = M_g C_g (0 - T_g) + M_w L$

According to the principle of conservation of energy, $Q_{\mathrm{lost}} + Q_{\mathrm{gained}} = 0$, we have:

Substituting the given values, we get:

$M_w = 71.43\ g$ The mass of unfrozen ice = 100 - 71.43 = 28.57 g

Exercise 05:

A 360.0-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron , and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution:

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat “lost” to the outside environment, then heat given off by rebar = - heat taken in by water, or:

$$q_{\mathrm{rebar}} = -q_{\mathrm{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{f,\text{rebar}} - T_{i,\text{rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{f,\text{water}} - T_{i,\text{water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$\begin{gathered}(0.449\,\text{J/g}\,^\circ\text{C}) \times (360.0\,\text{g}) \times (42.7^\circ\text{C} - T_{i,\text{rebar}}) = \\ -(4.184\,\text{J/g}\,^\circ\text{C}) \times (425\,\text{g}) \times (42.7^\circ\text{C} - 24.0^\circ\text{C})\end{gathered}$$

$$T_{i,\text{rebar}} = \frac{(4.184\,\text{J/g}\,^\circ\text{C}) \times (425\,\text{g}) \times (42.7^\circ\text{C} - 24.0^\circ\text{C})}{(0.449\,\text{J/g}\,^\circ\text{C}) \times (360.0\,\text{g})} + 42.7^\circ\text{C}$$

Solving this gives $T_{i,\text{rebar}} = 248^\circ\text{C}$, so the initial temperature of the rebar was 248°C.

Check Your Learning

A 248-g piece of copper is dropped into 390 mL of water at 22.6°C. The final temperature of the water was measured as 39.9°C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

ANSWER: The initial temperature of the copper was 335.6 °C.

Check Your Learning

A 248-g piece of copper initially at 314°C is dropped into 390 mL of water initially at 22.6°C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

ANSWER: The final temperature (reached by both copper and water) is 38.7 °C.

Exercise 06:

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0°C. The final temperature is 28.5°C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution:

Assuming perfect heat transfer, heat given off by metal = − heat taken in by water, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{f,\text{metal}} - T_{i,\text{metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{f,\text{water}} - T_{i,\text{water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0°C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\,\text{g})(28.5°\text{C} - 100.0°\text{C}) = -(4.18\,\text{J/g °C})(60.0\,\text{g})(28.5°\text{C} - 22.0°\text{C})$$

Solving this:

$$c_{\text{metal}} = -\frac{(4.184\,\text{J/g °C})(60.0\,\text{g})(6.5°\text{C})}{(59.7\,\text{g})(-71.5°\text{C})} = 0.38\,\text{J/g °C}$$

Comparing this with known values , our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Check Your Learning

A 92.9-g piece of a silver/gray metal is heated to 178.0°C, and then quickly transferred into 75.0 mL of water initially at 24.0°C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7°C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

ANSWER: $c_{\text{metal}} = 0.13\,\text{J/g °C}$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

Exercise 06:

When 50.0 mL of 1.00 M HCl(aq) and 50.0 mL of 1.00 M NaOH(aq), both at 22.0°C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9°C. What is the approximate amount of heat produced by this reaction?

$$\text{HCl(aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$

Solution:

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0°C. The HCl and NaOH then react until the solution temperature reaches 28.9°C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and the outside environment.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.184 J/g°C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184\,\text{J/g°C}) \times (1.0 \times 10^2\,\text{g}) \times (28.9\text{°C} - 22.0\text{°C}) = 2.9 \times 10^3\,\text{J}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.9 \times 10^3\,\text{J}$$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat.)

Check Your Learning

When 100 mL of 0.200 M NaCl(aq) and 100 mL of 0.200 M $AgNO_3$(aq), both at 21.9°C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5°C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

ANSWER:1.34×10^3 kJ; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water.

Exercise 07:

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack”. When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9°C in a calorimeter, the temperature decreases to 20.3°C.

Calculate the value of q for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.

Solution :

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{\text{rxn}} = -q_{\text{soln}}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$q_{\text{rxn}} = -q_{\text{soln}} = -(c\times m\times\Delta T)_{\text{soln}} = -[(4.184\,\text{J/g}\cdot{}^\circ\text{C})\times(53.2\,\text{g})\times(20.3\,{}^\circ\text{C}-24.9\,{}^\circ\text{C})]$$

$$= -[(4.184\,\text{J/g}\cdot{}^\circ\text{C})\times(53.2\,\text{g})\times(-4.6\,{}^\circ\text{C})] = +1.0\times10^3\,\text{J} = +1.0\,\text{kJ}$$

The positive sign for q indicates that the dissolution is an endothermic process.

Check Your Learning

When a 3.00 g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05°C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

ANSWER: 1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water.

Exercise 08:

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8°C to 35.6°C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution :

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.) The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\ &= -\left[(4.184\,\text{J/g}\ {}^\circ\text{C})\times(775\,\text{g})\times(35.6^\circ C-23.8^\circ C)+893\,\text{J/}{}^\circ\text{C}\times(35.6^\circ C-23.8^\circ C)\right] \\ &= -(38,300\,\text{J}+10,500\,\text{J}) \\ &= -48,800\,\text{J} = -48.8\,\text{kJ} \end{aligned}$$

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

Check Your Learning

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the benzene sample?

ANSWER: $q_{\text{rx}} = -39.0\,\text{kJ}$ (the reaction produced 39.0 kJ of heat)

Chapter 3

The first principle of thermodynamics

3.1 Introduction

Thermodynamics is based on four principles that stem from observation and experience. The first principle of thermodynamics states that the amount of energy exchanged between the system and the surrounding environment in the form of work and heat is constant regardless of the transformation undergone.

$$Q + W = \Delta E = \text{Constant}$$

Where ΔE denotes the change in the total energy of the system.

$$\Delta E = \Delta E_c + \Delta E_p + \Delta U$$

With:

- ΔE_c: Variation of the kinetic energy of the system (motion) - ΔE_p: Variation of the potential energy of the system (position) - ΔU: Variation of the internal energy of the system

If the system is at rest: $\Delta E_c = \Delta E_p = 0$

It follows that: $Q + W = \Delta U$

The internal energy U represents the sum of energies (kinetic and potential) of all particles on a microscopic scale (atoms and/or molecules). U is an extensive quantity.

$$[U] : \text{J or cal}$$

3.2 Other statements of the first principle

3.2.1 Conservation principle

For an isolated system, we have: $Q = W = 0$, consequently:

$$Q + W = \Delta U = 0 \implies U_1 = U_2$$

The internal energy of an isolated system remains constant. This means that the isolated system can undergo energy transformations from one form to another, but the sum of the different forms of energy remains constant.

3.2.2 Equivalence principle

Consider a closed system undergoing a cyclic transformation. The initial state and the final state coincide. Therefore: $U_1 = U_2$

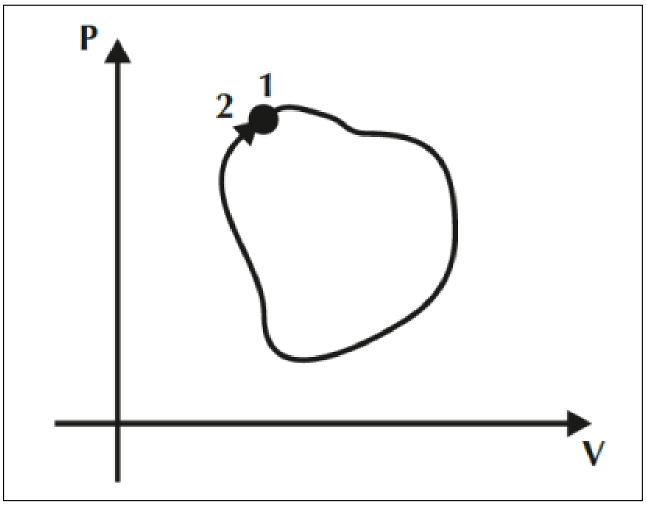

Figure 3.1: Equivalence principle

According to the expression of the first principle, we have: $Q + W = \Delta U = 0 \implies Q = -W$ Work is equivalent to heat.

3.2.3 Principle of initial and final states

According to the statement of the first principle, the variation in internal energy ΔU remains constant regardless of the nature of the transformation. Consider a set of transformations that take a system from an initial equilibrium state 1 to a final equilibrium state 2.

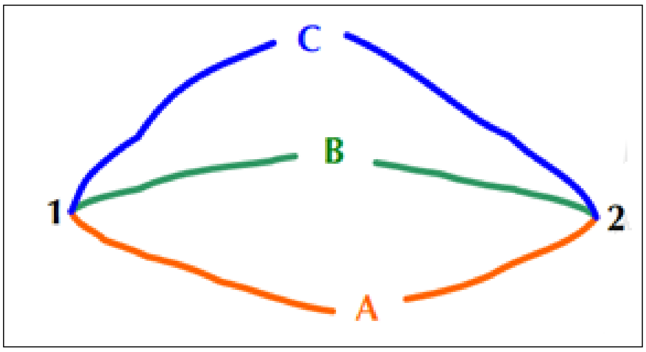

Figure 3.2: Principle of initial and final states

- Path A: $U_2 - U_1 = Q_A + W_A$
- Path B: $U_2 - U_1 = Q_B + W_B$
- Path C: $U_2 - U_1 = Q_C + W_C$

$U_2 - U_1 = Q_A + W_A = Q_B + W_B = Q_C + W_C$
This equality does not necessarily imply that:
$Q_A = Q_B = Q_C$ and $W_A = W_B = W_C$
Therefore, when there are multiple types of transformations to take a system from an equilibrium state 1 to an equilibrium state 2, the sum of energies $W + Q$ is independent of the type of transformation "path followed" and depends only on the initial and final states. This principle implies that internal energy U is a state function, meaning that the change in internal energy U depends only on the initial and final states. But Q and W are not state functions.

3.3 First Law of Joule: Variation of the internal energy of an ideal gas

Consider a rigid cylinder perfectly insulated, separated by a partition into two compartments C_1 and C_2. C_1 contains an ideal gas in the initial state characterized by the variables P_1, T_1, V_1, and C_2 is empty. The partition is removed, and the gas expands to occupy the entire cylinder. At equilibrium, the gas is in a final state characterized by P_2, T_2, V_2.

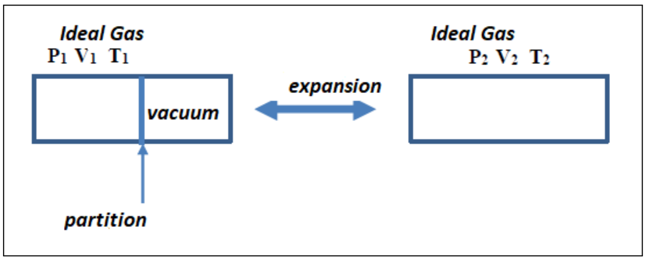

Figure 3.3: Ideal gas expansion

At constant temperature ($T_1 = T_2$), it is observed that $P_2 < P_1$ and $V_2 > V_1$. The cylinder is rigid and perfectly insulated, so $W = 0$ and $Q = 0$.

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

This results in $\Delta U = 0$ (U remains constant). At constant temperature, the change in internal energy of an ideal gas is zero. Consequently, the internal energy of an ideal gas depends only on its temperature and is independent of pressure and volume. According to the first law of Joule, the change in internal energy is therefore:

$dU = nc_v dT$

$$\int dU = \int_{T_1}^{T_2} nc_v dT \implies \Delta U = nc_v(T_2 - T_1) \implies \Delta U = nc_v \Delta T$$

3.4 Transformation of ideal gases "Closed System"

3.4.1 Isothermal transformation: $Q + W = \Delta U$

An isothermal transformation is a transformation with constant internal energy.

We have $T =$ Const. hence

$$\Delta U = nc_V \int_{T_1}^{T_2} \frac{dT}{T} = 0 = Q_T + W$$

Therefore,

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

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

3.4.2 Isochoric transformation ($V_1 = V_2 = V$)

$\Delta U = Q + W$

For an isochoric transformation (constant volume (V = constant $\Longrightarrow dV = 0$)), hence the work: $W = 0$, consequently, the heat exchanged (Q_V) is equal to the change in internal energy (ΔU): $Q_V = \Delta U$

$$Q_V = \Delta U = \int_{T_1}^{T_2} nc_v dT = nc_v(T_2 - T_1)$$

3.4.3 Isobaric transformation ($P_2 = P_1 = P$)

$\Delta U = Q + W$

We have P = const. hence $W = -P(V_2 - V_1)$. After substitution, we find:

$Q - P(V_2 - V_1) = U_2 - U_1$

It follows that:

$Q_P = (U_2 + P_2V_2) - (U_1 + P_1V_1)$

3.4.3.1 Enthalpy Function

We define a new thermodynamic function, enthalpy, denoted by H.

H is a state function and an extensive quantity.

H = U + PV

It follows that: $Q_P = H2\check{\ }H1 = \Delta H$

3.4.3.2 Second Law of Joule

At constant temperature, the change in enthalpy of an ideal gas is zero. Consequently, the enthalpy of an ideal gas depends only on its temperature; it is independent of pressure and volume.

Hence: $dH = nc_p dT$

$\int dH = \int_{T_1}^{T_2} nc_p dT \Longrightarrow \Delta H = nc_p(T_2 - T_1) \Longrightarrow \Delta H = nc_p \Delta T$

3.4.4 Relationship between Q_P and Q_V

The first law of thermodynamics leads to: $\Delta U = W + Q_P \rightarrow Q_P = \Delta U - W$

For an isochoric transformation: $\Delta U = Q_V$, $Q_P = Q_V - W$

As well as:

$$\frac{Q_P}{Q_V} = \frac{\Delta H}{\Delta U} = \frac{nc_p(T_2 - T_1)}{nc_v(T_2 - T_1)} = \frac{c_p}{c_v} = \gamma$$

3.4.5 Mayer's Relation

Consider an ideal gas undergoing an isobaric transformation from equilibrium state 1 to equilibrium state 2. According to the first law of thermodynamics, $\Delta U = Q + W$. By assumption, "isobaric transformation":

$$\begin{aligned} H &= U + PV \\ dH &= d(U + PV) \\ dH &= dU + d(PV) \end{aligned}$$

$$\begin{cases} dH = dQ = nc_P dT \\ dU = nc_V dT \\ (PV) = nRT \end{cases} \implies dH = d(U + PV)$$

After substitution, we find that:

$$nc_P dT = nc_V dT + nRdT \implies nc_P(T_2 - T_1) = nc_V(T_2 - T_1) + nR(T_2 - T_1)$$

Therefore,

$$c_P = c_V + R \quad \text{and} \quad c_P - c_V = R$$

We have:

$$R = c_P - c_V \quad \text{and} \quad \gamma = \frac{c_P}{c_V}$$

We find that:

$$c_p = \frac{R}{(\gamma - 1)} \quad \text{and} \quad c_v = \frac{R\gamma}{(\gamma - 1)}$$

3.4.6 Adiabatic transformation of an ideal gas

Consider an ideal gas undergoing an adiabatic transformation, meaning the system is thermally isolated $\delta Q = 0$, the only exchange with the surroundings is in the form of work.

According to the first principle:
we have; $\delta U = \delta w + \delta Q$
Therefore;

$$dU = \delta w$$

$$dU = nc_v dT = n\left(\frac{R}{\gamma - 1}\right) dT \quad \text{and} \quad \delta W = -PdV = \frac{-nRT}{V} dV$$

$$n\left(\frac{R}{\gamma-1}\right)dT=-nRT\frac{dV}{V}\implies\frac{dT}{T}=-(\gamma-1)\frac{dV}{V}$$

$$\implies\int_{T_1}^{T_2}\frac{dT}{T}=-(\gamma-1)\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\implies\ln\frac{T_2}{T_1}=-(\gamma-1)\ln\frac{V_2}{V_1}\implies\ln\frac{T_2}{T_1}=\ln\left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\implies\frac{T_2}{T_1}=\ln\left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

Therfore:

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

We will then have this formula which describes the equation of state for adiabatics:

$$T_1V_1^{\gamma-1}=T_2V_2^{\gamma-1}=\text{Constant}$$

We can also describe this equation in terms of pressure and volume as well as temperature in terms of pressure.

We have: $PV=nRT\implies T=\frac{PV}{nR}$

$$T_1V_1^{\gamma-1}=T_2V_2^{\gamma-1}=\text{Constant}$$

$$\frac{P_1V_1}{(nR)}V_1^{\gamma-1}=\frac{P_2V_2}{(nR)}V_2^{\gamma-1}$$

Therefore;

$$P_1V_1^{\gamma}=P_2V_2^{\gamma}=\text{Constant}$$

This formula is called Laplace's formula.

Also we have;

$$P_1^{\frac{(1-\gamma)}{\gamma}}T_1=P_2^{\frac{(1-\gamma)}{\gamma}}T_2$$

Calculation of work done by pressure forces during an adiabatic (reversible) transformation of an ideal gas:

The work is;

$$W_{1\to2}=-P\int_1^2 dV$$

We have: $dU=\delta W+\delta Q$

Since: $\delta Q = 0$ so $dU = \delta W = nc_v dT$

$$\Longrightarrow W_{1\to 2} = \Delta U = \int_1^2 dU = nC_v \int_1^2 dT = nC_v(T_2 - T_1)$$

$$c_v = \frac{R}{(\gamma - 1)} \quad \text{So} \quad W = \Delta U = n\frac{R}{(\gamma - 1)}(T_2 - T_1) \quad \text{or} \quad W = \Delta U = \frac{nRT_2 - nRT_1}{(\gamma - 1)}$$

$$\Longrightarrow W = \Delta U = \frac{P_2V_2 - P_1V_1}{\gamma - 1}.$$

Exercise 01

10 liters of nitrogen at 20 ° C and 1 atm: the temperature is raised to 100 °C with constant volume.

- Calculate the pressure as well as the quantities of energy exchanged in the form of work and heat.
- Same question if the transformation occurs at constant pressure.

Solution: I. The initial state is characterized by: $V_1 = 10$ liters; $P_1 = 1$ atm; $T_1 = 20°C$.

a. Isochoric transformation ($dV = 0$):

$V_1 = V_2 = 10$ liters; the final temperature is $T_2 = 100°C$.

Calculation of the final pressure :

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \implies P_2 = \frac{P_1 T_2}{T_1} \implies P_2 = \frac{1 \cdot 100}{20} \implies P_2 = 5 \quad atm$$

Calculation of the work :

$$W = \int -PdV \implies W = 0$$

Calculation of the quantity of heat:

$$Q = nc_v \int_{T_1}^{T_2} dt \implies Q = nc_v(T_2 - T_1)$$

$$P_1V_1 = nRT_1 \implies n = \frac{P_1V_1}{RT_1} \implies n = \frac{1 \text{ atm} \times 10 \text{ L}}{0.082 \times (20 + 273)} \implies n = 0.42 \text{ mol}$$

Nitrogen is a diatomic gas, therefore :

$$c_v = \frac{5}{2}R \quad \text{and} \quad c_p = \frac{7}{2}R$$

$$Q = 0.42(\frac{5}{2})8.314(373 - 293) \implies Q = 419.026\text{Joule}$$

b. Isobaric transformation: (dP = 0)

$$P_1 = P_2 = 1\text{atm}$$

Calculation of the final volume :

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \implies V_2 = \frac{V_1 \cdot T_2}{T_1} \implies V_2 = \frac{10 \cdot 100}{20} \implies V_2 = 50 \quad \text{liters}$$

Calculation of the work :

$$W = \int -PdV \implies W = -P \int_{V_1}^{V_2} dV \implies W = -P(V_2 - V_1)$$

$$W = 1 \cdot 1.013 \cdot 10^5(50 - 10) \cdot 10^{-3} \implies W = -4052 \quad Joules$$

Exercise 02

The initial state A of one mole of monoatomic ideal gas is characterized by $P_A = 2.105$ Pascals and $V_A = 14$ liters. This gas undergoes successively the following three transformations:

- A→B: An isobaric expansion, doubling its volume.
- B→C: An isothermal compression, returning it to its initial volume.
- C→A: An isochoric cooling, returning it to the initial state (P_A, V_A).

1) At what temperature does the isothermal compression occur? Deduce the maximum pressure reached. Represent the transformation cycle in the P-V diagram.

2) Calculate the work, heat, and change in internal energy exchanged by the system during each transformation? Perform the cycle balance (ΔU_{TOT}, W_{TOT}, Q_{TOT}).

Given: $R = 8.314$ J.mol^{-1}.K^{-1}, $C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$.

Solution:

(1) The isothermal compression is performed at the temperature $T_B = T_C$.

- The state variables at A are: $P_A = 2.10^5$ Pascals, $V_A = 14$ liters, and $T_A =?$.

$$P_A{\cdot}V_A = n{\cdot}R{\cdot}T_A \implies T_A = \frac{P_A \cdot V_A}{n \cdot R} \implies T_A = \frac{2.10^5\,\text{Pa} \cdot 14 \times 10^{-3}\,\text{m}^3}{1 \cdot 8.314}$$
$$\implies T_A = 336.78\,\text{K}$$

- The state variables at B are: $V_B = 2{\cdot}V_A \implies V_B = 28\,\text{liters} = 28{\times}10^{-3}$ m^3.

The transformation from state A to state B is an isobaric expansion (the pressure is constant), so: $P_B = P_A = 2.10^5$ Pascals.

Let's calculate the temperature at state B:

$$P_B \cdot V_B = n \cdot R \cdot T_B \implies T_B = \frac{P_B \cdot V_B}{n \cdot R} \implies T_B = \frac{P_B \cdot 2 \cdot V_A}{n \cdot R} \implies T_B = 2 \cdot T_A \implies T_B = 673.56 \text{ K}.$$

Therefore, the isothermal compression occurs at the temperature $T_B = 673.56$ K.

- The state variables at C are: $T_C = T_B = 673.56$ K; $V_C = 14$ liters.

Let's calculate the pressure at state C:

$$P_C{\cdot}V_C = n{\cdot}R{\cdot}T_C \implies P_C = \frac{n \cdot R \cdot T_C}{V_C} \implies P_C = \frac{1 \cdot 8.314 \cdot 673.56}{14 \times 10^{-3}} \implies P_C = 4 \times 10^5 \text{ Pascals}.$$

Therefore, the maximum pressure is that of state C, $P_C = 4{\times}10^5$ Pascals.

2) Calculation of the energies exchanged, in the form of work, heat, and the change in internal energy, by the system during each transformation.

a- An isobaric expansion from A to B

The work: W_1
$W_1 = -\int_{V_A}^{V_B} P_A dV \implies W_1 = -P_A(V_B - V_A)$
$\implies W_1 = -2.10^5(28 - 14) \times 10^{-3} \implies W_1 = -2800$ J (joules).
The quantity of heat: Q_1

$$Q_1 = Q_P = nc_P \int_{T_A}^{T_B} \frac{dT}{T}$$

$$\implies Q_2 = nc_P(T_B - T_A)$$

$$\implies Q_1 = 1.52 \times 8.314(673.56 - 336.78) \implies Q_1 = 6999.97\,\text{Joules}$$

The change in internal energy: ΔU_1

$$\Delta U = Q + W = nc_v \int_{T_A}^{T_B} \frac{dT}{T}$$

$$\begin{aligned} &\implies \Delta U_1 = Q_1 + W_1 = nc_v(T_B - T_A) \\ &\implies \Delta U_1 = 6999.99 - 2800 \\ &\implies \Delta U_1 = 4199.99\,\text{Joules} \end{aligned}$$

b- An isothermal compression from B to C ($dT = 0$)
The work: W_2

$$\begin{aligned} W_2 &= -\int_{V_B}^{V_C} P\,dV = -nRT_B \ln\left(\frac{V_C}{V_B}\right) \\ &= -1 \times 8.314 \times 673.56 \times \ln\left(\frac{14}{28}\right) \\ &= 3881.61\,\text{Joules} \end{aligned}$$

The change in internal energy: ΔU_2

$$\Delta U_2 = nc_v \int_{T_B}^{T_C} \frac{dT}{T} \implies \Delta U_2 = 0$$

The quantity of heat: Q_2

$$\begin{aligned} \Delta U_2 &= Q_2 + W_2 \\ &\implies 0 = Q_2 + W_2 \\ &\implies Q_2 = -W_2 \\ &\implies Q_2 = -3881.61\,\text{Joules} \end{aligned}$$

c- An isochoric cooling from C to A ($dV = 0$)
The work: W_3

$$W_3 = -\int_{V_A}^{V_B} P\,dV = 0$$

The change in internal energy ΔU_3 and the quantity of heat Q_3

$$\Delta U_3 = nc_v \int_{T_A}^{T_C} \frac{dT}{T} = Q_3 + W_3 \implies Q_3 = \Delta U_3 = nc_v(T_A - T_C)$$

$$\implies Q_3 = \Delta U_3 = 1\times\frac{3}{2}\times 8.314\times(336.78-673.56) \implies Q_3 = \Delta U_3 = -4199.99\,\text{Joules}$$

d- For the cycle :
The work: W_T

$$W_{\text{TOT}} = W_{\text{cycle}} = W_1 + W_2 + W_3 \implies W_{\text{cycle}} = 2081.61\,\text{Joules}$$

The quantity of heat: Q_T

$$Q_{\text{TOT}} = Q_{\text{cycle}} = Q_1 + Q_2 + Q \implies Q_{\text{cycle}} = -1081.61\,\text{Joules}$$

The change in internal energy: ΔU_T

$$\Delta U_{\text{TOT}} = \Delta U_{\text{cycle}} = W_{\text{cycle}} + Q_{\text{cycle}} = 0$$

Exercise 03

Consider one mole of a diatomic gas (assumed to be perfect, $C_p = \frac{7}{2}R$, $C_v = \frac{5}{2}R$, and $\gamma = 1.4$) in an initial thermodynamic state A defined by $P_A = 1\,\text{atm}$ and $T_A = 293\,\text{K}$. This gas undergoes a series of four reversible transformations represented on a (T, V) diagram by the rectangle (ABCD) in the following figure.

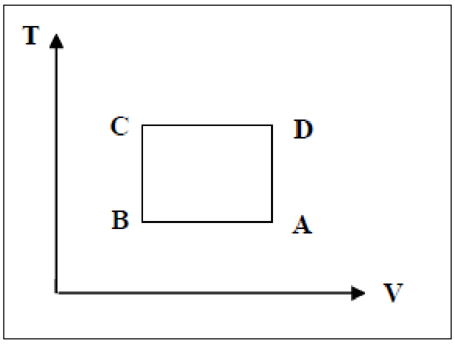

Figure 3.4: Diagram transformation

The pressure of state B is $P_B = 6\,\text{atm}$ and the temperature of state C is $T_C = 439.5\,\text{K}$.

1. Identify the nature and direction of these four transformations.

2. Calculate the variables for each state.

3. Qualitatively represent this cycle on a $P-V$ diagram.
4. Calculate, for each transformation and for the cycle, the work W, the heat Q, the internal energy ΔU, and the enthalpy ΔH. Is the first law of thermodynamics satisfied?

Solution :

1) The nature and direction of each transformation are as follows:

- Transformation from state A to state B (A→B) is an isothermal compression.
- Transformation from B to C (B→C) is an isochoric heating.
- Transformation from C to D (C→D) is an isothermal expansion.
- Transformation from D to A (D→A) is an isochoric cooling.

2) Calculation of the Variables for Each State :

- State A: $P_A = 1\,\text{atm}; \quad T_A = 293\,\text{K};$

Calculating the volume of state A:

$$P_A \cdot V_A = n \cdot R \cdot T_A \implies V_A = \frac{n \cdot R \cdot T_A}{P_A}$$

$$\implies V_A = \frac{1 \cdot 0.082 \cdot 293}{1} \implies V_A = 24\,\text{liters}$$

- State B: $T_B = T_A = 293\,\text{K}; \quad P_B = 6\,\text{atm}$

For an isothermal transformation, we have:

- State A to State B:

$$P_A \cdot V_A = P_B \cdot V_B \implies V_B = \frac{P_A \cdot V_A}{P_B}$$

$$\implies V_B = \frac{1 \cdot 24}{6} \implies V_B = 4\,\text{liters}$$

- State C: $T_C = 439.5\,\text{K}; \quad V_C = V_B = 4\,\text{liters}$

For an isochoric transformation, we have:

- State C to State D:

$$\frac{P_C}{T_C} = \frac{P_B}{T_B} \implies P_C = P_B \cdot \frac{T_C}{T_B}$$

$$\implies P_C = 6 \cdot \frac{439.5}{293} \implies P_C = 9\,\text{atm}$$

- State D: $T_D = T_C = 439.5\,\text{K}$; $V_D = V_A = 24\,\text{liters}$

The pressure of state D is calculated using the following relation:

$$P_D \cdot V_D = n \cdot R \cdot T_D \implies P_D = \frac{n \cdot R \cdot T_D}{V_D}$$

$$\implies P_D = \frac{1 \cdot 0.082 \cdot 439.5}{24} \implies P_D = 1.5\,\text{atm}$$

Calculation of Work, Heat, Change in Internal Energy, and Enthalpy:

a- Isothermal Compression from A to B ($dT = 0$):

The work: W_1

$$\begin{aligned} W_1 &= -\int_{V_A}^{V_B} P\,dV \\ &= -nRT_A \ln\left(\frac{V_B}{V_A}\right) \\ &= -1 \times 8.314 \times 293 \ln\left(\frac{424}{24}\right) \\ &= 4364.73\,\text{Joules} \end{aligned}$$

The change in internal energy: ΔU_1

$$\Delta U_1 = nc_v \int_{T_A}^{T_B} \frac{dT}{T} = 0$$

The amount of heat: Q_1

$$\begin{aligned} \Delta U_1 &= Q_1 + W_1 \\ &= 0 \\ &\Rightarrow Q_1 = -W_1 \\ &= -4364.73\,\text{Joules} \end{aligned}$$

The enthalpy: ΔH_1

$$\Delta H_1 = nc_p \int_{T_A}^{T_B} \frac{dT}{T} = 0$$

b- Isochoric Heating from B to C ($dV = 0$):

- Isothermal Expansion from C to D: The work: W_2

$$W_2 = -\int_{V_B}^{V_C} PdV \implies W_3 = 0$$

- The change in internal energy ΔU_2 **and the amount of heat** Q_2

$$\begin{aligned}\Delta U_2 &= nc_v \int_{T_B}^{T_C} \frac{dT}{T} \\ &= Q_2 + W_2 \\ &\Rightarrow Q_2 = \Delta U_2 = nc_v(T_C - T_B) \\ &= \Delta U_2 = 1 \times (\frac{5}{2}) \times 8.314 \times (439.5 - 293) \\ &= \Delta U_2 = 3045 \, \text{Joules}\end{aligned}$$

The enthalpy: ΔH_2

$$\begin{aligned}\Delta H_2 &= nc_p \int_{T_B}^{T_C} \frac{dT}{T} \\ &= nc_p(T_C - T_B) \\ &= 1 \times (\frac{7}{2}) \times 8.314 \times (439.5 - 293) \\ &= 4263 \, \text{Joules}\end{aligned}$$

c- D :

The work: W_3

$$\begin{aligned}W_3 &= -\int_{V_C}^{V_D} P \, dV \\ &= -nRT_C \ln\left(\frac{V_D}{V_C}\right) \\ &= -1 \times 8.314 \times 439.5 \ln\left(\frac{24}{4}\right) \\ &= -6547.09 \, \text{Joules}\end{aligned}$$

- The change in internal energy: ΔU_3

$$\Delta U_3 = nc_v \int_{T_C}^{T_D} \frac{dT}{T} = 0$$

- The amount of heat: Q_3

$$\begin{aligned}\Delta U_3 &= Q_3 + W_3 \\ &= 0 \\ &\Rightarrow Q_3 = -W_3 \\ &= 6547.09 \, \text{Joules}\end{aligned}$$

- **The enthalpy:** ΔH_3

$$\Delta H_3 = nc_p \int_{T_C}^{T_D} \frac{dT}{T} = 0$$

d- Isochoric Cooling from D to A:

- **The work:** W_4

$$W_4 = -\int_{V_D}^{V_A} P\,dV = 0$$

- **The change in internal energy** ΔU_4 **and the amount of heat** Q_4:

$$\begin{aligned}\Delta U_4 &= nc_v \int_{T_D}^{T_A} \frac{dT}{T}\\ &= Q_4 + W_4\\ &\Rightarrow Q_4 = \Delta U_4 = nc_v(T_A - T_D)\\ &= \Delta U_4 = 1 \times (\frac{5}{2}) \times 8.314 \times (293 - 439.5)\\ &= \Delta U_4 = -3045\,\text{Joules}\end{aligned}$$

- **The enthalpy:** ΔH_4

$$\begin{aligned}\Delta H_4 &= nc_p \int_{T_A}^{T_D} \frac{dT}{T}\\ &= nc_p(T_A - T_D)\\ &= 1 \times (\frac{7}{2}) \times 8.314 \times (293 - 439.5)\\ &= \Delta H_4 = -4263\,\text{Joules}\end{aligned}$$

e- For the cycle:

- **The work:** W_T

$$\begin{aligned}W_T &= W_{cycle} = W_1 + W_2 + W_3 + W_4\\ &= -2182.36\,\text{Joules}\end{aligned}$$

- **The amount of heat:** Q_T

$$\begin{aligned}Q_T &= Q_{cycle} = Q_1 + Q_2 + Q_3 + Q_4\\ &= 2182.36\,\text{Joules}\end{aligned}$$

- **The change in internal energy:** ΔU_T

$$\Delta U_T = \Delta U_{cycle} = W_{cycle} + Q_{cycle} = 0$$

- **The enthalpy: ΔH_T**

$$\Delta H_T = \Delta H_{cycle} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = 0$$

Exercise 04

During a thermodynamic process, a system moves from state A to state B, it is supplied with 400 J of heat and does 100 J of work. (a) For this transition, what is the system's change in internal energy? (b) If the system then moves from state B back to state A, what is its change in internal energy? (c) If in moving from A to B along a different path, $W'_{AB} = 400\,\mathrm{J}$ of work is done on the system, how much heat does it absorb?

Strategy

The first law of thermodynamics relates the internal energy change, work done by the system, and the heat transferred to the system in a simple equation. The internal energy is a function of state and is therefore fixed at any given point regardless of how the system reaches the state.

Solution

From the first law, the change in the system's internal energy is

$$\Delta E_{\mathrm{int}_{AB}} = Q_{AB} - W_{AB} = 400\,\mathrm{J} - 100\,\mathrm{J} = 300\,\mathrm{J}.$$

Consider a closed path that passes through the states A and B. Internal energy is a state function, so ΔE_{int} is zero for a closed path. Thus

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{int}_{AB}} + \Delta E_{\mathrm{int}_{BA}} = 0,$$

and

$$\Delta E_{\mathrm{int}_{AB}} = -\Delta E_{\mathrm{int}_{BA}}.$$

This yields

$$\Delta E_{\mathrm{int}_{BA}} = -300\,\mathrm{J}.$$

The change in internal energy is the same for any path, so

$$\Delta E_{\mathrm{int}_{AB}} = 300\,\mathrm{J} = \Delta E'_{\mathrm{int}_{AB}} = Q'_{AB} - W'_{AB} = Q'_{AB} - (-400\,\mathrm{J}),$$

and the heat exchanged is

$$Q'_{AB} = -100\,\mathrm{J}.$$

The negative sign indicates that the system loses heat in this transition.

Significance

When a closed cycle is considered for the first law of thermodynamics, the change in internal energy around the whole path is equal to zero. If friction were to play a role in this example, less work would result from this heat added.

Exercise 05

A machinist polishes a 0.50-kg copper fitting with a piece of emery cloth for 2.0 min. He moves the cloth across the fitting at a constant speed of 1.0 m/s by applying a force of 20 N, tangent to the surface of the fitting. (a) What is the total work done on the fitting by the machinist? (b) What is the increase in the internal energy of the fitting? Assume that the change in the internal energy of the cloth is negligible and that no heat is exchanged between the fitting and its environment. (c) What is the increase in the temperature of the fitting?

Strategy

The machinist's force over a distance that can be calculated from the speed and time given is the work done on the system. The work, in turn, increases the internal energy of the system. This energy can be interpreted as the heat that raises the temperature of the system via its heat capacity. Be careful with the sign of each quantity.

Solution

The power created by a force on an object or the rate at which the machinist does frictional work on the fitting is $F \cdot v = -Fv$. Thus, in an elapsed time Δt (2.0 min), the work done on the fitting is

$$W = -Fv\Delta t = -(20\,\mathrm{N})(1.0\,\mathrm{m/s})(1.2 \times 10^2\,\mathrm{s}) = -2.4 \times 10^3\,\mathrm{J}.$$

By assumption, no heat is exchanged between the fitting and its environment, so the first law gives for the change in the internal energy of the fitting:

$$\Delta E_{\text{int}} = -W = 2.4 \times 10^3\,\mathrm{J}.$$

Since ΔE_{int} is path independent, the effect of the $2.4 \times 10^3\,\mathrm{J}$ of work is the same as if it were supplied at atmospheric pressure by a transfer of heat. Thus,

$$2.4 \times 10^3\,\mathrm{J} = mc\Delta T = (0.50\,\mathrm{kg})(3.9 \times 10^2\,\mathrm{J/kg \cdot {}^\circ C})\Delta T,$$

and the increase in the temperature of the fitting is

$$\Delta T = 12^\circ C,$$

where we have used the value for the specific heat of copper, $c = 3.9 \times 10^2\,\mathrm{J/kg \cdot {}^\circ C}$.

Significance

If heat were released, the change in internal energy would be less and cause less of a temperature change than what was calculated in the problem.

Exercise 06

Heat is added to 1 mol of an ideal monatomic gas confined to a cylinder with a movable piston at one end. The gas expands quasi-statically at a constant temperature of 300 K until its volume increases from V to $3V$. (a) What is the change in internal energy of the gas? (b) How much work does the gas do? (c) How much heat is added to the gas?

Strategy

(a) Because the system is an ideal gas, the internal energy only changes when the temperature changes.

(b) The heat added to the system is therefore purely used to do work that has been calculated in Work, Heat, and Internal Energy.

(c) Lastly, the first law of thermodynamics can be used to calculate the heat added to the gas.

Solution

We saw in the preceding section that the internal energy of an ideal monatomic gas is a function only of temperature. Since $\Delta T = 0$, for this process, $\Delta E_{\text{int}} = 0$.

The quasi-static isothermal expansion of an ideal gas was considered in the preceding section and was found to be

$$\begin{aligned} W &= nRT \ln\left(\frac{V_2}{V_1}\right) \\ &= nRT \ln\left(\frac{3V}{V}\right) \\ &= (1.00\,\text{mol})(8.314\,\text{J/K}\cdot\text{mol})(300\,\text{K})\,(\ln 3) \\ &= 2.74 \times 10^3\,\text{J}. \end{aligned}$$

With the results of parts (a) and (b), we can use the first law to determine the heat added:

$$\Delta E_{\text{int}} = Q - W = 0,$$

which leads to

$$Q = W = 2.74 \times 10^3\,\text{J}.$$

Significance

An isothermal process has no change in the internal energy. Based on that, the first law of thermodynamics reduces to $Q = W$.

Exercise 07

When 1.00 g of water at 100°C changes from the liquid to the gas phase at atmospheric pressure, its change in volume is $1.67 \times 10^{-3}\,\text{m}^3$. (a) How much heat must be added to vaporize the water? (b) How much work is done by the water against the atmosphere in its expansion? (c) What is the change in the internal energy of the water?

Strategy

We can first figure out how much heat is needed from the latent heat of vaporization of the water. From the volume change, we can calculate the work done from $W = p\Delta V$ because the pressure is constant. Then, the first law of thermodynamics provides us with the change in the internal energy.

Solution

With L_v representing the latent heat of vaporization, the heat required to vaporize the water is

$$Q = mL_v = (1.00\,\mathrm{g})(2.26 \times 10^3\,\mathrm{J/g}) = 2.26 \times 10^3\,\mathrm{J}.$$

Since the pressure on the system is constant at $1.00\,\mathrm{atm} = 1.01 \times 10^5\,\mathrm{N/m^2}$, the work done by the water as it is vaporized is

$$W = p\Delta V = (1.01 \times 10^5\,\mathrm{N/m^2})(1.67 \times 10^{-3}\,\mathrm{m^3}) = 169\,\mathrm{J}.$$

From the first law, the thermal energy of the water during its vaporization changes by

$$\Delta E_{\text{int}} = Q - W = 2.26 \times 10^3\,\mathrm{J} - 169\,\mathrm{J} = 2.09 \times 10^3\,\mathrm{J}.$$

Significance

We note that in part (c), we see a change in internal energy, yet there is no change in temperature. Ideal gases that are not undergoing phase changes have the internal energy proportional to temperature. Internal energy in general is the sum of all energy in the system.

Exercise 08

1g of water at 373 K is converted into steam at the same temperature. The volume of water becomes 1671 ml on boiling. Calculate the change in the internal energy of the system if the heat of vaporization is 540 cal/g.

Solution:

As the vaporization takes place against a constant pressure of 1 atmosphere, work done for an irreversible process, w, is:

$$\begin{aligned} w &= p(V_2 - V_1) \\ &= nRT \\ &= \frac{1}{18} \times 1.987 \times 373 \\ &= 41 \text{ cal/g} \end{aligned}$$

$$q = 540 \text{ cal/g}$$

$$\begin{aligned} \Delta E &= q - w \text{ (First Law)} \\ \Delta E &= 540 - 41 \\ \Delta E &= 499 \text{ cal/g} \end{aligned}$$

Exercise 09

A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 liters to a volume of

10 liters. In doing so it absorbs 400 J thermal energy from its surroundings. Determine ΔE for the process.

Solution:

$$\Delta E = q - w$$

Here, $q = 400$ J
$w = -p(V_2 - V_1) = -(1)(10 - 5)$
$= -5$ atm
$= -506$ J [1 atm = 101.2 J]

Substituting values in (1):

$$\begin{aligned}\Delta E &= 400 \text{ J} - (-506 \text{ J}) \\ &= 400 + 506 \\ &= 906 \text{ J}\end{aligned}$$

Exercise 10

Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 to one atmosphere at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy? Also, calculate ‘q’.

Solution:

$$w = -2.303 nRT \log\left(\frac{P_2}{P_1}\right)$$

$$\begin{aligned}n &= \frac{10}{5} = 5 \text{ moles} \\ T &= 273 \text{ K} \\ P_1 &= 20 \text{ atm} \\ P_2 &= 1 \text{ atm}\end{aligned}$$

Substituting the values we get:

$$w = -2.303 \times 5 \times 1.987 \times 273 \log\frac{20}{1} = -8126.65 \text{ cal.}$$

Since there is no change in temperature:

$$\Delta E = 0$$

Hence:

$$\begin{aligned}q &= \Delta E + w \\ &= 0 + (-8126.65) \\ &= -8126.65 \text{ cal.}\end{aligned}$$

Chapter 4

Applications of the first law of thermodynamics to thermochemistry

4.1 Introduction

Thermochemistry is a branch of thermodynamics that deals with the laws governing the transformations of a system with chemical reactions. These laws allow us to determine the amount of heat involved in a chemical reaction and also provide information about the evolution of this reaction under imposed operating conditions (temperature and pressure).

4.2 Chemical Reaction

A chemical reaction is a transformation of reactants into products under a temperature T and atmospheric pressure ($P = 1$ atm):

$$aA + bB \rightarrow cC + dD$$

Such as:

- a, b, c, and d: represent stoichiometric coefficients.
- A and B are chemical species representing the reactants (initial state under T and P).
- C and D are chemical species representing the products (final state under T and P).

The reaction indicates that a moles of A react with b moles of B to give c moles of C and d moles of D.

In general, a chemical reaction occurs at a constant temperature T, meaning: the temperature of the products = temperature of the reactants ($T_A = T_B = T_C = T_D = T$, it is called the temperature of the chemical reaction).

The initial state is characterized by the internal energy and enthalpy of the reactants (U_1 and H_1 respectively), and the final state is characterized by the internal energy and enthalpy of the products (U_2 and H_2). The reaction is assumed to be complete.

4.3 Heat of a Chemical Reaction

The heat of a chemical reaction (or enthalpy of reaction) at a temperature T is defined as the heat energy exchanged (released or absorbed) with the external surroundings during the transformation of reactants into chemical products during a chemical reaction.

If heat is supplied by the reaction ($Q < 0$), then this reaction is Exothermic (Release of heat). Conversely, if heat is absorbed by the chemical reaction ($Q > 0$), then this reaction is Endothermic (absorbs heat).

4.3.1 Heat at Constant Volume

Consider a chemical reaction that occurs at constant volume (isochoric transformation). According to the first law of thermodynamics, we have:

$$Q_V + W = \Delta U$$

where the work $W = 0$ for an isochoric transformation (V is constant). Therefore:

$$Q_V = \Delta U = U_{\text{Products}} - U_{\text{Reactants}}$$

Example: $\mathrm{Cl_2}(g) + \mathrm{H_2}(g) \rightarrow 2\mathrm{HCl}(g)$

The number of moles of gaseous species remains constant (Number of moles of reactants in the gaseous state = number of moles of products in the gaseous state).

4.3.2 Heat at Constant Pressure

Consider a chemical reaction that occurs at constant pressure (isobaric transformation). According to the first law of thermodynamics, for an isobaric transformation, we have:

$$Q_P = \Delta U = U_{\text{Products}} - U_{\text{Reactants}}$$

IV-3-3- Relation between Q_P and Q_V:

Consider the following chemical reaction that occurs in the gaseous phase at temperature T: $aA + bB \longrightarrow cC + dD$

At constant pressure, we have:

$$\Delta U = Q_P + W \implies Q_P = \Delta U - W$$

We also have: $\Delta U = Q_V$ and $W = -(PV_2 - PV_1)$

Therefore, it follows that:

$$Q_P = Q_V + (PV_2 - PV_1)$$

The reactants and products are in the gaseous state (assumed ideal gas): $PV_1 = n_{\text{reactants}} RT = (a+b)RT$ and $PV_2 = n_{\text{products}} RT = (c+d)RT$

After substitution, we find that:

$$Q_P = Q_V + RT(n_{\text{products}} - n_{\text{reactants}})$$

Thus:

$$Q_P = Q_V + \Delta nRT$$

Where: $\Delta n = n_{\text{products}} - n_{\text{reactants}}$

The following relation can be established between the enthalpy of a reaction and the change in internal energy:

$$\Delta H_R = \Delta U + \Delta nRT$$

4.4 The standard state

It is necessary to specify the conditions of temperature and pressure under which chemical reactions are carried out; therefore, a standard state is defined.

The standard state or standard conditions of temperature and pressure (STP) of a chemical compound taken in its pure state are defined under a pressure of one atmosphere (1 atm) and at the standard temperature of 25°C.

The standard enthalpy of the reaction is noted; it represents the change in enthalpy of a reaction carried out at a temperature of 298 K where the reactants and products are taken in their standard states (298 K and 1 atm).

4.5 The standard enthalpy of formation (ΔH_f^0)

4.5.1 Simple substances and compound substances

A substance is a material composed of molecules which are a union of atoms: If the atoms are identical, then the substance is considered a simple substance (H_2, O_2, N_2, ...). If the atoms are different, then the substance is considered a compound substance (NH_3, CH_4, HCl, ...).

4.5.2 Standard enthalpy of formation of a compound

The standard enthalpy of formation, denoted as ΔH_f°, of a chemical compound is the corresponding change in enthalpy for the reaction of forming one mole of that compound under standard conditions from its elements in their standard states as well ($P = 1\,\text{atm}$ and $T = 298\,\text{K}$).

Note: The standard enthalpy of formation of pure simple substances in the standard state is zero, such as:

$$\begin{aligned}\Delta H_f^0(O_2)_g &= \Delta H_f^0(N_2)_g\\ &= \Delta H_f^0(H_2)_g\\ &= \Delta H_f^0(fe)_s\\ &= \Delta H_f^0(C_{\text{graphite}})_s\\ &= \Delta H_f^0(Cl)_g\\ &= 0\end{aligned}$$

Example: The standard enthalpy of formation of water in the gaseous state.

Water is formed from hydrogen and oxygen.

In the standard state, hydrogen is in the form of $H_2\,(g)$ and oxygen is in the form of $O_2\,(g)$, hence:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)} \quad \Delta H_f^0(H_2O,\,298K)_g = -57.8\,\text{Kcal}\cdot\text{mol}^{-1}$$

4.5.3 Enthalpy of dissociation

The energy of a chemical bond (enthalpy of dissociation of a bond) is defined as the change in enthalpy of the reaction that dissociates one mole of such bonds.

Example:

At 25°C and 1 bar, it takes 436 kJ of heat to dissociate one mole of dihydrogen gas entirely into two moles of hydrogen atoms:

$$\mathrm{H}_2(g) \longrightarrow 2\mathrm{H}(g) \quad \Delta H = +436\ \text{kJ}$$

The energy of the H-H bond = enthalpy of the dissociation reaction of $\mathrm{H}_2 = 436$ kJ/mol

4.5.4 Enthalpy of physical state change

In thermodynamics, the enthalpy of physical state change (also known as latent heat of state change) of a pure substance is the change in enthalpy accompanying the transition of the system from one physical state 1 to another physical state 2.

Example:

- The transition from the solid state to the liquid state is referred to as the enthalpy of fusion (ΔH_{fus} or L_{f}). The reverse of this transformation is solidification, so we talk about the enthalpy of solidification ($\Delta H_{\text{sol}} = -\Delta H_{\text{fus}}$).
- The transition from the liquid state to the gaseous state is referred to as the enthalpy of vaporization (ΔH_{vap} or L_{vap}). The reverse of this transformation is liquefaction ($\Delta H_{\text{liq}} = -\Delta H_{\text{vap}}$).
- The transition from the solid state to the gaseous state is referred to as the enthalpy of sublimation (ΔH_{sub} or L_{sub}). The reverse of this transformation is condensation ($\Delta H_{\text{cond}} = -\Delta H_{\text{sub}}$).

4.5.5 The enthalpy of a chemical reaction ΔH_R^0:

The enthalpy of a chemical reaction is calculated by two methods, direct and indirect.

4.5.5.1 Direct Method

a- Determination of the enthalpy of the reaction from the enthalpies of formation of the compounds:

Consider the following reaction at the temperature of 298 K:

$$aA + bB \to cC + dD$$

Knowing the enthalpies of formation of the products and reactants, we can determine the enthalpy of the reaction using the following relationship:

$$\Delta H_R^0(298\,\text{K}) = \sum \Delta H_f^0(\text{Products}) - \sum \Delta H_f^0(\text{Reactants})$$

$$\Delta H_R^0(298\,\text{K}) = (c\Delta H_f^0(C) + d\Delta H_f^0(D)) - (a\Delta H_f^0(A) + b\Delta H_f^0(B))$$

Example:

$$C_2H_4(g)+H_2O(liq) \to C_2H_5OH(liq)\Delta H_R^0 = \Delta H_f^0(C_2H_5OH)-(\Delta H_f^0(C_2H_4)+\Delta H_f^0(H_2O))$$

b- Determination of the enthalpy of the reaction from the bond formation energies:

A molecule is a union of atoms. When two atoms come into contact, each atom contributes one electron to form a bond. There are several types of bonds: single bond $H-H$ (H_2), double bond $C=C$ (C_2H_4), triple bond $C \equiv C$ (C_2H_2).

The bond energy $A-B$ between atoms A and B, denoted as E_{A-B}, is the energy released during the formation of a covalent bond from the atoms taken in the gaseous state under standard conditions ($P = 1$ atm and $T = 298$ K).

It is equal to the enthalpy change ΔH_{A-B} required to carry out the formation reaction of this chemical bond.

$$\text{Atome } A(g) + \text{Atome } B(g) \rightarrow \text{Molecule } A\check{}B(g) + E_{A-B}$$

$E_{A-B} = \Delta H_{A-B}(298\,\mathrm{K})$ (bond formation energy or bond enthalpy).

ΔH_{A-B} is expressed in cal/mol or J/mol, it is always negative ($\Delta H_{A-B} < 0$). Therefore, bond formation is exothermic (on the contrary, bond breaking is endothermic).

The enthalpy of any chemical reaction can be determined using bond formation enthalpy values. It is equal to the difference between the bond energies of the products and the bond energies of the reactants.

$$aA + bB \rightarrow cC + dD$$

$$\Delta H^0_R(298\,\mathrm{K}) = (c\sum E_C + d\sum E_D) - (a\sum E_A + b\sum E_B)$$

Example:

$$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$$

$$\Delta H^0_R(298\,\mathrm{K}) = (E_{C-C} + 6E_{C-H}) - (E_{C\equiv C} + 2E_{C-H} + 2E_{H-H})$$

4.5.5.2 Indirect Method: Hess's Law

If we consider the reaction $R \rightarrow P$ for which we seek the enthalpy of the chemical reaction (where R represents one or more reactants and P represents one or more products).

Knowing the enthalpies of the following secondary reactions: $R \rightarrow X$ and $X \rightarrow P$.

This means that the reaction from R to P occurs through the intermediary X.

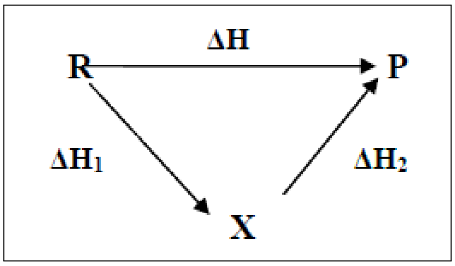

Figure 4.1: Indirect Method

The enthalpy ΔH is a state function; it depends only on the initial and final states and not on the path followed. It follows that:

$$\Delta H_R^0(298K) = \Delta H_1 + \Delta H_2$$

Therefore: The enthalpy of the reaction is the sum of the enthalpies of intermediate transformations.

$$\Delta H_R^0(298K) = \sum \Delta H_i$$

Example:
We are trying to calculate $\Delta H_R^0(298K)$ of the following reaction:

$$\mathrm{CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (liq)\ \ (1)}\ \ \Delta H_R^0(298K) = ?$$

Knowing the enthalpies of other chemical reactions.

$$\mathrm{C\ (g) + 2H_2\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (liq)\ \ (2)}\ \ \Delta H_1$$

$$\mathrm{C\ (g) + 2H_2\ (g) \rightarrow CH_4\ (g)\ \ (3)}\ \ \Delta H_2$$

We observe that reaction (2) is the sum of reactions (1) and (3).
Therefore, by conducting an energy balance, we will have:

$$\Delta H_1 = \Delta H_\mathrm{R} + \Delta H_2 \implies \Delta H_\mathrm{R} = \Delta H_1 - \Delta H_2$$

We have: $\Delta H_1 = \Delta H_\mathrm{f}^0(\mathrm{CO_2(g)}) + \Delta H_\mathrm{f}^0(\mathrm{H_2O(liq)})$
And $\Delta H_2 = \Delta H_\mathrm{f}^0(\mathrm{CH_4(g)})$
Therefore:

$$\Delta H_\mathrm{R} = \Delta H_\mathrm{f}^0(\mathrm{CO_2(g)}) + \Delta H_\mathrm{f}^0(\mathrm{H_2O(liq)}) - \Delta H_\mathrm{f}^0(\mathrm{CH_4(g)})$$

4.5.5.3 Variation of the enthalpy of the reaction with temperature (Kirchhoff's Law)

Consider the following reaction:

$$aA + bB \longrightarrow cC + dD$$

Knowing the standard enthalpy of this chemical reaction at the temperature 298 K, we can calculate the enthalpy of this reaction at another temperature T.

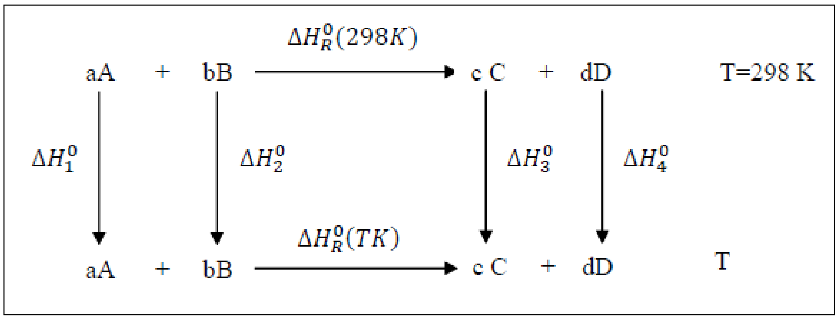

Figure 4.2: Kirchhoff's Law

We know that: $\sum \Delta H_i^0(\text{cycle}) = 0$

$$\text{So: } \Delta H_R^0(298K) + \Delta H_4 + \Delta H_3 - \Delta H_1 - \Delta H_2 - \Delta H_R^0(TK) = 0$$

$$\Longrightarrow \Delta H_R^0(TK) = \Delta H_R^0(298K) + \Delta H_4 + \Delta H_3 - \Delta H_1 - \Delta H_2 \ldots (1)$$

$$\Delta H_1^0 = \int_{298}^{T} acp_A dT$$

$$\Delta H_2^0 = \int_{298}^{T} bc_{PB} dT$$

$$\Delta H_3^0 = \int_{298}^{T} cc_{PC} dT$$

$$\Delta H_4 = \int_{298}^{T} dc_{PD} dT$$

$$(1) \Longrightarrow \Delta H_R^0(TK) = \Delta H_R^0(298K) + \int_{298}^{T} \left[(cc_{PC} + dc_{PD}) - (ac_{PA} + bc_{PB})\right] dT$$

$$\text{Then: } \Delta H_R^0(TK) = \Delta H_R^0(298K) + \int_{298}^{T} \Delta c_P dT \text{ (Kirchhoff's Law)}$$
$$\text{Where: } \Delta c_P = (cc_{PC} + dc_{PD}) - (ac_{PA} + bc_{PB})$$
$$\text{In general: } \Delta c_P = \sum n_i cp_i(\text{Products}) - \sum n_j cp_j(\text{Reactifs}))$$

Exercise 1:

Calculate the standard heat of combustion $\Delta H_r^{0,298K}$ of solid oxalic acid ($C_2H_2O_4$, s) at 25°C and atmospheric pressure, using the standard molar enthalpies of formation. Given that:

$\Delta H_f^{0,298}(C_2H_2O_4, s) = -1822.2\,\text{kJ/mol}$

$\Delta H_f^{0,298}(CO_2, g) = -393\,\text{kJ/mol}$

$\Delta H_f^{0,298}(H_2O, l) = -285.2\,\text{kJ/mol}$

Solution:

The combustion reaction of oxalic acid is: $C_2H_2O_4(s) + 12O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$ We calculate the heat of combustion (enthalpy of combustion reaction) using the direct method:

$$\begin{aligned}
\Delta H_\mathrm{r}^0(298\,\mathrm{K}) &= \sum \Delta H_\mathrm{f}^0(\text{Products}) - \sum \Delta H_\mathrm{f}^0(\text{Reactants}) \\
&\implies \Delta H_\mathrm{r}^0(298\,\mathrm{K}) = 2\Delta H_\mathrm{f}^0(CO_2(g)) + \Delta H_\mathrm{f}^0(H_2O(l)) - \Delta H_\mathrm{f}^0(C_2H_2O_4(s)) \\
&\implies \Delta H_\mathrm{r}^0(298\,\mathrm{K}) = 2 \cdot (-393) + (-286.2) - (-1822.2) \\
&\implies \Delta H_\mathrm{r}^0(298\,\mathrm{K}) = 750\,\mathrm{kJ}
\end{aligned}$$

Exercise 2:

Consider the following reaction: $CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$

1- Calculate the standard enthalpy $\Delta H^\circ_{r,298\mathrm{K}}$ of this reaction. Is the reaction endothermic or exothermic?

2- Deduce the value of the internal energy $\Delta U^\circ_{r,298\mathrm{K}}$ of the same reaction.

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

$$\begin{aligned}
CO(g) + \frac{1}{2}O_2(g) &\longrightarrow CO_2(g) & \Delta H_\mathrm{r}^0(298\,\mathrm{K}, 1) &= -283\,\mathrm{kJ} \\
H_2(g) + \frac{1}{2}O_2(g) &\longrightarrow H_2O(g) & \Delta H_\mathrm{r}^0(298\,\mathrm{K}, 2) &= -241.8\,\mathrm{kJ} \\
C_2H_4(g) + 2O_2(g) &\longrightarrow CO_2(g) + 2H_2O(g) & \Delta H_\mathrm{r}^0(298\,\mathrm{K}, 3) &= -803.2\,\mathrm{kJ}
\end{aligned}$$

Solution:

1. The studied reaction is obtained by the following summation: Reaction

1 + 3 × reaction 2 - reaction 3 Therefore:

$$\begin{aligned}\Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K}) &= \Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K},1) + 3\cdot\Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K},2) - \Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K},3)\\ &\Longrightarrow\ \Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K}) = (-283) + 3\cdot(-241.8) - (-803.2)\\ &\Longrightarrow\ \Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K}) = -205.2\,\mathrm{kJ}\end{aligned}$$

Since $\Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K}) < 0$, the reaction is exothermic.

2. Calculation of the change in internal energy using the relation:

$$\Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K}) = \Delta U_{\mathrm{r}}^{0} + \Delta n\cdot R\cdot T \implies \Delta U_{\mathrm{r}}^{0} = \Delta H_{\mathrm{r}}^{0}(298\,\mathrm{K}) - \Delta n\cdot R\cdot T$$

where $\Delta n = n_{\text{Products}} - n_{\text{Reactants}}$.

$\Delta n = (1+1) - (3+1) \implies \Delta n = -2$ moles
$\Delta U_{\mathrm{r}}^{0} = (-205.2) - (-2)\cdot 8.314\cdot 10^{-3}\cdot 298 \implies \Delta U_{\mathrm{r}}^{0} = -200.25\,\mathrm{kJ}$

Exercise 3:
We consider the oxidation reaction of ammonia by oxygen as follows:

$$2\,NH_3(g) + 5/2\,O_2(g) \longrightarrow 2\,NO(g) + 3\,H_2O(g) \quad \Delta H_r^{0}(298\,K) = -109\,\mathrm{kJ}$$

Calculate the standard molar enthalpy of formation of NH_3 (g) knowing the standard molar enthalpies of formation of NO (g) and H_2O (g).
Given:

$$\Delta H_f^{0}(298\,K; NO) = 21.5\,\mathrm{kJ/mol} \quad \text{and} \quad \Delta H_f^{0}(298\,K; H_2O) = -58\,\mathrm{kJ/mol}$$

Solution:
We apply the following relation:

$$\Delta H_r^{0}(298\,K) = 2\cdot\Delta H_f^{0}(298\,K; NO) + 3\cdot\Delta H_f^{0}(298\,K; H_2O) - 2\cdot\Delta H_f^{0}(298\,K; NH_3)$$

$$\implies \Delta H_f^{0}(298\,K; NH_3) = \frac{2\cdot\Delta H_f^{0}(298\,K; NO) + 3\cdot\Delta H_f^{0}(298\,K; H_2O) - \Delta H_r^{0}(298\,K)}{2}$$

$$\implies \Delta H_f^{0}(298\,K; NH_3) = \frac{109 + (2\cdot 21.5) + (3\cdot(-58))}{2}$$

$$\implies \Delta H_f^{0}(298\,K; NH_3) = -11\,\mathrm{kJ/mol}$$

Exercise 4:
The combustion reaction of one mole of ethylene under standard pressure and temperature conditions is given by the equation:

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H_r^0(298\,K) = -1387.8\,kJ$$

1. Calculate the standard molar enthalpy of formation of $C_2H_4(g)$ knowing that $\Delta H_f^0(298\,K; H_2O) = -284.2\,kJ/mol$ and $\Delta H_f^0(298\,K; CO_2) = -393\,kJ/mol$.

2. Using the bond energies (presented in the table) as well as the enthalpy of sublimation of carbon $C(s) \rightarrow C(g) \quad \Delta H^\circ_{\text{sub}}(C, s) = 171.2\,\text{kcal mol}^{-1}$, calculate the C=C bond energy in $C_2H_4(g)$.

Bond	Δh°_{298} (bond) $(\text{kJ} \cdot \text{mol}^{-1})$
H-H	-434.7
C-H	-413.8
C-C	-263.3

Solution :

1. We calculate the standard molar enthalpy of formation of $\text{C}_2\text{H}_4(g)$ using the following relation:

$$\Delta H_r^0(298\,\text{K}) = 2 \cdot \Delta H_f^0(298\,\text{K}; \text{CO}_2) + 2 \cdot \Delta H_f^0(298\,\text{K}; \text{H}_2\text{O}) - \Delta H_f^0(298\,\text{K}; \text{C}_2\text{H}_4)$$

$$\Longrightarrow \Delta H_f^0(298\,\text{K}; \text{C}_2\text{H}_4) = 2 \cdot \Delta H_f^0(298\,\text{K}; \text{CO}_2) + 2 \cdot \Delta H_f^0(298\,\text{K}; \text{H}_2\text{O}) - \Delta H_r^0(298\,\text{K})$$

$$\Longrightarrow \Delta H_f^0(298\,\text{K}; \text{C}_2\text{H}_4) = 2 \cdot (-393) + 2 \cdot (-284.2) - (-1387.8)$$

$$\Longrightarrow \Delta H_f^0(298\,\text{K}; \text{C}_2\text{H}_4) = 33.4\,\text{kJ}$$

2- Calculate the bond energy of C = C in C_2H_4 (g).

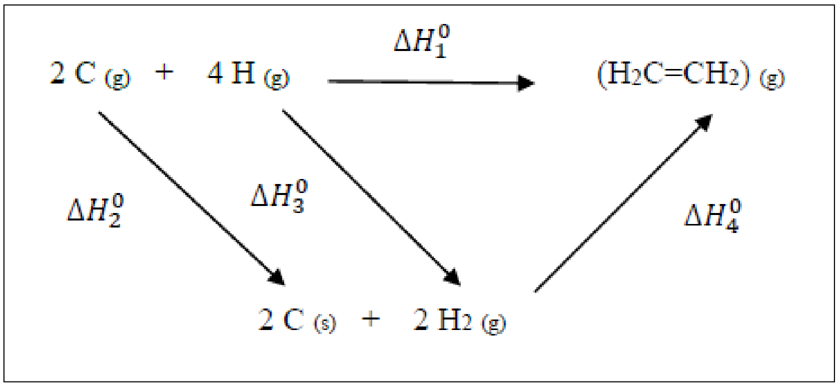

Figure 4.3

For the obtained cycle, we have:

$$\sum \Delta H_i^0 = 0 \Longrightarrow \Delta H_1^0 - \Delta H_2^0 - \Delta H_3^0 - \Delta H_4^0 = 0$$

$$\Delta H_1^0 = \Delta h_{298}^0(C = C) + 4\Delta h_{298}^0(C - H)$$

$$\Delta H_2^0 = -\Delta h_{\text{sub},298}^0(C, s)$$

$$\Delta H_3^0 = 2\Delta h_{298}^0(H - H)$$

$$\Delta H_4^0 = \Delta H_f^0(298\,\text{K}; \text{C}_2\text{H}_4)$$

After substitution, we find that:

$$\begin{aligned}
\Delta h_{298}^0(C = C) &= \Delta H_f^0(298\,\text{K}; \text{C}_2\text{H}_4) + 2\Delta h_{298}^0(H - H) \\
&\quad - 2 \cdot \Delta h_{\text{sub},298}^0(C, s) - 4\Delta h_{298}^0(C - H) \\
&= 33.4 + (2 \cdot (-434.7)) - 2 \cdot (171.2 \cdot 4.18) - (4 \cdot (-413.8)) \\
&\implies \Delta h_{298}^0(C = C) = -612.03\,\text{kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

Exercise 5:

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Write a thermochemical equation for the reaction of one mole of sucrose:

$$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq}) + 8\text{KClO}_3(\text{aq}) \longrightarrow 12\text{CO}_2(\text{g}) + 11\text{H}_2\text{O}(\text{l}) + 8\text{KCl}(\text{aq})$$

Solution

The present exercise does not involve the reaction of stoichiometric amounts of reactants, and so the limiting reactant must be identified (it limits the yield of the reaction and the amount of thermal energy produced or consumed).

The provided amounts of the two reactants are:

$$(2.67\,\text{g})\left(\frac{1\,\text{mol}}{342.3\,\text{g}}\right) = 0.00780\,\text{mol C}_{12}\text{H}_{22}\text{O}_{11}$$
$$(7.19\,\text{g})\left(\frac{1\,\text{mol}}{122.5\,\text{g}}\right) = 0.0587\,\text{mol KClO}_3$$

The provided molar ratio of perchlorate-to-sucrose is then:

$$\frac{0.0587\,\text{mol KClO}_3}{0.00780\,\text{mol C}_{12}\text{H}_{22}\text{O}_{11}} = 7.52$$

The balanced equation indicates 8 mol $KClO_3$ are required for reaction with 1 mol $C_{12}H_{22}O_{11}$. Since the provided amount of KClO3 is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

$$\Delta H = \frac{-43.7\,\text{kJ}}{0.0587\,\text{mol KClO}_3} = -744\,\text{kJ/mol KClO}_3$$

Because the equation, as written, represents the reaction of 8 mol $KClO_3$, the enthalpy change is:

$$(-744\,\text{kJ/mol KClO}_3)(8\,\text{mol KClO}_3) = -5960\,\text{kJ}$$

The enthalpy change for this reaction is $-5960\,\text{kJ}$, and the thermochemical equation is:

$$C_{12}H_{22}O_{11} + 8KClO_3 \longrightarrow 12CO_2 + 11H_2O + 8KCl \quad \Delta H = -5960\,\text{kJ}$$

Check Your Learning

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_2$(s) and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2$(s) is produced?

ANSWER:$\Delta H = -338\,\text{kJ}$

Exercise 6:

Ozone, O_3(g), forms from oxygen, O_2(g), by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, ΔH_f°, of ozone from the following information:

$$3O_2(g) \rightarrow 2O_3(g) \quad \Delta H^\circ = +286\,\text{kJ}$$

Solution

ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, ΔH_f° for O_3(g) is the enthalpy change for the reaction:

$$\frac{3}{2}O_2(g) \rightarrow O_3(g)$$

For the formation of 2 mol of O_3(g), $\Delta H^\circ = +286\,\text{kJ}$. This ratio, $\left(\frac{286\,\text{kJ}}{2\,\text{mol O}_3}\right)$, can be used as a conversion factor to find the heat produced when 1 mole of O_3(g) is formed, which is the enthalpy of formation for O_3(g):

$$\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1\,\text{mol O}_3 \times \frac{286\,\text{kJ}}{2\,\text{mol O}_3} = 143\,\text{kJ}$$

Therefore, $\Delta H_f^\circ[O_3(g)] = +143\,\text{kJ/mol}$.

Check Your Learning

Hydrogen gas, H_2, reacts explosively with gaseous chlorine, Cl_2, to form hydrogen chloride, HCl(g). What is the enthalpy change for the reaction of 1 mole of $H_2(g)$ with 1 mole of $Cl_2(g)$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of HCl(g) is $-92.3\,\mathrm{kJ/mol}$.

ANSWER:$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g) \quad \Delta H^\circ = -184.6\,\mathrm{kJ}$

Exercise 7:

Determine the enthalpy of formation, ΔH_f°, of $FeCl_3(s)$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\begin{aligned} Fe(s) + Cl_2(g) &\longrightarrow FeCl_2(s) & \Delta H^\circ &= -341.8\,\mathrm{kJ} \\ FeCl_2(s) + \frac{1}{2}Cl_2(g) &\longrightarrow FeCl_3(s) & \Delta H^\circ &= -57.7\,\mathrm{kJ} \end{aligned}$$

Solution

We are trying to find the standard enthalpy of formation of $FeCl_3(s)$, which is equal to ΔH° for the reaction:

$$Fe(s) + \frac{3}{2}Cl_2(g) \longrightarrow FeCl_3(s) \quad \Delta H_f^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their ΔHs:

$$\begin{aligned} Fe(s) + Cl_2(g) &\longrightarrow FeCl_2(s) & \Delta H^\circ &= -341.8\,\mathrm{kJ} \\ FeCl_2(s) + \frac{1}{2}Cl_2(g) &\longrightarrow FeCl_3(s) & \Delta H^\circ &= -57.7\,\mathrm{kJ} \\ Fe(s) + \frac{3}{2}Cl_2(g) &\longrightarrow FeCl_3(s) & \Delta H^\circ &= -399.5\,\mathrm{kJ} \end{aligned}$$

$$\frac{\Delta H^\circ = -57.7}{\Delta H^\circ = -399.5} = -399.5\,\mathrm{kJ/mol}.$$

The enthalpy of formation, ΔH_f°, of $FeCl_3(s)$ is $-399.5\,\mathrm{kJ/mol}$.

Check Your Learning

Calculate ΔH for the process:

$$N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)$$

from the following information:

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad \Delta H = 180.5\,\mathrm{kJ}$$

$$NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g) \quad \Delta H = -57.06\,\mathrm{kJ}$$

ANSWER:66.4 kJ

Exercise 8:

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

$$\text{(i)}\quad \mathrm{ClF\,(g)} + \mathrm{F_2(g)} \longrightarrow \mathrm{ClF_3(g)} \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH° for reaction (i):

$$\begin{aligned}
&\text{(ii)} && 2\,\mathrm{OF_2(g)} \longrightarrow \mathrm{O_2(g)} + 2\,\mathrm{F_2(g)} \quad \Delta H^\circ_{\text{(ii)}} = -49.4\,\mathrm{kJ}\\
&\text{(iii)} && 2\,\mathrm{ClF\,(g)} + \mathrm{O_2(g)} \longrightarrow \mathrm{Cl_2O\,(g)} + \mathrm{OF_2(g)} \quad \Delta H^\circ_{\text{(iii)}} = +214.0\,\mathrm{kJ}\\
&\text{(iv)} && \mathrm{ClF_3(g)} + \mathrm{O_2(g)} \longrightarrow \frac{1}{2}\mathrm{Cl_2O\,(g)} + \frac{3}{2}\mathrm{OF_2\,(g)} \quad \Delta H^\circ_{\text{(iv)}} = +236.2\,\mathrm{kJ}
\end{aligned}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that ClF (g) is needed as a reactant. This can be obtained by multiplying reaction (iii) by 12, which means that the ΔH° change is also multiplied by 12:

$$\mathrm{ClF\,(g)} + 12\,\mathrm{O_2(g)} \longrightarrow 12\,\mathrm{Cl_2O\,(g)} + 12\,\mathrm{OF_2(g)} \quad \Delta H^\circ = 12(214.0) = +107.0\,\mathrm{kJ}$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction (ii), which means that the ΔH° changes sign and is halved:

$$\frac{1}{2}\mathrm{O_2\,(g)} + \mathrm{F_2(g)} \longrightarrow \mathrm{OF_2(g)} \quad \Delta H^\circ = +24.7\,\mathrm{kJ}$$

To get ClF_3 as a product, reverse (iv), changing the sign of ΔH°:

$$\frac{1}{2}\mathrm{Cl_2O\,(g)} + \frac{3}{2}\mathrm{OF_2\,(g)} \longrightarrow \mathrm{ClF_3(g)} + \mathrm{O_2(g)}(1) \quad \Delta H^\circ = -236.2\,\mathrm{kJ}$$

Now check to make sure that these reactions add up to the reaction we want:

$$\begin{aligned}
&\mathrm{ClF\,(g)} + \frac{1}{2}\mathrm{O_2\,(g)} + \frac{1}{2}\mathrm{F_2\,(g)} \longrightarrow \mathrm{ClF_3(g)}(2) && \Delta H^\circ = +107.0\,\mathrm{kJ}\\
&\frac{1}{2}\mathrm{O_2\,(g)} + \frac{1}{2}\mathrm{F_2\,(g)} \longrightarrow \mathrm{OF_2(g)}(3) && \Delta H^\circ = +24.7\,\mathrm{kJ}
\end{aligned}$$

$$\frac{\Delta H^\circ = -236.2\,\mathrm{kJ}}{\Delta H^\circ = -104.5\,\mathrm{kJ}}$$

Reactants $\frac{1}{2}O_2$ and $\frac{1}{2}O_2$ cancel out product O_2; product $\frac{1}{2}Cl_2O$ cancels reactant $\frac{1}{2}Cl_2O$; and reactant $\frac{3}{2}OF_2$ is cancelled by products $\frac{1}{2}OF_2$ and OF_2. This leaves only reactants $\mathrm{ClF(g)}$ and $\mathrm{F_2(g)}$ and product $\mathrm{ClF_3(g)}$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH° values will give the desired ΔH°:

$$\Delta H^\circ = (+107.0\,\mathrm{kJ}) + (24.7\,\mathrm{kJ}) + (-236.2\,\mathrm{kJ}) = -104.5\,\mathrm{kJ}$$

Exercise 9:
Both graphite and diamond burn.

$$\mathrm{C(s, diamond) + O_2(g) \longrightarrow CO_2(g)}$$

For the conversion of graphite to diamond:

$$\mathrm{C(s, graphite) \longrightarrow C(s, diamond)} \quad \Delta H^\circ_{298} = 1.90\,\mathrm{kJ}$$

Which produces more heat, the combustion of graphite or the combustion of diamond?
ANSWER: Diamond
Exercise 10:
Calculate ΔH for the process

$$\mathrm{Hg_2Cl_2(s) \longrightarrow 2\,Hg\,(l) + Cl_2(g)}$$

from the following information:

$$\mathrm{Hg\,(l) + Cl_2(g) \longrightarrow HgCl_2(s)} \quad \Delta H = -224\,\mathrm{kJ}$$

$$\mathrm{Hg\,(l) + HgCl_2(s) \longrightarrow Hg_2Cl_2(s)} \quad \Delta H = -41.2\,\mathrm{kJ}$$

ANSWER: 265 kJ
Exercise 11: Calculate the enthalpy for this reaction:

$$\mathrm{2C\,(s) + H_2(g) \rightarrow C_2H_2(g)} \quad \Delta H^\circ = ???\,\mathrm{kJ}$$

Given the following thermochemical equations:

$$\begin{aligned}
\mathrm{C_2H_2(g)} + \frac{5}{2}\mathrm{O_2\,(g) \rightarrow 2CO_2(g) + H_2O\,(l)} &\qquad \Delta H^\circ = -1299.5\,\mathrm{kJ} \\
\mathrm{C\,(s) + O_2(g) \rightarrow CO_2(g)} &\qquad \Delta H^\circ = -393.5\,\mathrm{kJ} \\
\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2\,(g) \rightarrow H_2O\,(l)} &\qquad \Delta H^\circ = -285.8\,\mathrm{kJ}
\end{aligned}$$

Solution:

1) Determine what we must do to the three given equations to get our target equation:

a) first eq: flip it so as to put C_2H_2 on the product side
b) second eq: multiply it by two to get 2C
c) third eq: do nothing. We need one H_2 on the reactant side and that's what we have.

2) Rewrite all three equations with changes applied:

$$\begin{aligned}
2CO_2(g) + H_2O\,(l) &\rightarrow C_2H_2(g) + \frac{5}{2}O_2(g) & \Delta H^\circ &= +1299.5\,\text{kJ}\\
2C\,(s) + 2O_2(g) &\rightarrow 2CO_2(g) & \Delta H^\circ &= -787\,\text{kJ}\\
H_2(g) + \frac{1}{2}O_2(g) &\rightarrow H_2O\,(l) & \Delta H^\circ &= -285.8\,\text{kJ}
\end{aligned}$$

Notice that the ΔH values changed as well.

3) Examine what cancels:

$2CO_2$ → first & second equation
H_2O → first & third equation
$\frac{5}{2}O_2$ → first & sum of second and third equation

4) Add up ΔH values for our answer:

$$+1299.5\,\text{kJ} + (-787\,\text{kJ}) + (-285.8\,\text{kJ}) = +226.7\,\text{kJ}$$

Exercise 12:

Calculate the enthalpy of the following chemical reaction:

$$CS_2(l) + 3\,O_2(g) \longrightarrow CO_2(g) + 2\,SO_2(g)$$

Given:

$$\begin{aligned}
C\,(s) + O_2(g) &\longrightarrow CO_2(g) \quad \Delta H = -393.5\,\text{kJ/mol}\\
S\,(s) + O_2(g) &\longrightarrow SO_2(g) \quad \Delta H = -296.8\,\text{kJ/mol}\\
C\,(s) + 2\,S\,(s) &\longrightarrow CS_2(l) \quad \Delta H = +87.9\,\text{kJ/mol}
\end{aligned}$$

Solution:

1) What to do to the data equations:

Leave equation 1 untouched (want CO_2 as a product).
Multiply the second equation by 2 (want to cancel 2S, also want $2SO_2$ on product side).
Flip the third equation (want CS_2 as a reactant).

2) The result:

$$C\,(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5\,\mathrm{kJ/mol}$$
$$2\,S\,(s) + 2\,O_2(g) \longrightarrow 2\,SO_2(g) \quad \Delta H = -593.6\,\mathrm{kJ/mol}$$
$$CS_2(l) \longrightarrow C\,(s) + 2\,S\,(s) \quad \Delta H = -87.9\,\mathrm{kJ/mol}$$

3) Add the three revised equations. C and 2S will cancel.
4) Add the three enthalpies for the final answer.

Exercise 13:

Given the following data:

$$\begin{aligned} SrO\,(s) + CO_2(g) &\longrightarrow SrCO_3(s) && \Delta H = -234\,\mathrm{kJ} \\ 2\,SrO\,(s) &\longrightarrow 2\,Sr\,(s) + O_2(g) && \Delta H = +1184\,\mathrm{kJ} \\ 2\,SrCO_3(s) &\longrightarrow 2\,Sr\,(s) + 2\,C(s, gr) + 3\,O_2(g) && \Delta H = +2440\,\mathrm{kJ} \end{aligned}$$

Find the ΔH of the following reaction:

$$C(s, gr) + O_2(g) \longrightarrow CO_2(g)$$

Solution:

1) Analyze what must happen to each equation:

a) first eq ⟶ flip it (this puts the CO_2 on the right-hand side, where we want it)

b) second eq ⟶ do not flip it, divide through by two (no flip because we need to cancel the SrO, divide by two because we only need to cancel one SrO)

c) third equation ⟶ flip it (to put the $SrCO_3$ on the other side so we can cancel it), divide by two (since we need to cancel only one $SrCO_3$)

Notice that what we did to the third equation also sets up the Sr to be cancelled. Why not also multiply first equation by two (to get 2 SrO for canceling)? Because we only want one CO_2 in the final answer, not two. Notice also that I ignored the oxygen. If everything is right, the oxygen will take care of itself.

2) Apply all the above changes (notice what happens to the ΔH values):

$$\begin{aligned} SrCO_3(s) &\longrightarrow SrO\,(s) + CO_2(g) && \Delta H = +234\,\mathrm{kJ} \\ SrO\,(s) &\longrightarrow Sr\,(s) + \frac{1}{2}O_2\,(g) && \Delta H = +592\,\mathrm{kJ} \\ Sr\,(s) + C(s, gr) + \frac{3}{2}O_2\,(g) &\longrightarrow SrCO_3(s) && \Delta H = -1220\,\mathrm{kJ} \end{aligned}$$

3) Here is a list of what is eliminated when everything is added:
$SrCO_3$, SrO, Sr, $\frac{1}{2}O_2$
The last one comes from $\frac{3}{2}O_2$ on the left in the third equation and $\frac{1}{2}O_2$ on the right in the second equation.

4) Add the equations and the ΔH values:

$$+234 + (+592) + (-1220) = -394$$

$$\mathrm{C(s,gr)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H_f = -394\,\mathrm{kJ}$$

Notice the subscripted f. This is the formation reaction for CO_2 and its value can be looked up, either in your textbook.

Exercise 14:

Given the following information:

$$2\,\mathrm{NO\,(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{NO_2(g)} \quad \Delta H = -116\,\mathrm{kJ}$$

$$2\,\mathrm{N_2(g)} + 5\,\mathrm{O_2(g)} + 2\,\mathrm{H_2O\,(l)} \longrightarrow 4\,\mathrm{HNO_3(aq)} \quad \Delta H = -256\,\mathrm{kJ}$$

$$\mathrm{N_2(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{NO\,(g)} \quad \Delta H = +183\,\mathrm{kJ}$$

Calculate the enthalpy change for the reaction below:

$$3\,\mathrm{NO_2(g)} + \mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{HNO_3(aq)} + \mathrm{NO\,(g)} \quad \Delta H = ???$$

Solution:

1) Analyze what must happen to each equation:

a) first eq ⟶ flip; multiply by $\frac{3}{2}$ (this gives $3NO_2$ as well as the 3NO which will be necessary to get one NO in the final answer)
b) second eq ⟶ divide by 2 (gives two nitric acid in the final answer)
c) third eq ⟶ flip (cancels 2NO as well as nitrogen)

2) Comment on the oxygens:

a) step 1a above puts $\frac{3}{2}O_2$ on the right
b) step 1b puts $\frac{5}{2}O_2$ on the left
c) step 1c puts $\frac{2}{2}O_2$ on the right
In addition, a and c give $\frac{5}{2}O_2$ on the right to cancel out the $\frac{5}{2}O_2$ on the left.

3) Apply all the changes listed above:

$$3\,\mathrm{NO_2(g)} \longrightarrow 3\,\mathrm{NO\,(g)} + \frac{3}{2}\mathrm{O_2\,(g)} \quad \Delta H = +174\,\mathrm{kJ}$$

$$\mathrm{N_2(g)} + \frac{5}{2}\mathrm{O_2\,(g)} + \mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{HNO_3(aq)} \quad \Delta H = -128\,\mathrm{kJ}$$

$$2\,\mathrm{NO\,(g)} \longrightarrow \mathrm{N_2(g)} + \mathrm{O_2(g)} \quad \Delta H = -183\,\mathrm{kJ}$$

4) Add the equations and the ΔH values:

$$+174 + (-128) + (-183) = -137\,\mathrm{kJ}$$

$$3\,\mathrm{NO_2(g)} + \mathrm{H_2O\,(l)} \longrightarrow 2\,\mathrm{HNO_3(aq)} + \mathrm{NO\,(g)} \quad \Delta H = -137\,\mathrm{kJ}$$

Exercise 15:

Calculate the value of ΔH° for the following reaction:

$$P_4O_{10}(s) + 6\,PCl_5(g) \longrightarrow 10\,Cl_3PO\,(g)$$

using the following four equations:
a) $P_4(s) + 6\,Cl_2(g) \longrightarrow 4\,PCl_3(g)\ \Delta H^\circ = -1225.6\,\mathrm{kJ}$
b) $P_4(s) + 5\,O_2(g) \longrightarrow P_4O_{10}(s)\ \Delta H^\circ = -2967.3\,\mathrm{kJ}$
c) $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)\ \Delta H^\circ = -84.2\,\mathrm{kJ}$
d) $PCl_3(g) + \frac{1}{2}O_2\,(g) \longrightarrow Cl_3PO\,(g)\ \Delta H^\circ = -285.7\,\mathrm{kJ}$

Solution:

1) We know that P_4O_{10} MUST be on the left-hand side in the answer, so let's reverse (b):
b) $P_4O_{10}(s) \longrightarrow P_4(s) + 5\,O_2(g)\ \Delta H^\circ = +2967.3\,\mathrm{kJ}$

2) We know that PCl_5 MUST be on the left-hand side in the answer, so let's reverse (c) and multiply it by 6:
c) $6\,PCl_5(g) \longrightarrow 6\,PCl_3(g) + 6\,Cl_2(g)\ \Delta H^\circ = +505.2\,\mathrm{kJ}$

3) We know that Cl_3PO MUST have a 10 in front of it:
d) $10\,PCl_3(g) + 5\,O_2(g) \longrightarrow 10\,Cl_3PO\,(g)\ \Delta H^\circ = -2857\,\mathrm{kJ}$

4) Now, write all four equations, but incorporate the revisions:
a) $P_4(s) + 6\,Cl_2(g) \longrightarrow 4\,PCl_3(g)\ \Delta H^\circ = -1225.6\,\mathrm{kJ}$
b) $P_4O_{10}(s) \longrightarrow P_4(s) + 5\,O_2(g)\ \Delta H^\circ = +2967.3\,\mathrm{kJ}$
c) $6\,PCl_5(g) \longrightarrow 6\,PCl_3(g) + 6\,Cl_2(g)\ \Delta H^\circ = +505.2\,\mathrm{kJ}$
d) $10\,PCl_3(g) + 5\,O_2(g) \longrightarrow 10\,Cl_3PO\,(g)\ \Delta H^\circ = -2857\,\mathrm{kJ}$

5) Now, we will add all four equations as well as the ΔH° values. Notice the following:
a) $P_4(s)$ cancels out (see equations a and b)
b) Cl_2 cancels out (see equations a and c)
c) O_2 cancels out (see equations b and d)
d) PCl_3 cancels out (see equations a+c and d)

6) The ΔH° values added together:

$$-1225.6\,\mathrm{kJ} + (+2967.3\,\mathrm{kJ}) + (+505.2\,\mathrm{kJ}) + (-2857\,\mathrm{kJ}) = -610.1\,\mathrm{kJ}$$

7) The answer:

$$P_4O_{10}(s) + 6\,PCl_5(g) \longrightarrow 10\,Cl_3PO\,(g) \quad \Delta H^\circ = -610.1\,\mathrm{kJ}$$

Chapter 5

The second law of thermodynamics

5.1 Introduction:

Among the shortcomings of the first law of thermodynamics, we can mention: It does not allow predicting the direction of a thermodynamic transformation system. It does not distinguish between work (transfer of ordered macroscopic energy) and heat (transfer of disordered microscopic energy).

The first law of thermodynamics, which is a principle of energy conservation (energy in the form of work and heat exchanged between a system and the external environment is conserved), does not allow predicting the direction of evolution of a transformation, it only allows determining ΔU and ΔH.

Example:

When a hot body and a cold body are in contact: heat passes from the hot body to the cold body until thermal equilibrium is reached. The reverse transformation (from the cold body to the hot body) never occurs spontaneously, yet this transformation is not prohibited by the first principle, as it only demands the conservation of energy.

$$\begin{gathered} A + B \rightarrow \text{mixture}(A+B) \\ T_A \quad T_B \quad T_{eq} \end{gathered}$$

It is important to know the direction of evolution of the transformation, which is why we have a second law of thermodynamics that can inform us about the direction of system evolutions. It is a principle of evolution based on the concept of entropy.

5.2 Statement of the Second Law of Thermodynamics

The second law arose as a necessity to explain especially irreversible phenomena. Let A and B be two equilibrium states of a system. The first law of thermodynamics does not predict whether the transformation of the system proceeds from A to B or the reverse (from B to A) spontaneously. This question can be answered using the second law of thermodynamics. It allows us to determine the true initial state and the true final state and to specify the nature of a transformation (reversible, irreversible), through a state function called entropy (S).

Physically, entropy is an abstract quantity that allows measuring the degree of disorder of a system at the microscopic scale.

5.3 Concept of reversibility and irreversibility

Consider a perfect gas under pressure P_1 undergoing compression to the final state characterized by pressure P_2. This gas transitions from P_1 to P_2 in a reversible (ideal) or irreversible (real) manner.

5.3.1 Reversible Transformation (Ideal)

The reversible transformation, also known as ideal, is a transformation that continuously allows reversing the direction of the transformation by passing through the same stages of direct transformation. Therefore, it would be possible to return from the final state to the initial state. It is a very slow transformation that passes through a succession of equilibrium states. During the evolution, we have:

$$P = P_e \quad \text{and} \quad T = T_e.$$

5.3.2 Irreversible Transformation (Real)

The irreversible transformation, also known as real, is a rapid transformation, during which P and T are not homogeneous; we have $P \neq P_e$ and $T \neq T_e$. It would not be possible to return from the final state to the initial state. It is a transformation that does not pass through a succession of equilibrium states. This is the case for any spontaneous thermodynamic transformation of a system left to itself.

5.4 Concept of Entropy

Entropy is an extensive quantity and is measured in J/K or J/(K·mol) when considered for one mole of the system. For a transformation of a system in thermal contact with a heat source from the initial state (A) to the final state (B) of the external environment, the change in entropy verifies the following relation:

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

5.4.1 Case of a Reversible Transformation

In the case of a reversible transformation, we define the entropy function as follows:

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

Let's consider a thermodynamic cycle composed of two reversible transformations from state A to state B (transformation 1) and from state B to state A (transformation 2).

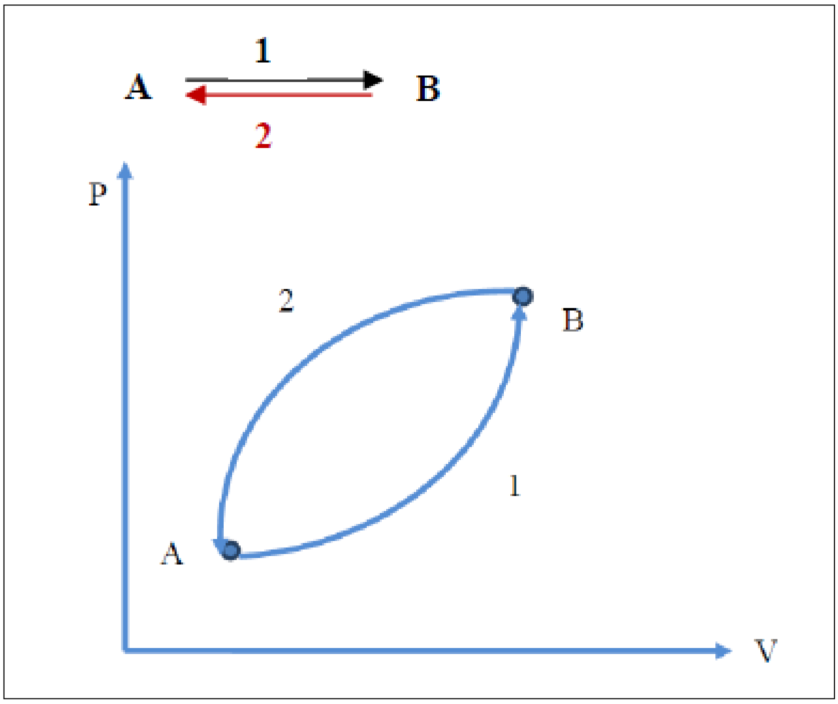

Figure 5.1: Reversible Transformation

Performing the energy balance on the cycle as follows:

$\frac{\sum dQ_T}{T} = \int_A^B \frac{dQ(1)}{T} + \int_B^A \frac{dQ(2)}{T} = 0$

$\Longrightarrow \int_A^B \frac{dQ(1)}{T} - \int_B^A \frac{dQ(2)}{T} = 0$

$$\Longrightarrow \int_A^B \frac{dQ(1)}{T} = \int_B^A \frac{dQ(2)}{T} = \int_A^B \frac{\delta Q_{rev}}{T}$$

We conclude that for a reversible transformation, the integral $\int_A^B \frac{\delta Q_{rev}}{T}$
It only depends on the initial state (A) and the final state (B).
It does not depend on the path taken.
Therefore, $\frac{dQ_{rev}}{T}$ is a state function called entropy (S).
So $dS = \frac{dQ_{rev}}{T}$.
The change in entropy is thus: $\Delta S = S_B - S_A = \int_A^B \frac{\delta Q_{rev}}{T}$

5.4.2 Case of an Irreversible Transformation

Consider the irreversible cycle formed by an irreversible transformation from the initial state (A) to the final state (B) and a reversible transformation from state B to state A.

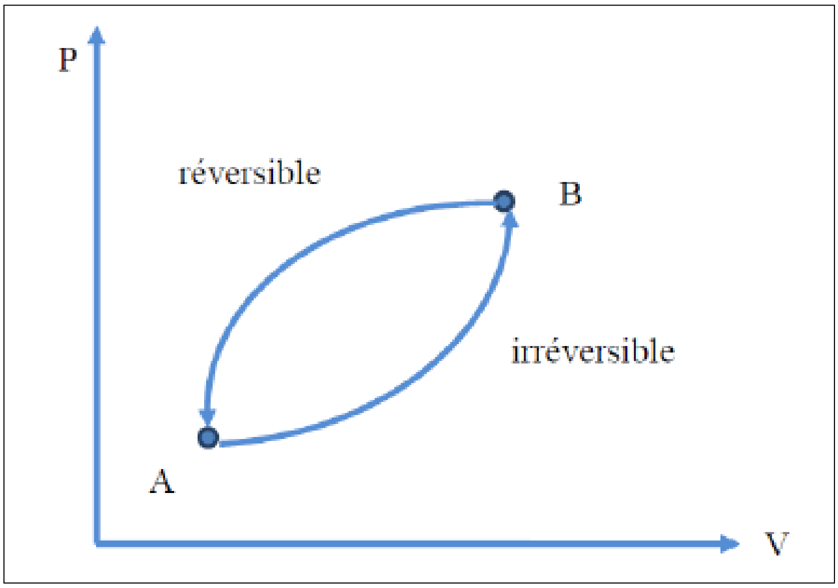

Figure 5.2: Irreversible Transformation

The energy balance on this irreversible cycle is:

$$\frac{\sum dQ_T}{T} = \int_A^B \frac{dQ_{irrev}}{T} + \int_A^B \frac{dQ_{rev}}{T} < 0$$
$$\implies \int_A^B \frac{dQ_{irrev}}{T} - \int_A^B \frac{dQ_{rev}}{T} < 0$$
$$\implies \int_A^B \frac{dQ_{irrev}}{T} < \int_A^B \frac{dQ_{rev}}{T}$$

Hence: $\dfrac{dQ_{irrev}}{T} < dS$ and thus: $\Delta S > \displaystyle\int_A^B \frac{\delta Q_{irrev}}{T}$

Entropy balance:

The term $\int_A^B \frac{dQ_{irrev}}{T}$ is called the change in exchange entropy ($\Delta S_{exchange}$). This term corresponds to the irreversible path, i.e., the path actually followed. For a system in thermal contact with a heat source, we have:

$$\Delta S_{exchange} = \int_A^B \frac{dQ_{irrev}}{T} = \frac{1}{T}\int_A^B dQ_{irrev} = \frac{Q_{irrev}}{T}$$

Entropy S is a state function, so we have: $\Delta S = \Delta S_{rev} + \Delta S_{irrev} > \int_A^B \frac{\delta Q_{irrev}}{T} \implies \Delta S > \Delta S_{exchange}$

Hence: $\Delta S = \Delta S_{exchange} + \Delta S_{system}$

$\Delta S_{exchange}$: Corresponds to the variation of exchanged entropy with the external environment.

$\Delta S_{created}$: Corresponds to the variation of entropy created due to internal transformations related to microscopic evolutions of the system.

ΔS : Corresponds to the variation of entropy of the system.

- $\Delta S_{system} = 0$: Therefore, the transformation from initial state A to final state B is reversible.
- $\Delta S_{system} > 0$: Therefore, the transformation from initial state A to final state B is spontaneous.
- $\Delta S_{system} < 0$: Therefore, the transformation from initial state A to final state B is not spontaneous.

5.5 Entropy as a function of the variables T and V

According to the first law of thermodynamics: $dU = dQ + dW$

According to the second law of thermodynamics: $dS = \dfrac{dQ_{rev}}{T}$

$dW = -PdV$ and $dU = nC_v dT \Rightarrow dU = TdS - PdV \Rightarrow nC_v dT = TdS - PdV$

According to the ideal gas law, for one mole we have: $PV = nRT \Rightarrow P = \dfrac{nRT}{V}$

So $C_v dT = \dfrac{TdS - nRTdV}{V}$

$\Rightarrow dS = \dfrac{C_v dT}{T} + \dfrac{RdV}{V}$ ....(1)

5.6 Entropy as a function of the variables T and P

According to the first law of thermodynamics: $dH = dU + d(PV)$

$\Rightarrow dH = dU + PdV + VdP$

We have: $dU = TdS - PdV \Rightarrow dH = TdS - PdV + PdV + VdP$

$\Rightarrow dH = TdS + VdP$

For one mole of ideal gas: $V = RT/P$; $dH = c_p dT$

Therefore: $dH = TdS + \dfrac{RT}{P} dP$

$\Rightarrow dS = c_p \dfrac{dT}{T} - R\dfrac{dP}{P}$ ....(2)

5.7 Entropy as a function of the variables V and P

According to expressions (1) and (2) representing the entropy variation (dS):

$$dS = c_v \frac{dT}{T} + R\frac{dV}{V} = c_p \frac{dT}{T} - R\frac{dP}{P}$$

$$\Longrightarrow R\frac{dV}{V} = (c_p - c_v)\frac{dT}{T} - R\frac{dP}{P}$$

We know that $(c_p - c_v) = R$ (Mayer's relation)

So: $R\dfrac{dV}{V} = R\dfrac{dT}{T} - R\dfrac{dP}{P}$

$\Rightarrow \dfrac{dV}{V} = \dfrac{dT}{T} - \dfrac{dP}{P}$

$\Rightarrow \dfrac{dT}{T} = \dfrac{dV}{V} + \dfrac{dP}{P}$ ....(3)

Replacing equation (3) into (1) or (2), we find: (1)

$\Rightarrow dS = c_v \left(\dfrac{dV}{V} + \dfrac{dP}{P}\right) + R\dfrac{dV}{V} = c_v \dfrac{dV}{V} + c_v \dfrac{dP}{P} + c_p \dfrac{dV}{V} - c_v \dfrac{dV}{V}$

$\Rightarrow dS = c_v \dfrac{dP}{P} + c_p \dfrac{dV}{V}$

5.8 Calculation of entropy change without phase change:

The entropy change of a system is calculated along the reversible path according to the type and nature of the transformation it undergoes.

$$\Delta S = \int_A^B \frac{dQ_{rev}}{T} = \int_A^B \frac{dQ}{T}$$

5.8.1 Case of solids and liquids

We know that in the case of solids and liquids, the amount of heat is defined by the relation: $dQ = nCdT$. Thus, the entropy change is given by:

$$\Delta S = \int_A^B \frac{dQ}{T} = \int_A^B \frac{nCdT}{T} = nC \int_A^B \frac{dT}{T} \implies \Delta S = nC \ln \frac{T_B}{T_A}$$

5.8.2 Case of perfect gases

In the case of perfect gases and according to the first law of thermodynamics, we have: $dQ = dU - dW$, where: $dU = nC_v dT$ and $dW = -PdV$. This results in: $dQ = nC_v dT + PdV$.

5.8.2.1 Isochoric transformation

For an isochoric transformation, we have $dV = 0$, hence: $dQ = nC_v dT$.

As a result: $\Delta S = \int_A^B \frac{dQ}{T} = \displaystyle\int_A^B \frac{nC_v dT}{T}$.

If C_v is constant between T_B and T_A, after integration we find:

$\Delta S = nC_v \ln \frac{T_B}{T_A}$.

5.8.2.2 Isothermal transformation

For an isothermal transformation, we have $dT = 0$, hence: $dQ = PdV = nRT\frac{dV}{V}$.

As a result: $\Delta S = \int_A^B \frac{dQ}{T} = \displaystyle\int_A^B \frac{nRTdV}{TV} = nR \int_A^B \frac{dV}{V}$.

After integration we find:

$\Delta S = nR \ln \frac{V_B}{V_A}$ or $\Delta S = nR \ln \frac{P_A}{P_B}$.

5.8.2.3 Isobaric transformation

For an isobaric transformation, we have $dQ = dH = nC_p dT$.

So: $\Delta S = \int_A^B \frac{dQ}{T} = \displaystyle\int_A^B \frac{nC_p dT}{T}$.

After integration we find: $\Delta S = nC_p \ln \frac{T_B}{T_A}$.

5.8.2.4 Reversible adiabatic transformation

We know that for an adiabatic transformation, the heat $dQ = 0$, hence: $\Delta S = 0$.

5.8.3 Irreversible adiabatic transformation

In the case of irreversible adiabatic transformation, we have $\Delta S = 0$; consequently: $\Delta S_{\text{exchange}} = \Delta S_{\text{creator}} > 0$. On the reversible path, we found that $\Delta S_{\text{exchange}} = 0$. However, on the irreversible path, we have $\Delta S_{\text{exchange}} > 0$. Hence, we disagree with the principle of initial and final states because entropy is a state function. Normally, we find that $\Delta S_{\text{rev}} = \Delta S_{\text{irrev}}$. That's why calculating the entropy change ΔS in the case of irreversible adiabatic transformation is done through intermediate paths and not through a direct path.

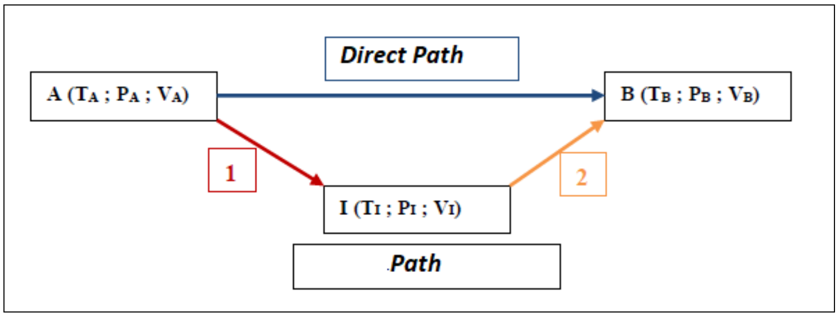

Figure 5.3: Irreversible adiabatic Transformation

Therefore: $\Delta S = \Delta S_1 + \Delta S_2$
Note:

$$\Delta S = \Delta S_{\text{isotherm}} + \Delta S_{\text{isobar}} = \Delta S_{\text{isotherm}} + \Delta S_{\text{isochore}} = \Delta S_{\text{isobar}} + \Delta S_{\text{isochore}}$$

5.8.3.1 Cyclical Transformation

For a cyclical transformation, the change in entropy $\Delta S = 0$, because entropy is a state function (entropy at the initial state equals entropy at the final state).

$$\Delta S = 0 \geq \int_A^B \frac{dQ}{T} \implies \int_A^B \frac{dQ}{T} \leq 0 \text{ (Clausius' inequality)}$$

5.9 Calculation of the entropy change during phase change of pure substances

The quantity of heat accompanying a change in the physical state of matter is called latent heat. It is well known that a phase change of a pure substance occurs at constant temperature, hence:

$$\Delta S = \int_A^B \frac{dQ_{\text{change of phase}}}{T_{\text{change of phase}}} = \frac{1}{T_{\text{change of phase}}} \int_A^B dQ_{\text{change of phase}}$$

$$\Delta S = \frac{Q_{\text{change of phase}}}{T_{\text{change of phase}}}$$

$$Q_{\text{change of phase}} = Q_{\text{rev}} = \Delta H$$

$$\Delta S = \frac{\Delta H}{T}$$

With:

ΔH : Latent Heat of Vaporization, Fusion, or Sublimation.

T : Temperature of the change of the physical state of matter.

ΔS_{f} : Change in entropy of fusion.

ΔS_{vap} : Change in entropy of vaporization.

ΔS_{sub} : Change in entropy of sublimation.

$$\Delta S_{\text{f}} = \frac{\Delta H_{\text{f}}}{T_{\text{f}}} = \frac{nL_{\text{f}}}{T_{\text{f}}}; \quad \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} = \frac{nL_{\text{vap}}}{T_{\text{vap}}}; \quad \Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}}} = \frac{nL_{\text{sub}}}{T_{\text{sub}}}$$

5.10 Calculation of the entropy change for the mixing of pure substances

5.10.1 Case of pure substances in the solid or liquid state

Let two substances A and B have temperatures T_A and T_B respectively. After contact between them, the equilibrium temperature reached is T_{eq}. The entropy change of mixing is expressed as: $\Delta S = \Delta S_A + \Delta S_B = n_A c_A \ln\left(\frac{T_{\text{eq}}}{T_A}\right) + n_B c_B \ln\left(\frac{T_{\text{eq}}}{T_B}\right)$.

5.10.2 Case of pure substances in the gaseous state

V-10-2- Case of pure substances in the gaseous state: Let a perfect gas A be characterized by the initial state variables (P_1, T_1, and V_1), and a perfect gas B be characterized by the initial state variables (P_2, T_2, and V_2). The mixture of the two gases is characterized by the variables (final state) P_m, T_m, and V_m. The entropy change of the mixture is expressed as: $\Delta S = \Delta S_A + \Delta S_B = (\Delta S_T + \Delta S_V)_A + (\Delta S_T + \Delta S_V)_B = (\Delta S_T + \Delta S_P)_A + (\Delta S_T + \Delta S_P)_B = (\Delta S_P + \Delta S_V)_A + (\Delta S_P + \Delta S_V)_B$

5.11 Heat Engines

A heat engine is a system capable of converting thermal energy into mechanical energy (work) and vice versa. This system undergoes a cyclic transformation.

Reversible heat engines must comply with the two principles of thermodynamics. There are two possible cases:

- When the work is negative ($W < 0$): it is a heat engine.
- When the work is positive ($W > 0$): it is a refrigeration machine or a heat pump.

5.11.1 Thermal Engines

These are machines that produce work, known as driving machines. A portion of the heat at high temperature is converted into mechanical work and the rest is lost, as shown in the figure below:

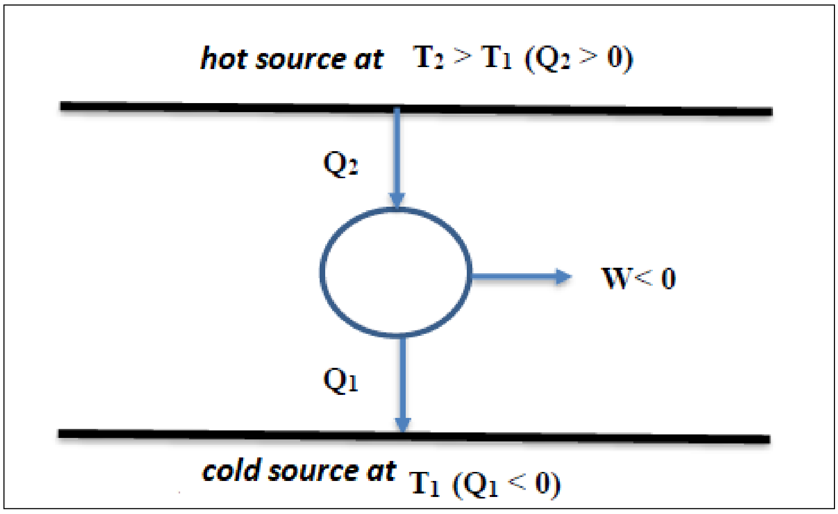

Figure 5.4: Operating principle of a heat engine

Note: A heat source refers to any body or system capable of exchanging heat while remaining at a constant temperature. Examples of thermodynamic machines include:

- Steam engines.
- Gasoline or diesel combustion engines.
- Thermal or nuclear power plants for electricity generation.

5.11.2 Refrigeration Machine

These are machines where heat transfer occurs from a cold source to a hot source, with additional work done to facilitate this transfer.

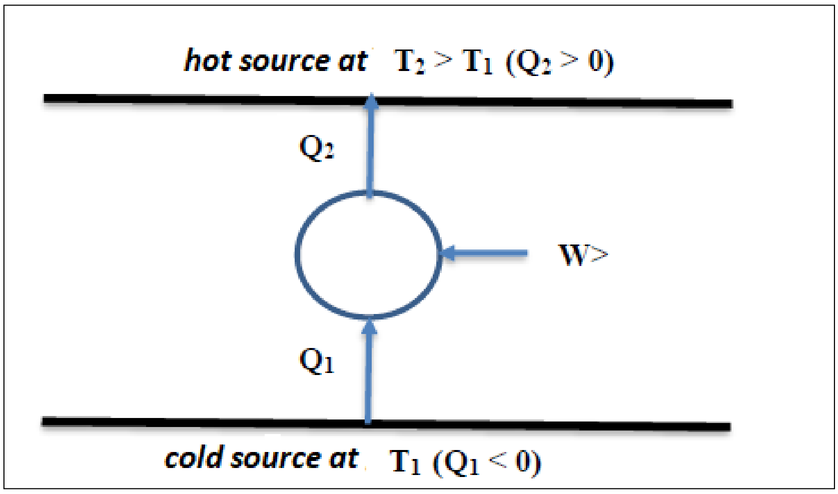

Figure 5.5: Operating principle of a Refrigeration Machine

In general, thermodynamic machines operate with several successive transformations and thus form a cycle. There are several thermodynamic cycles; in the following, we mention the Carnot cycle.

5.11.3 Applications of the Carnot cycle

V-11-3- Applications of the Carnot cycle: The Carnot cycle is referred to as a diathermic and reversible cycle, meaning two heat sources. It consists of two isothermal transformations and two reversible adiabatic transformations.

To provide work to the external environment, a diathermic machine must necessarily receive heat from the hot source and provide it to the cold source.

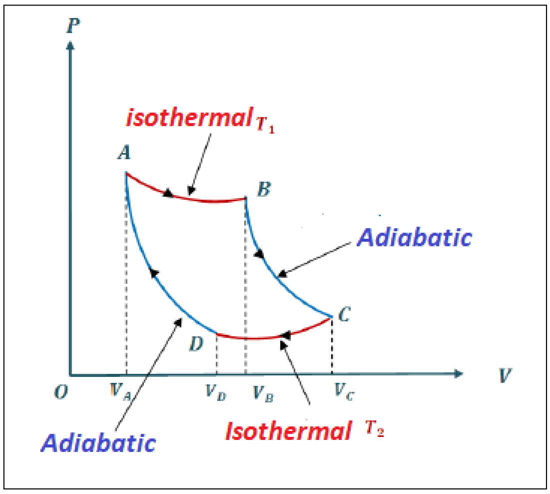

Figure 5.6: The Carnot cycle

- AB: Isothermal transformation at temperature T_1
- BC: Adiabatic transformation: from T_1 to T_2
- CD: Isothermal transformation at temperature T_2
- DA: Adiabatic transformation: from T_2 to T_1

Heat Exchange Balance

Isothermal Transformation A → B

For 1 mole: $dU = nC_V dT = 0 = dQ + dW$

$Q_1 = Q_{AB} = -W_{AB}$

$PV = RT \rightarrow P = \frac{RT}{V}; T = T_1$

$W_{AB} = \int_{V_A}^{V_B} \frac{(-RT_1)}{V} dV \Rightarrow W_{AB} = -RT_1 \int_{V_A}^{V_B} \frac{dV}{V} \Rightarrow W_{AB} = -RT_1 \ln \frac{V_B}{V_A}$

$dU = C_V dT = 0 = dQ + dW \Rightarrow\Rightarrow Q_1 = Q_{AB} = -W_{AB}$

$Q_1 = Q_{AB} = RT_1 \ln \frac{V_B}{V_A}$

Adiabatic Transformation B → C

$Q_{BC} = 0$

$$\begin{aligned} dU &= dw + dQ, \\ dQ &= 0, \\ dU &= nC_V dT \end{aligned}$$

$\rightarrow dw = nC_V dT$

$W_{BC} = \int_{T_1}^{T_2} C_V dT \Rightarrow W_{BC} = C_V(T_2 - T_1) \Rightarrow W_{BC} = C_V \Delta T$
Replacing C_V with $C_V = \dfrac{R}{(\gamma - 1)}$,
$W_{BC} = \dfrac{R}{(\gamma - 1)} \Delta T \Rightarrow W_{BC} = \dfrac{R}{(\gamma - 1)}(T_2 - T_1)$

Isothermal Transformation C → D

$$\begin{gathered} dU = nC_V dT = 0 = \delta Q + \delta W, \\ Q_2 = Q_{CD} = -W_{CD} \\ W_{CD} = -RT_2 \ln \frac{V_D}{V_C} \\ Q_2 = Q_{CD} = RT_2 \ln \frac{V_D}{V_C} \end{gathered}$$

Adiabatic Transformation D → A
$Q_{DA} = 0$
$W_{DA} = \dfrac{R}{(\gamma - 1)}(T_1 - T_2)$

Heat Exchange Balance

- Isothermal Transformation AB → $Q_1 = Q_{AB} = RT_1[\ln \dfrac{V_B}{V_A}]$
- Adiabatic Transformation BC → $Q_{BC} = 0$
- Isothermal Transformation CD → $Q_2 = Q_{CD} = RT_2[\ln \dfrac{V_D}{V_C}]$
- Adiabatic Transformation DA → $Q_{DA} = 0$

Sign of heat quantities:

$$Q_1 = RT_1 \left[\ln \frac{V_B}{V_A} \right] > 0, \quad Q_2 = RT_2 \ln \frac{V_D}{V_C} < 0$$

The relation between temperatures T_1 and T_2 and volumes V_A, V_B, V_C, and V_D is given by:

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma} = Constant \quad \text{(for ideal gases)}$$

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} = Constant \quad \text{and} \quad T_2^{\gamma} P_1^{1-\gamma} = T_1^{\gamma} P_1^{1-\gamma} = Constant \quad \text{(for adiabatic processes)}$$

For the adiabatic transformation B→C
we have: $T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}$.
And for the adiabatic transformation D→A,we have
$T_2 V_D^{\gamma-1} = T_1 V_A^{\gamma-1} \Rightarrow \dfrac{T_1 V_B^{\gamma-1}}{T_1 V_A^{\gamma-1}} = \dfrac{T_2 V_C^{\gamma-1}}{T_2 V_D^{\gamma-1}} \Rightarrow \dfrac{V_B^{\gamma-1}}{V_A^{\gamma-1}} = \dfrac{V_C^{\gamma-1}}{V_D^{\gamma-1}}$

$\Rightarrow \left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1}$
$\Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}.$

- $Q_1 = RT_1\left[\ln\frac{V_B}{V_A}\right] \Rightarrow \frac{Q_1}{T_1} = R\left[\ln\frac{V_B}{V_A}\right]$
- $Q_2 = -RT_2\left[\ln\frac{V_C}{V_D}\right] \Rightarrow \frac{Q_2}{T_2} = -R\left[\ln\frac{V_C}{V_D}\right] = -R\left[\ln\frac{V_B}{V_A}\right]$

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2}$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

This relation is known as the Carnot-Clausius identity.

For a reversible cycle

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

For an irreversible cycle

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0$$

5.11.4 Efficiency

1st principle: $\Delta U = W + Q_1 + Q_2 = 0 \rightarrow W = -(Q_1 + Q_2)$
2nd principle: $\frac{Q_1}{T_1} + \frac{Q_2}{Q_2} = 0 \rightarrow \frac{Q_1}{T_1} = -\frac{Q_2}{Q_2}$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

The efficiency of the Carnot cycle depends only on the temperatures of the cold and hot sources.

- The efficiency of the heat engine is defined by the ratio of the work done (W_{done}) to the heat it received from the hot source (Q_{HS}).

$$\rho = -\frac{W_{\text{done}}}{Q_{\text{HS}}} = -\frac{-(Q_1 + Q_2)}{Q_1} = 1 + \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\rho = 1 + \frac{Q_2}{Q_1} \quad \rho = 1 - \frac{T_2}{T_1}$$

- The efficiency of heat engine depends only on the temperatures T_1 and T_2 and not on the nature of the fluid.

- For an irreversible heat engine: $\rho_{\text{irrev}} < 1 - \dfrac{T_2}{T_1}$
- In the case of Refrigeration machines, the desired effect is the amount of heat Q_2 removed from the cold source. The efficiency or coefficient of refrigeration effect is given by:

$$\varepsilon_{\text{rev}} = \frac{Q_2}{W} = \frac{Q_2}{-(Q_1+Q_2)} \Rightarrow \varepsilon_{\text{rév}} = \frac{T_2}{T_1 - T_2} \Rightarrow \varepsilon_{\text{rev}} = \frac{T_2}{T_1} - 1$$

Exercise 1:

Small glass beads with a total mass of $m_1 = 50g$ are placed in an oven maintained at a temperature $T_1 = 80°C$. They are then immersed in a calorimeter containing a mass $m_2 = 100g$ of water at a temperature $T_2 = 20°C$. Heat transfers take place inside the adiabatic enclosure constituting the calorimeter under atmospheric pressure.

1. Calculate the final equilibrium temperature T_f.

2. Determine the variation in overall entropy.

Given data: The relevant thermal capacities are provided: Water (mass-specific): $c_{\text{water}} = 4.18\,\text{J K}^{-1}\ \text{g}^{-1}$; Glass (mass-specific): $c_{\text{glass}} = 0.87\,\text{J K}^{-1}\ \text{g}^{-1}$; Calorimeter: $C = 150\,\text{J K}^{-1}$.

Solution:

1-

$$\Sigma Q_i = 0 \Rightarrow Q_{\text{verre}} + Q_{\text{eau}} + Q_{\text{cal}} = 0 \quad (1)$$

The heat quantity of the glass beads is: $Q_{\text{verre}} = m_1 c_{\text{verre}}(T_f - T_1)$

$$\Rightarrow Q_{\text{verre}} = 50 \times 0.87(T_f - 353) \Rightarrow Q_{\text{verre}} = 43.5T_f - 15355.5$$

The heat quantity of the water is: $Q_{\text{eau}} = m_2 c_{\text{eau}}(T_f - T_2)$

$$\Rightarrow Q_{\text{eau}} = 100 \times 4.18(T_f - 293) \Rightarrow Q_{\text{eau}} = 418T_f - 122474$$

The heat quantity of the calorimeter is: $Q_{\text{cal}} = C(T_f - T_2)$

$$\Rightarrow Q_{\text{cal}} = 150(T_f - 293) \Rightarrow Q_{\text{cal}} = 150T_f - 43950$$

$$(1) \Rightarrow 43.5T_f - 15355.5 + 418T_f - 122474 + 150T_f - 43950 = 0$$

$$\Rightarrow 611.5T_f - 14840 = 0 \Rightarrow T_f = 297.27K = 24.27°C$$

2-

Determination of the variation in overall entropy:

$$\Delta S = \Delta S_{\text{verre}} + \Delta S_{\text{eau}} + \Delta S_{\text{cal}}$$

The entropy variation of the glass beads is: $\Delta S_{\text{verre}} = \int_{T_1}^{T_2} \delta Q_{\text{verre}} \frac{1}{T}$

$$\Rightarrow \Delta S_{\text{verre}} = m_1 c_{\text{verre}} \ln \frac{T_f}{T_1} \Rightarrow \Delta S_{\text{verre}} = 50 \times 0.87 \ln \frac{297.27}{353}$$

$$\Rightarrow \Delta S_{\text{verre}} = -7.48JK^{-1}$$

The entropy variation of the water is: $\Delta S_{\text{eau}} = \int_{T_1}^{T_2} \delta Q_{\text{eau}} \frac{1}{T}$

$$\Rightarrow \Delta S_{\text{eau}} = m_2 c_{\text{eau}} \ln \frac{T_f}{T_2} \Rightarrow \Delta S_{\text{eau}} = 100 \times 4.18 \ln \frac{297.27}{293}$$

$$\Rightarrow \Delta S_{\text{eau}} = 6.05JK^{-1}$$

The entropy variation of the calorimeter is: $\Delta S_{\text{cal}} = \int_{T_1}^{T_2} \delta Q_{\text{cal}} \frac{1}{T}$

$$\Rightarrow \Delta S_{\text{cal}} = C \ln \frac{T_f}{T_2} \Rightarrow \Delta S_{\text{cal}} = 150 \ln \frac{297.27}{293}$$

$$\Rightarrow \Delta S_{\text{cal}} = 2.17 J K^{-1} \Rightarrow \Delta S = 6.05 + 2.17 - 7.48 \Rightarrow \Delta S = 0.74 J K^{-1}$$

Exercise 02:

Consider 2 moles of ideal gas expanding from 30 to 50 liters in an isothermal and irreversible manner.

1. Calculate the entropy change of the gas.
2. Calculate the created entropy.

Solution:

For the isothermal transformation ($\delta T = 0$),
we have: $\delta U = \delta Q + \delta W = 0 \Rightarrow \delta Q = -\delta W$ And $\delta W = -PdV$

1. The entropy change of the system (gas) is:

$$\begin{aligned}
\Delta S_{\text{system}} &= \int_{T_1}^{T_2} \frac{\delta Q_{\text{system}}}{T} \\
&= \int_{T_1}^{T_2} \frac{PdV}{T} \\
&= \int_{T_1}^{T_2} \frac{nRTdV}{TV} \\
&= \int_{T_1}^{T_2} \frac{nRdV}{V} \\
&= nR \ln \frac{V_2}{V_1} \\
&= 2 \times 8.314 \ln \frac{50}{30} \\
&= 8.49\, J\, K^{-1}
\end{aligned}$$

2. The created entropy:

$$\begin{aligned}
\Delta S_{\text{exchange}} &= \frac{Q_{\text{irreversible}}}{T} = -\frac{W_{\text{irreversible}}}{T} \\
&= P_{final}\Delta V\frac{1}{T} \\
&= nRT\frac{\Delta V}{V_2T} \\
&= nR\frac{\Delta V}{V_2} \\
&= 2\times 8.314\frac{20}{50} \\
&= 6.65\,J\,K^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta S_{\text{system}} &= \Delta S_{\text{exchange}} + \Delta S_{\text{created}} \\
\Delta S_{\text{created}} &= \Delta S_{\text{system}} - \Delta S_{\text{exchange}} \\
&= 8.49 - 6.65 \\
&= 1.84\,J\,K^{-1}
\end{aligned}$$

Exercise 03:

In an adiabatic enclosure, 360 g of water at $25°C$ is mixed with 36 g of ice at $0°C$.

1. Calculate the temperature of thermal equilibrium.
2. Calculate the entropy change accompanying this transformation.

Given: Molar specific heat of liquid water: $C_{\text{water}}(H_2O,l) = 75.25\,J\cdot mol^{-1}\cdot K^{-1}$ Enthalpy change of fusion of ice: $\Delta h^{\circ}_{\text{fusion},273}(H_2O,s) = 5.94\,kJ\cdot mol^{-1}$

Solution:

1- Calculation of the equilibrium temperature of the mixture:

Liquid water ($m_1 = 360\,\text{g}$) with $T_1 = 25°\text{C}$ + Ice ($m_2 = 36\,\text{g}$) with $T_2 = 0°\text{C}$ (water in solid state).

After thermal equilibrium $\longrightarrow$ liquid mixture with an equilibrium temperature T_{eq}

$$Ice(36g,0°C) \xrightarrow{fusion} Liquid(0°C) \xrightarrow{heating} mixture(liq,T_eq) \xleftarrow{cooling} (360g,25°C)water$$

In calculating the number of moles of liquid water: $n_1 = \dfrac{m_1}{M_{\text{water}}}$, thus $n_1 = \dfrac{360}{18}$, therefore $n_1 = 20$ moles of liquid water at $T = 25\,°\text{C} = 298\,\text{K}$.

The number of moles of ice at $T = 0°\text{C} = 273\,\text{K}$: $n_2 = \dfrac{m_2}{M_{\text{water}}}$, $n_2 = \dfrac{36}{18}$, $n_2 = 2\,\text{moles}$.

We have: $Q_1 = n_1 c_{\text{water}}(T_{\text{eq}} - T_1)$: cooling of hot water,
$Q_1 = 20 \times 75.25(T_{\text{eq}} - 298) = 1505T_{\text{eq}} - 448490$.
$Q_2 = n_2 L_f$: ice melting,
$Q_2 = 2 \times 5.94 \times 10^3 = 11.88 \times 10^3$.
And $Q_3 = n_2 c_{\text{water}}(T_{\text{eq}} - T_2)$,
$Q_3 = 2 \times 75.25(T_{\text{eq}} - 273) = 150.5T_{\text{eq}} - 41086.5$.
$\Sigma Q_i = 0 \rightarrow Q_1 + Q_2 + Q_3 = 0$

$$\Rightarrow 1505\,T_{\text{eq}} - 448490 + 11880 + 150.5\,T_{\text{eq}} - 41086.5 = 0$$

$$\Rightarrow 1655.5\,T_{\text{eq}} - 477696.5 = 0 \Rightarrow T_{\text{eq}} = 288.55\,\text{K} = 15.55\,°\text{C}$$

2- Calculation of the entropy change of the transformation:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

The entropy change of the liquid water is:

$$\Delta S_1 = n_1 c_{\text{water}} \ln \frac{T_{\text{eq}}}{T_1} \Rightarrow \Delta S_1 = 20 \times 75.25 \ln \frac{288.55}{298} \Rightarrow \Delta S_1 = -48.50\,\text{J K}^{-1}$$

The entropy change of the ice is:

$$\Delta S_2 = \frac{n_2 L_f}{T_{\text{eq}}} \Rightarrow \Delta S_2 = \frac{2 \times 5.94 \times 10^3}{288.55} \Rightarrow \Delta S_2 = 41.17\,\text{J K}^{-1}$$

$$\Delta S_3 = n_2 c_{\text{water}} \ln \frac{T_{\text{eq}}}{T_2} \Rightarrow \Delta S_3 = 2 \times 75.25 \ln \frac{288.55}{273} \Rightarrow \Delta S_3 = 8.35\,\text{J K}^{-1}$$

$$\Rightarrow \Delta S = 41.14 + 8.35 - 48.50 \Rightarrow \Delta S = 1.02\,\text{J K}^{-1}$$

Exercise 04:

Calculate ΔS°_{298} for the following changes:

1. $SnCl_4(l) \rightarrow SnCl_4(g)$
2. $CS_2(g) \rightarrow CS_2(l)$
3. $Cu(s) \rightarrow Cu(g)$
4. $H_2O(l) \rightarrow H_2O(g)$
5. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
6. $2HCl(g) + Pb(s) \rightarrow PbCl_2(s) + H_2(g)$
7. $Zn(s) + CuSO_4(s) \rightarrow Cu(s) + ZnSO_4(s)$

ANSWER: 107 J/K; −86.4 J/K; 133.2 J/K; 118.8 J/K; −326.6 J/K; −171.9 J/K; (g) −7.2 J/K

Exercise 04:

The entropy change for the process

$$H_2O(s) \to H_2O(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system.

Is the process spontaneous at $-10.00\,^\circ\mathrm{C}$?

Is it spontaneous at $+10.00\,^\circ\mathrm{C}$?

Solution:

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, $\Delta S_{\text{sys}} = 22.1\,\mathrm{J/K}$ and $q_{\text{surr}} = -6.00\,\mathrm{kJ}$. At $-10.00\,^\circ\mathrm{C}$ (263.15 K), the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = 22.1\,\mathrm{J/K} - \frac{6.00 \times 10^3\,\mathrm{J}}{263.15\,\mathrm{K}} = -0.7\,\mathrm{J/K}$$

Since $\Delta S_{\text{univ}} < 0$, melting is nonspontaneous (not spontaneous) at $-10.0\,^\circ\mathrm{C}$.

At $10.00\,^\circ\mathrm{C}$ (283.15 K), the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} = 22.1\,\mathrm{J/K} - \frac{6.00 \times 10^3\,\mathrm{J}}{283.15\,\mathrm{K}} = +0.9\,\mathrm{J/K}$$

Since $\Delta S_{\text{univ}} > 0$, melting is spontaneous at $10.00\,^\circ\mathrm{C}$.

Check Your Learning

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of ΔS_{univ}?

ANSWER Entropy is a state function, so $\Delta S_{\text{freezing}} = -\Delta S_{\text{melting}} = -22.1\,\mathrm{J/K}$ and $q_{\text{surr}} = +6.00\,\mathrm{kJ}$. At $-10.00\,^\circ\mathrm{C}$, spontaneous, $+0.7\,\mathrm{J/K}$; at $+10.00\,^\circ\mathrm{C}$, nonspontaneous, $-0.9\,\mathrm{J/K}$.

Exercise 05:

A gas is isothermally (20°C) compressed and the work done on the gas is equal to −1850 J. Calculate the change of entropy which the gas experiences.

Solution :

$$\Delta S = \int_1^2 \frac{dQ}{T} = \frac{1}{T}Q = \frac{1}{T}W = -\frac{1850}{293} = -6.3\,\mathrm{J/K}.$$

Exercise 06:

You decide to take a nice hot bath but discover that your thoughtless roommate has used up most of the hot water. You fill the tub with 195 kg of 30.0 degrees C water and attempt to warm it further by pouring in 5.00 kg of boiling water from the stove. The heat capacity of water is 4190 J/(kg·K).

(a) Is this a reversible or an irreversible process? Explain.

(b) Calculate the final temperature of the bath water.

(c) Calculate the net change in entropy of the system+surroundings (bath water + boiling water), assuming no heat exchange with the air or the tub itself. Explain the result.

Solution :

(a) Because the heat transfer occurs over a finite temperature difference it is irreversible.

(b) As the water mixes: heat will be transferred from the hot to the cold water. Call the final temperature T_f and solve for T_f using $Q = mc\Delta T$. $m_c c(T_f - T_c) = m_b c(T_b - T_f)$,

where m_c and m_b are the masses of the cold and boiling water respectively (same subscripts used for the temperatures). Solving yields: $T_f = 31.75\,°\mathrm{C}$.

(c) $\Delta S = mc \ln \dfrac{T_f}{T_i} = m_c c \ln \dfrac{T_f}{T_c} + m_b c \ln \dfrac{T_f}{T_b} = 471\,\mathrm{J/K}$. So $\Delta S_{\text{system}} > 0$ indeed, as it should be.

Exercise 07:

A lonely party balloon with a volume of 2.40 L and containing 0.100 mol of air is left behind to drift in the temporarily uninhabited and depressurized International Space Station. Sunlight coming through a porthole heats and explodes the balloon, causing the air in it to undergo a free expansion into the empty station, whose total volume is 425 m^3. Calculate the entropy change of the air during the expansion.

Solution:

The entropy change of a free expansion is: $\Delta S = nR \ln \dfrac{V_f}{V_i} = 10.0\,\mathrm{J/K}$. So $\Delta S_{\text{system}} > 0$ (irreversible process).

A certain heat engine operating on a Carnot cycle absorbs 410 J of heat per cycle at its hot reservoir at 135°C and has a thermal efficiency of 22.0%. (a) How much work does this engine do per cycle? (b) How much heat does the engine waste each cycle? (c) What is the temperature of the cold reservoir? (d) Show that the total change of entropy for the Carnot cycle is equal to 0.

Answer

1. From the definition of the efficiency of a heat engine we find: $W = \eta Q_H = 90.2\,\mathrm{J}$ per cycle.

2. For a heat engine: $Q_H + Q_C = W$ ($Q_C < 0$ because heat leaves the system!). So using the result from (a) we find $Q_C = -320\,\mathrm{J}$. So the machine wastes 320 J every cycle.

3. $\dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H}$, so $T_C = -T_H \cdot \dfrac{Q_C}{Q_H} = 318\,\mathrm{K}$.

4. $\Delta S = \frac{|Q_H|}{T_H} + \frac{|Q_C|}{T_C} = 0$. Because the entropy change is zero the Carnot cycle must be reversible.

Chapter 6

Statement of the Third Principle of Thermodynamics, Absolute Entropy at Zero Kelvin (0 K)

6.1 Statement of the Third Principle: Absolute entropy at zero Kelvin (0 K)

The third principle of thermodynamics, also known as Nernst's theorem (1906), states that at absolute zero (-273°C) the entropy of pure substances (perfectly crystallized) is zero. Therefore, the third principle establishes a reference for entropy. In the case of a pure substance, there is no thermal agitation at this temperature, and the crystal is perfect.

6.2 The standard molar absolute entropy of a pure substance $S^\circ_{\mathbf{ST}}$:

The value of the entropy of a substance depends on pressure (for example, high pressure would confine a gas to a smaller volume, thus reducing its entropy). Therefore, it is common to choose a standard pressure and provide the standard molar entropy.

The third principle of thermodynamics assigns an absolute molar entropy to any pure substance at temperature T. In the standard state, the absolute molar entropy is denoted by S°_{ST}. That is, the molar entropy of a substance in its standard state (pure substance under 1 atm).

At constant pressure, for example, $p = p^\circ = 1$ atm, knowledge of the heat capacity $c_p(T, P)$, denoted by $c_p^\circ(T)$, allows access, through integration, to S_T°:

$$S^\circ(T) - S^\circ(T=0) = \int_{T=0}^{T} c_p^\circ(T)\frac{dT}{T}$$

Where:

- $S^\circ(T)$ represents the absolute molar entropy of compound A at temperature T.
- $S^\circ(T=0)$ represents the absolute molar entropy of compound A at temperature 0 K.

According to the third principle, $S^\circ(T=0) = 0$, so:

$$S^\circ(T) = \int_{T=0}^{T} c_p^\circ(T)\frac{T}{T}dT$$

6.3 The change in absolute entropy during a chemical reaction $\Delta S_{\mathbf{R}}^\circ$

The evolution of a thermodynamic system is governed by the entropy function, which can be positive or zero. In the case of chemical reactions, entropy is positive if the reaction is spontaneous and zero if it is reversible (at equilibrium). Consider the following reaction under standard conditions ($P = 1$ atm and $T = 298$ K):

$$\mathrm{aA} + \mathrm{bB} \longrightarrow \mathrm{cC} + \mathrm{dD}$$

$$\Delta S_{\mathrm{R,298K}}^\circ = (cS_{\mathrm{298K,C}}^\circ + dS_{\mathrm{298K,D}}^\circ) - (aS_{\mathrm{298K,A}}^\circ + bS_{\mathrm{298K,B}}^\circ)$$

Where S_{298K}° denotes the molar entropy of the chemical species expressed in cal. K^{-1}. mol^{-1}. In general, the change in entropy of a chemical reaction under standard conditions is given by the following relation:

$$\Delta S_{\mathrm{R,298}}^\circ = \sum n_i S_{i,298}^\circ(\text{Products}) - \sum n_j S_{j,298}^\circ(\text{Reactants})$$

6.4 The change in entropy of a chemical reaction at temperature T, $\Delta S_{\mathbf{R}}(T)$

Given the change in entropy of a chemical reaction $\Delta S_{\mathrm{R,298}}^\circ$, we can calculate the change in entropy of this reaction at another temperature T, $\Delta S_{\mathrm{R},T}^\circ$, using the Kirchoff's relation:

$$\Delta S_{\mathrm{R},T}^\circ = \Delta S_{\mathrm{R,298}}^\circ + \int_{298}^{T} \Delta c_p \frac{dT}{T}$$

Where: $\Delta c_p = \sum c_{p,i}(\text{Products}) - \sum c_{p,j}(\text{Reactants})$.

6.5 The Gibbs free energy of a chemical reaction

6.5.1 Definition

- The condition of maximum entropy is a suitable criterion for the equilibrium of an isolated system:

◇ $\Delta S > 0$: Processes spontaneous (irreversible)

◇ $\Delta S = 0$: **Processes reversible**

- In the case of a non-isolated system:
  - It is necessary to consider the variations in entropy (of the system and the external surroundings).
  - It is necessary to find a new state function characteristic of the system according to two criteria:

1. **Criterion of maximum entropy:** The system evolves towards the state with the highest statistical probability (number of microstates).
2. **Criterion of minimum energy:** The system evolves towards the state of lowest energy (the most stable).

Introduction of the state function called Free Enthalpy: $G = H - TS$
The free enthalpy (G) is an indispensable function for the study of chemical reactions; it allows predicting if a chemical reaction performed at T and P is theoretically possible and in which direction it evolves.

At constant temperature: $dG = dH - TdS$ So: $\Delta G = \Delta H - T\Delta S$

6.5.2 Condition for the evolution of a system:

Consider a system that evolves spontaneously (in an irreversible way) from an initial state to a final state at $T =$ constant. In this case, we have:

$$dS > \frac{dQ_{\text{irrev}}}{T} \implies dS - \frac{dQ_{\text{irrev}}}{T} > 0$$

. So: $TdS - dQ_{\text{irrev}} > 0$.

For a finite transformation between the initial and final states (at constant T and P), we can write:

$$T\Delta S - \Delta H > 0 \implies \Delta H - T\Delta S < 0$$

. Where: $\Delta G = \Delta H - T\Delta S$.

A non-isolated system at constant T and P evolves spontaneously in the direction where $\Delta G < 0$ ($dG < 0$).

6.5.3 Calculation of the variation of free enthalpy during a chemical reaction

Free enthalpy (G) is an essential function for the study of chemical reactions; it allows predicting if a chemical reaction performed at T and P is theoretically possible and in which direction it evolves.

6.5.3.1 Standard free enthalpy of formation $\Delta G^\circ_{f,T}$

It is the change in free enthalpy accompanying the formation of one mole of a compound from its constituents taken in their standard reference state.

$$\Delta G^\circ_{f,T} = \Delta H^\circ_{f,T} - T\Delta S^\circ_{f,T}$$

6.5.3.2 Standard Gibbs free energy of reaction $\Delta G^\circ_{R,T}$

The following relation represents the state function known as the Gibbs function, called free enthalpy:

$$\Delta G^\circ_{298} = \Delta H^\circ_{298} - 298\Delta S^\circ_{298}$$

.

$\Delta G^\circ_{R,298}$ can also be calculated using the following expression:

$$\Delta G^\circ_{R,298} = \sum \Delta G^\circ_{298}(\text{Products}) - \sum \Delta G^\circ_{298}(\text{Reactants})$$

.

$\Delta G^\circ_{R,T}$ can also be calculated at temperature T by the following relation:

$$\Delta G^\circ_{R,T} = \Delta H^\circ_{R,T} - T\Delta S^\circ_{R,T}$$

. Where ΔH°_T and ΔS°_T are calculated by applying Kirchhoff's law.

The standard free enthalpy of all simple substances is zero; $\Delta G^\circ_{R,T} = 0$.

- $\Delta G^\circ_{R,T} < 0$ implies the reaction is spontaneous.
- $\Delta G^\circ_{R,T} > 0$ implies the reaction is non-spontaneous.
- $\Delta G^\circ_{R,T} = 0$ implies the reaction is at equilibrium (there is no evolution of the system).

6.6 Molar free enthalpy - Equilibrium

6.6.1 Variation of molar free enthalpy with pressure

During a transformation, the pressure of the system may vary. These variations do not have any influence on the state of condensed phases. However, in the case of gases, the effect of pressure is very important. The molar free enthalpy G is expressed in terms of other thermodynamic functions by the relation:

$$G = H - TS = U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

Now, $dW = -PdV$ and $dQ = TdS$ for a reversible process. Hence:

$$dU = dQ - PdV = TdS - PdV$$

Thus:

$$dG = VdP - SdT$$

For an isothermal transformation, we can write:

$$dG = VdP$$

For a finite variation in pressure from P_1 to P_2:

$$\Delta G = G_T^{P2} - G_T^{P1} = \int_{P_1}^{P_2} VdP$$

For n moles of ideal gas:

$$V = \frac{nRT}{P} \implies \Delta G = G_T^{P2} - G_T^{P1} = nRT \int_{P_1}^{P_2}$$

$$\implies G_T^{P2} - G_T^{P1} = nRT \ln \frac{P_2}{P_1}$$

If we choose $P_1 = 1$ bar (standard state), For one mole of a pure gas, the molar free enthalpy at pressure P is:

$$G_T^P = G_T^\circ + RT \ln P$$

For one mole of gas i in a mixture, the molar free enthalpy is a function of the partial pressure P_i:

$$G_T^P = G_T^\circ + RT \ln P_i$$

This relation is applicable in the case of ideal gases, and can be generalized to systems with any constituents in the form:

$$G_T^P(i) = G_T^\circ(i) + RT \ln a_i$$

where a_i is the activity (concentration, pressure, etc.) of constituent i.

6.6.2 Chemical equilibrium

6.6.2.1 Definition

A chemical system is in equilibrium when it undergoes a reversible reaction, that is, a reaction that is not total. The establishment of equilibrium requires the coexistence of all constituents, products, and reactants at a constant temperature, pressure, and with uniform compositions that remain constant over time.

6.6.2.2 Mass action law (Guldberg and Waage relation for homogeneous equilibria) and equilibrium constants

A homogeneous equilibrium is any mixture that results in the formation of a single solid, liquid, or gaseous phase. This phase is homogeneous: its properties are identical regardless of the location within this phase. In 1865, Guldberg and Waage, inspired by Berthollet's propositions, experimentally demonstrated that there was a relation between the concentrations of species present at equilibrium in solution; the equilibrium constant they defined was called the Guldberg and Waage constant or the mass action law constant. Consider a chemical reaction in solution,

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

At equilibrium, the concentrations of the constituents satisfy the relation:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where K_c is the equilibrium constant relative to concentrations. $[A]$ is the molar concentration of constituent A.

In the case where the constituents are in the gaseous state, we use the equilibrium constant relative to partial pressures:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

6.6.2.3 Relation between K_P and K_c

The molar concentration of a constituent:

$$[A] = \frac{n_A}{V} = \frac{P_A}{RT}; [B] = \frac{n_B}{V} = \frac{P_B}{RT}; [C] = \frac{n_C}{V} = \frac{P_C}{RT}; [D] = \frac{n_D}{V} = \frac{P_D}{RT}$$

$$Thus : n_A = a; n_B = b; n_C = c; n_D = d$$

After replacing the concentrations of the different constituents (in the gaseous state) in the expression of K_c, we find that:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_P\,(RT)^{\Delta n(g)}$$

Where: $\Delta n(g) = (c + d) - (a + b)$

6.6.2.4 Relation between the equilibrium constant and the standard free enthalpy change

Consider a chemical reaction occurring between ideal gases:

$$a\mathrm{A(g)} + b\mathrm{B(g)} \rightleftharpoons c\mathrm{C(g)} + d\mathrm{D(g)}$$

The change in free enthalpy between the initial state and any state before equilibrium:

$$\Delta G_{r,T} = c \cdot G_T(C) + d \cdot G_T(D) - a \cdot G_T(A) - b \cdot G_T(B)$$

Applying for each constituent the relation:

$$G_T P = G_T^\circ + RT \ln P_i$$

We obtain:

$$\Delta G_{r,T} = \Delta G_{r,T}^\circ + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

With:

$$\Delta G_{r,T}^\circ = c \cdot G_T^\circ(C) + d \cdot G_T^\circ(D) - a \cdot G_T^\circ(A) - b \cdot G_T^\circ(B)$$

At equilibrium:

$$\Delta G_{r,T} = 0 \implies \Delta G_{r,T}^\circ + RT \ln \left(\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right) = 0$$

$$\implies \Delta G_{r,T}^\circ = -RT \ln \left(\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right)$$

$$\implies \Delta G_{r,T}^\circ = -RT \ln K_P$$

$$\ln K_P = -\frac{\Delta G_{r,T}^\circ}{RT} \implies K_P = \exp\left(-\frac{\Delta G_{r,T}^\circ}{RT} \right)$$

The equilibrium constant depends only on the temperature and has no dimension.

6.6.3 Displacement of the equilibrium

6.6.3.1 Le Chatelier's Principle

When a chemical system is subjected to a disturbance by changing one of the equilibrium factors, the equilibrium shifts in a direction that reduces the effect of the disturbance.

Equilibrium always tends to oppose the changes we want to impose on it. This is the law of moderation.

We will study the effect of a disturbance on a system in equilibrium by changing an equilibrium factor and predicting its evolution.

6.6.3.2 Variation of K_P with T: Influence of Temperature: Van 't Hoff Law

$$\Delta G^\circ_{\mathrm{r},T} = \Delta H^\circ_\mathrm{r} - T\Delta S^\circ_\mathrm{r} = -RT\ln K_P$$

$$\ln K_P = -\frac{\Delta H^\circ_\mathrm{r}}{RT} + \frac{\Delta S^\circ_\mathrm{r}}{R}$$

If we plot $\ln K_P$ against $1/T$, we directly obtain the values of $\Delta H^\circ_\mathrm{r}$ and $\Delta S^\circ_\mathrm{r}$. This relationship can be written in differential form:

$$\frac{d(\ln K_P)}{dT} = \frac{\Delta H^\circ_\mathrm{r}}{RT^2} \quad \text{Van 't Hoff Law}$$

$$d(\ln K_P) = \frac{dT}{T^2}\cdot\frac{\Delta H^\circ_\mathrm{r}}{R}$$

$$\Longrightarrow \int_{(K_P(T_1))}^{(K_P(T_2))} d(\ln K_p) = \int_{T_1}^{T_2}\frac{dT}{T^2}\cdot\frac{\Delta H^\circ_\mathrm{r}}{R}$$

$$lnk_p]_{kp(T_1)}^{kp(T_2)} = \frac{\Delta H^\circ}{R}\left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

$$\Longrightarrow \ln\left(\frac{K_P(T_2)}{K_P(T_1)}\right) = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

The Vant'Hoff relation allows for an easy prediction of the influence of temperature (T) on an equilibrium. RT^2 is a term that is necessarily positive.

- If $\Delta H^\circ_\mathrm{r} < 0$ (exothermic reaction): $d(\ln K_P)$ and dT have opposite signs, so if T increases, K_P decreases (and vice versa).
- If $\Delta H^\circ_\mathrm{r} > 0$ (endothermic reaction): $d(\ln K_P)$ and dT have the same signs, so if T increases, K_P increases (and vice versa).

An increase in temperature (K_P increases) thus favors the direction corresponding to the endothermic reaction. Conversely, a decrease in temperature (K_P decreases) favors the direction corresponding to the exothermic reaction.

6.6.3.3 Influence of Partial Pressure

The equilibrium shifts in the direction of disappearance of the components whose pressure has been increased.

$$K_P = \frac{P_C^c\cdot P_D^d}{P_A^a\cdot P_B^b} = constant$$

- If P_A increases (nA and [A] increase). For K_P to remain constant, the equilibrium shifts in direction 1 (forward direction).

- If P_C increases. For K_P to remain constant, the equilibrium shifts in direction 2 (reverse direction).

In general

- If the reactant pressures increase, the product pressures decrease {Sense 1
- If the reactant pressures decrease, the product pressures increase {Sense 2

6.6.3.4 Dissociation coefficients in homogeneous phases

If a chemical reaction involves only one reactant (homogeneous medium), such as: $AB(g) \rightleftharpoons A(g) + B(g)$ It is called a **dissociation reaction**. The dissociation rate α (dissociation coefficient), ranging from 0 to 1, is defined as follows:

$$\alpha = \frac{n'}{n_0}$$

where n' is the number of moles dissociated and n_0 is the initial number of moles.

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

at $t = 0:\ n_0, 0, 0$ at equilibrium: $n_0 - n', n', n'$, $\quad K_P = \frac{P_A P_B}{P_{AB}}$

Total number of moles at equilibrium: $n_t = n_{AB} + n_A + n_B = (n_0 - n') + n' + n' \quad n' = n_0\alpha$

So: $n_t = (n_0 - n_0\alpha) + n_0\alpha + n_0\alpha = n_0 + n_0\alpha = n_0(1+\alpha) \quad \alpha = 0\% \rightarrow 100\%$

t	AB	A	B	a
0	n_0	0	0	0
à l'équilibre	$n_0(1-\alpha)$	$n_0\alpha$	$n_0\alpha$	α
n_t	$n_0(1+\alpha)$			1

$$K_P = \frac{P_A P_B}{P_{AB}} \Rightarrow \ln K_P = -\frac{\Delta G^\circ}{RT}$$

$$P_A = X_A P_t = \frac{n_A}{n_t} P_t = \frac{n_0\alpha}{n_0(1+\alpha)} P_t = \frac{\alpha}{1+\alpha} P_t$$

$$P_B = X_B P_t = \frac{n_B}{n_t} P_t = \frac{n_0\alpha}{n_0(1+\alpha)} P_t = \frac{\alpha}{1+\alpha} P_t$$

$$P_{AB} = X_{AB} P_t = \frac{n_{AB}}{n_t} P_t = \frac{n_0(1-\alpha)}{n_0(1+\alpha)} P_t = \frac{1-\alpha}{1+\alpha} P_t$$

$$K_P = \left(\frac{\alpha}{1+\alpha} P_t\right)\left(\frac{\alpha}{1+\alpha} P_t\right) / \left(\frac{1-\alpha}{1+\alpha} P_t\right) = \frac{\alpha^2 P_t}{(1+\alpha)(1-\alpha)} = \frac{\alpha^2 P_t}{1-\alpha^2}$$

$$K_P = \frac{\alpha^2 P_t}{1-\alpha^2} \Rightarrow \alpha^2 = K_P(1-\alpha^2) = \alpha^2 P_t \Rightarrow K_P = \alpha^2(K_P + P_t)$$

$$\alpha^2 = \frac{K_P}{K_P + P_t} \Rightarrow \alpha = \sqrt{\frac{K_P}{K_P + P_t}}$$

Exercise 01

1. What is the standard molar absolute entropy of water at 25°C, knowing that:

$s^\circ_{273}(\mathrm{H_2O},\, s) = 10.26\,\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$

$\Delta h^\circ_{\text{fusion, }273}(\mathrm{H_2O},\, s \rightleftharpoons \mathrm{H_2O},\, l) = 1440\,\mathrm{cal\cdot mol^{-1}}$

$C_p(\mathrm{H_2O},\, l) = 11.2 + 7.17\times10^{-3}T\,\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$.

2. What is the standard molar entropy of formation of water at 25°C, knowing that:

$s^\circ_{298}(\mathrm{H_2},\, g) = 31.21\,\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$

$s^\circ_{298}(\mathrm{O_2},\, g) = 49.00\,\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$.

Solution:

1−Calculation of the absolute molar entropy of water at 25°C:

$S^0_{298}(\mathrm{H_2O}, l)$

$\mathrm{H_2O}$ (s, 273 K) → $\mathrm{H_2O}$ (l, 273 K) → $\mathrm{H_2O}$ (l, 298 K)

$$\Delta S^0 = S^0_{298}(\mathrm{H_2O}, l) - S^0_{273}(\mathrm{H_2O}, s)$$

$$S^0_{298}(\mathrm{H_2O}, l) = \Delta S^0 + S^0_{273}(\mathrm{H_2O}, s)$$

$$\Delta S^0 = \Delta S^0(273, \text{fusion}) + \Delta S^0(\text{heating})$$

$$\Delta S^0(273, \text{fusion}) = \frac{\Delta H^0_{273,\text{fusion}}}{T_{\text{fusion}}};\Delta S^0(\text{heating}) = \int_{273}^{298} C_p(\mathrm{H_2O}, l)\frac{dT}{T}$$

$$S^0_{298}(\mathrm{H_2O}, l) = \frac{\Delta H^0_{273,\text{fusion}}}{T_{\text{fusion}}} + \int_{273}^{298} C_p(\mathrm{H_2O}, l)\frac{dT}{T} + S^0_{273}(\mathrm{H_2O}, s)$$

$$S^0_{298}(\mathrm{H_2O}, l) = 10.26 + \frac{1440}{273} + \int_{273}^{298} (\frac{11.2}{T} + 7.17\times10^{-3})dT$$

$$S^0_{298}(\mathrm{H_2O}, l) = 15.54 + 11.2\ln\frac{298}{273} + 1.17\times10^{-3}(298-273)$$

$$S^0_{298}(\mathrm{H_2O}, l) = 15.66\,\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$$

Calculation of the standard entropy of formation of water at 298 K:$\Delta S_{\mathrm{f},298}(\mathrm{H_2O},\, l)$

$\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{H_2O}$ (l) at 298 K

$$\Delta S^0_{\mathrm{r},298} = \Delta S^0_{\mathrm{f},298}(\mathrm{H_2O},\, l) \implies \Delta S^0_{\mathrm{f},298}(\mathrm{H_2O},\, l) = S^0_{298}(\mathrm{H_2O},\, l) - S^0_{298}(\mathrm{H_2,g}) - \frac{1}{2}S^0_{298}(\mathrm{O_2,g})$$

$$\Delta S^0_{\mathrm{f},298}(\mathrm{H_2O},\, l) = 15.66 - 31.21 - \frac{1}{2}\times 49$$

$$\Delta S^0_{\mathrm{f},298}(\mathrm{H_2O},\, l) = -40.05\,\mathrm{cal\cdot mol^{-1}\cdot K^{-1}}$$

Exercise 02

Consider the formation reaction of one mole of MgO:

$$\mathrm{Mg\ (s)} + \frac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{MgO\ (s)}$$

Assume that $\Delta H_{\mathrm{r}}^{0} = -602\,\mathrm{kJ}$ and $\Delta S_{\mathrm{r}}^{0} = -108\,\mathrm{J}\cdot\mathrm{K}^{-1}$ are independent of temperature.

1. Calculate $\Delta G_{\mathrm{r}}^{0}$ for the formation of MgO (s) at $0\,^{\circ}\mathrm{C}$. Is the reaction possible or impossible at this temperature?
2. At what temperature is the formation of MgO impossible?

Solution:

1- Calculation of the standard Gibbs free energy of formation of MgO:

$$\Delta G_{\mathrm{r}}^{0} = \Delta H_{\mathrm{r}}^{0} - T\Delta S_{\mathrm{r}}^{0}$$
$$\Delta G_{\mathrm{r}}^{0} = -602 - 273 \times (-108 \times 10^{-3})$$
$$\Delta G_{\mathrm{r}}^{0} = -572.52\,\mathrm{kJ}$$

We observe that $\Delta G_{\mathrm{r}}^{0} < 0$, so the formation reaction of MgO is possible.

2- Calculation of the temperature at which formation is impossible:
The reaction is impossible, so $\Delta G_{\mathrm{r}}^{0} = 0$:

$$\Delta H_{\mathrm{r}}^{0} - T\Delta S_{\mathrm{r}}^{0} = 0$$
$$T\Delta S_{\mathrm{r}}^{0} = \Delta H_{\mathrm{r}}^{0}$$
$$T = \frac{\Delta H_{\mathrm{r}}^{0}}{\Delta S_{\mathrm{r}}^{0}}$$
$$T = \frac{-602}{-108 \times 10^{-3}}$$
$$T = 5574.07\,\mathrm{K}$$

Therefore, the reaction is impossible, i.e., non-spontaneous at $T > 5574.07\,\mathrm{K}$.

Exercise 03

Calculate the standard entropy change for the combustion of methanol, CH_3OH at 298 K:

$$2\mathrm{CH_3OH(l)} + 3\mathrm{O_2(g)} \longrightarrow 2\mathrm{CO_2(g)} + 4\mathrm{H_2O(l)}$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients. The standard entropy of formations are found in specific Table.

$$\begin{aligned}\Delta S^0 &= \Delta S^0_{298}\\ &= \sum \nu S^0_{298}(\text{products}) - \sum \nu S^0_{298}(\text{reactants})\\ &= [2S^0_{298}(\mathrm{CO_2(g)}) + 4S^0_{298}(\mathrm{H_2O(l)})] - [2S^0_{298}(\mathrm{CH_3OH(l)}) + 3S^0_{298}(\mathrm{O_2(g)})]\\ &= [(2 \times 213.8) + (4 \times 70.0)] - [(2 \times 126.8) + (3 \times 205.03)]\\ &= -161.6\,\mathrm{J/mol \cdot K}\end{aligned}$$

Exercise 03

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2\mathrm{CH_3OH(l)} + 3\mathrm{O_2(g)} \rightarrow 2\mathrm{CO_2(g)} + 4\mathrm{H_2O(l)}$$

Solution

Calculate the entropy change using standard entropies as shown above:

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

$$\begin{aligned}&[2\text{mol} \times S^\circ(\mathrm{CO_2(g)}) + 4\text{mol} \times S^\circ(\mathrm{H_2O(l)})] - [2\text{mol} \times S^\circ(\mathrm{CH_3OH(l)}) + 3\text{mol} \times S^\circ(\mathrm{O_2(g)})]\\ &= [2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\\ &= -161.6\,\mathrm{J/K}\end{aligned}$$

Check Your Learning

Calculate the standard entropy change for the following reaction:

$$\mathrm{Ca(OH)_2(s)} \rightarrow \mathrm{CaO(s)} + \mathrm{H_2O(l)}$$

ANSWER: 24.7 J/K