الجمهوريـــــــــــــــــة الجزائريــــــــة الديمقراطيـــــــة الشعبيـــــة

وزارة التعليـــــــــــم العــــــــــالي والبحـــــــــث العلـــــــمي

جامعة تيسمسيلت – أحمد بن يحيى الونشريسي

Algerian Democratic and Popular Republic

Ministry of Higher Education and Scientific Research

Tissemsilt University – Ahmed Ben Yahia El-Wancharissi

Faculty of Sciences and Technologies

Department of Sciences and Technologies

Intended for 1st Year Undergraduate Students in Sciences and Technologies

Course Handout Entitle:

THERMODYNAMICS I

Prepared by:

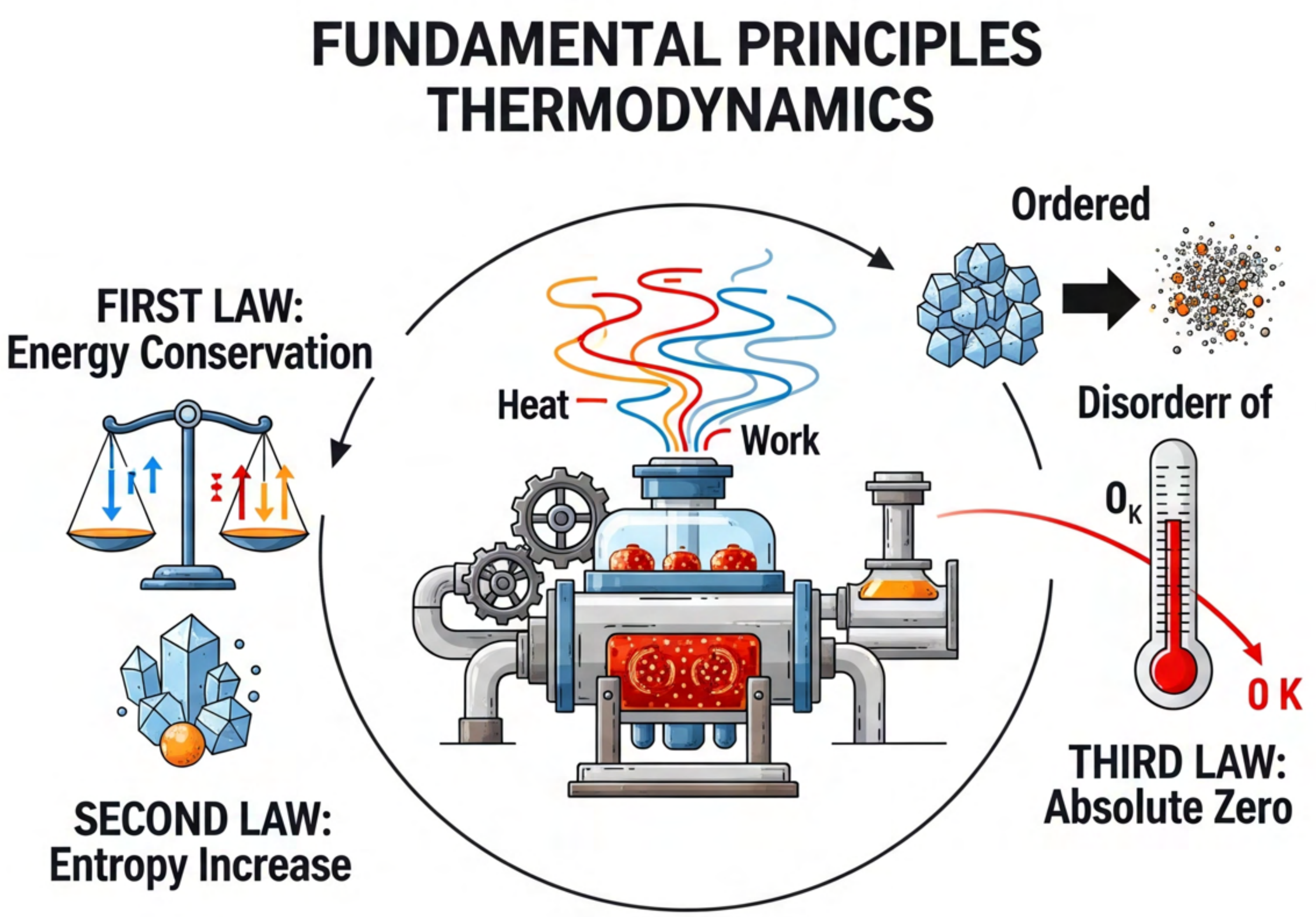
Dr. ABDI Mohamed

Academic year: 2025-2026

THERMODYNAMICS

Intended for 1st Year Undergraduate Students in Sciences and Technologies (ST)

Prepared by :
Dr. ABDI Mohamed



Semestre: 2

Unité d'enseignement: UEF 1.2

Matière 3: Thermodynamique

VHS: 67h30 (Cours: 3h00; TD: 1h30)

Crédits: 6

Coefficient: 3

Objectifs de l'Enseignement

Donner les bases nécessaires de la thermodynamique classique en vue des applications à la combustion et aux machines thermiques. Homogénéiser les connaissances des étudiants. Les compétences à appréhender sont : L'acquisition d'une base scientifique de la thermodynamique classique ; L'application de la thermodynamique à des systèmes variés ; L'énoncé, l'explication et la compréhension des principes fondamentaux de la thermodynamique.

Connaissances Préalables Recommandées

Mathématiques de base.

Contenu de la Matière

Chapitre 1. Généralités sur la Thermodynamique (3 Semaines)

1. Propriétés fondamentales des fonctions d'état. 2. Définitions des systèmes thermodynamiques et le milieu extérieur. 3. Description d'un système thermodynamique. 4. Evolution et états d'équilibre thermodynamique d'un système. 5. Transferts possibles entre le système et le milieu extérieur. 6. Transformations de l'état d'un système (opération, évolution). 7. Rappels des lois des gaz parfaits.

Chapitre 2. 1er Principe de la Thermodynamique (3 Semaines)

1. Le travail, la chaleur, L'énergie interne, Notion de conservation de l'énergie. 2. Le 1er principe de la thermodynamique : énoncé, notion d'énergie interne d'un système, application au gaz parfait, la fonction enthalpie, capacité calorifique, transformations réversibles (isochore, isobare, isotherme, adiabatique).

Chapitre 3. Applications du Premier Principe de la Thermodynamique à la Thermochimie (3 Semaines)

Chaleurs de réaction, l'état standard, l'enthalpie standard de formation, l'enthalpie de dissociation, l'enthalpie de changement d'état physique, l'enthalpie d'une réaction chimique, loi de Hess, loi de Kirchoff.

Chapitre 4. 2 ^{ème} Principe de la Thermodynamique (3 Semaines)

1. Le 2 ^{ème} principe pour un système fermé. 2. Enoncé, du 2 ^{ème} principe : Entropie d'un système isolé fermé. 3. calcul de la variation d'entropie : transformation isotherme réversible, transformation isochore réversible, transformation isobare réversible, transformation adiabatique, au cours d'un changement d'état, au cours d'une réaction chimique.

Chapitre 5. Le 3ème Principe et Entropie Absolue (1 Semaine)

Chapitre 6. Energie et Enthalpie Libres – Critères d'Evolution d'un Système (2 Semaines)

1. Introduction. 2. Energie et enthalpie libre. 3. Les équilibres chimiques.

Mode d'Évaluation :

Contrôle continu: 40% ; **Examen:** 60% .

Références Bibliographiques :

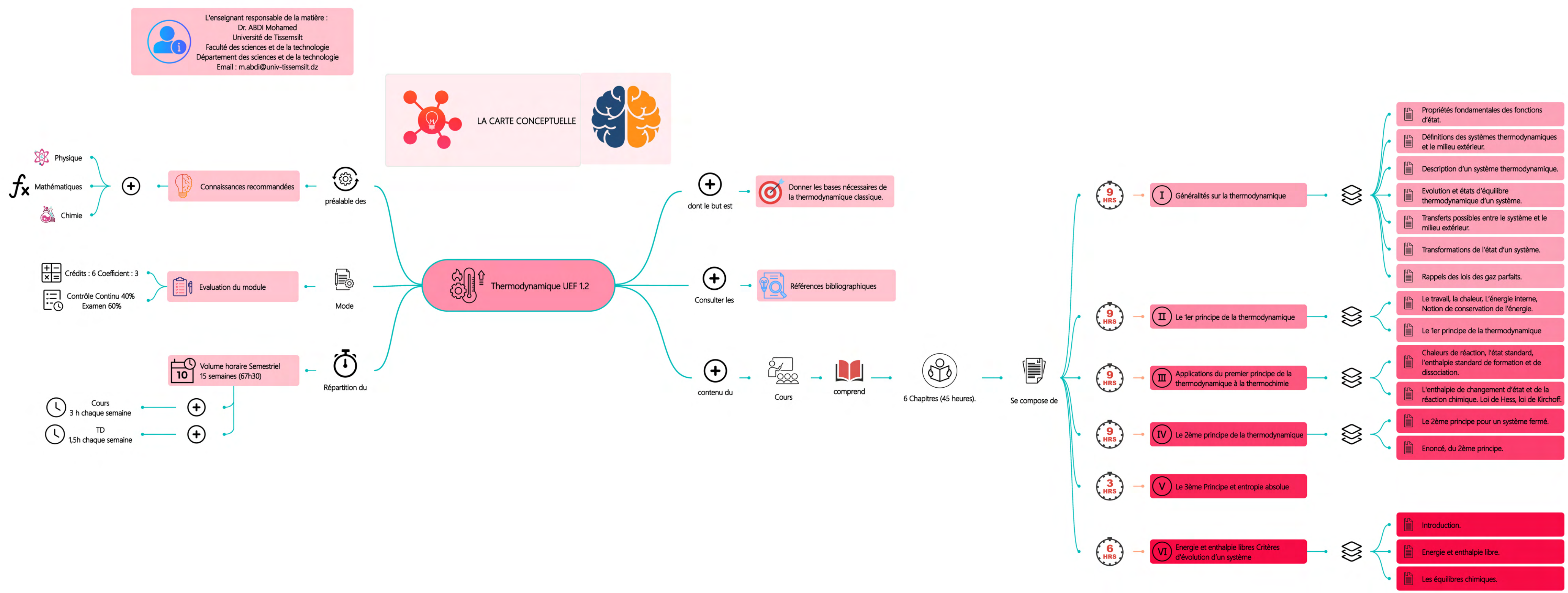
1. C. Coulon, S. Le Boiteux S. et P. Segonds, Thermodynamique Physique - Cours et exercices avec solutions, Edition Dunod.

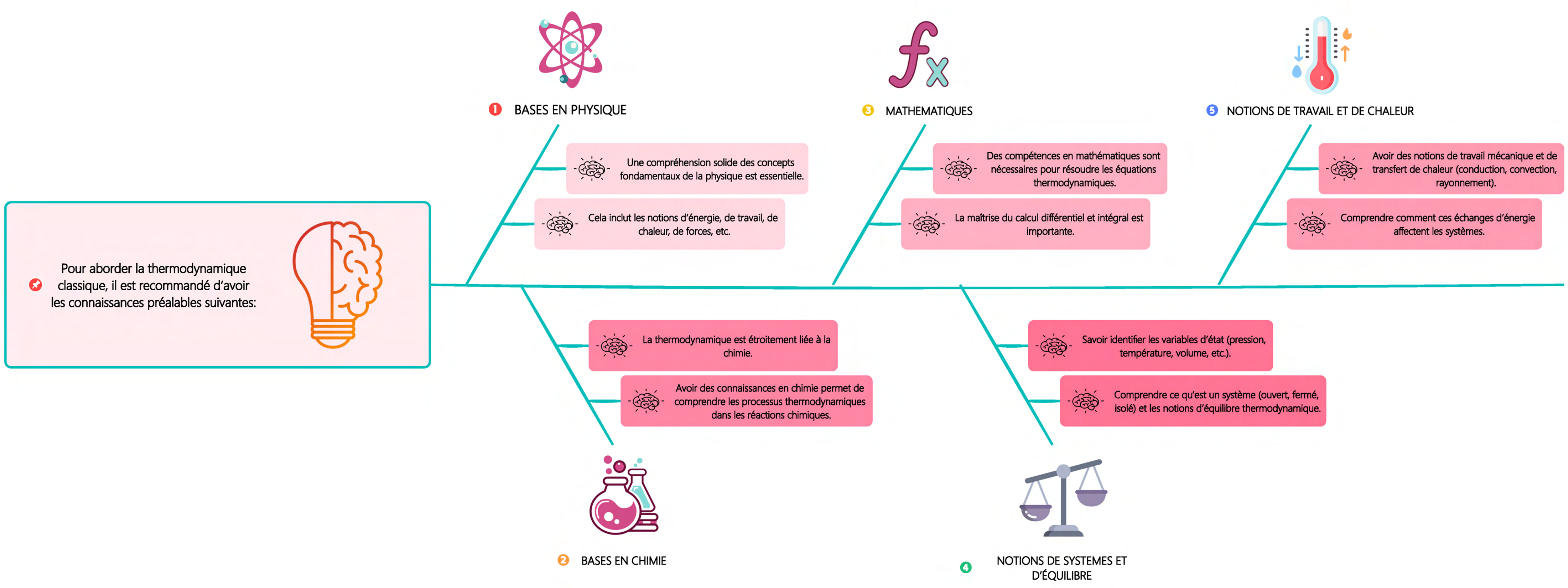
2. H.B. Callen, Thermodynamics, Cours, Edition John Wiley and Sons, 1960.

3. R. Clerac, C. Coulon, P. Goyer, S. Le Boiteux and C. Rivenc, Thermodynamics, Cours et travaux dirigés de thermodynamique, Université Bordeaux 1, 2003.

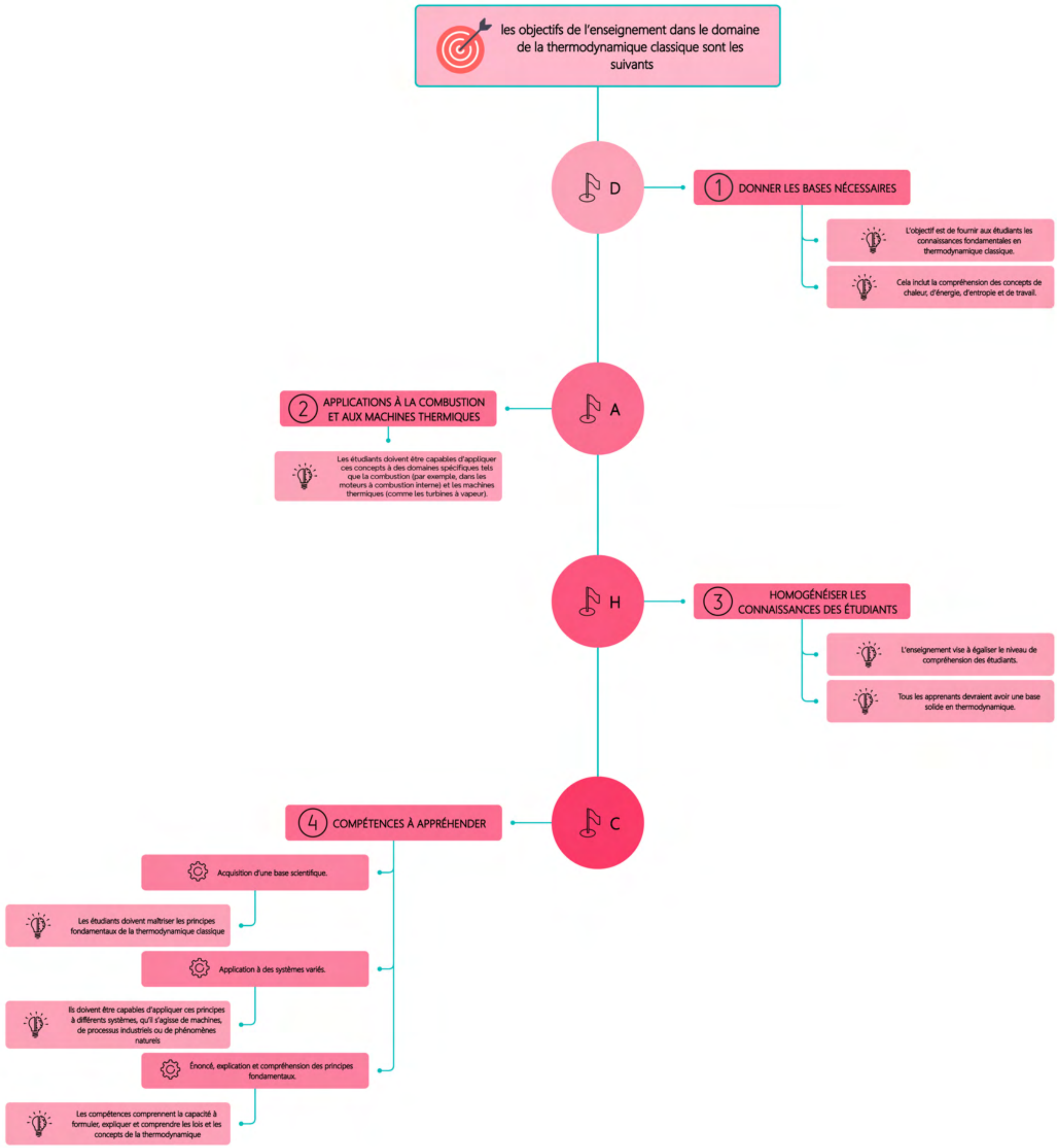
4. O. Perrot, Cours de Thermodynamique I.U.T. de Saint-Omer Dunkerque, 2011.

5. C. L. Huillier, J. Rous, Introduction à la thermodynamique, Edition Dunod.


L'enseignant responsable de la matière :
Dr. ABDI Mohamed
Université de Tissemsilt
Faculté des sciences et de la technologie
Département des sciences et de la technologie
Email : m.abdi@univ-tissemsilt.dz
LA CARTE CONCEPTUELLE
Thermodynamique UEF 1.2
préalable des
Connaissances recommandées
Physique
Mathématiques
Chimie
Mode
Evaluation du module
Crédits : 6 Coefficient : 3
Contrôle Continu 40%
Examen 60%
Répartition du
Volume horaire Semestriel
15 semaines (67h30)
Cours
3 h chaque semaine
TD
1,5h chaque semaine
dont le but est
Donner les bases nécessaires de la thermodynamique classique.
Consulter les
Références bibliographiques
contenu du
Cours
comprend
6 Chapitres (45 heures).
Se compose de
9 HRS
I Généralités sur la thermodynamique
Propriétés fondamentales des fonctions d'état.
Définitions des systèmes thermodynamiques et le milieu extérieur.
Description d'un système thermodynamique.
Evolution et états d'équilibre thermodynamique d'un système.
Transferts possibles entre le système et le milieu extérieur.
Transformations de l'état d'un système.
Rappels des lois des gaz parfaits.
9 HRS
II Le 1er principe de la thermodynamique
Le travail, la chaleur, L'énergie interne, Notion de conservation de l'énergie.
Le 1er principe de la thermodynamique
9 HRS
III Applications du premier principe de la thermodynamique à la thermochimie
Chaleurs de réaction, l'état standard, l'enthalpie standard de formation et de dissociation.
L'enthalpie de changement d'état et de la réaction chimique. Loi de Hess, loi de Kirchoff.
9 HRS
IV Le 2ème principe de la thermodynamique
Le 2ème principe pour un système fermé.
Enoncé, du 2ème principe.
3 HRS
V Le 3ème Principe et entropie absolue
6 HRS
VI Energie et enthalpie libres Critères d'évolution d'un système
Introduction.
Energie et enthalpie libre.
Les équilibres chimiques.



Pour aborder la thermodynamique classique, il est recommandé d'avoir les connaissances préalables suivantes:
1 BASES EN PHYSIQUE
Une compréhension solide des concepts fondamentaux de la physique est essentielle.
Cela inclut les notions d'énergie, de travail, de chaleur, de forces, etc.
2 BASES EN CHIMIE
La thermodynamique est étroitement liée à la chimie.
Avoir des connaissances en chimie permet de comprendre les processus thermodynamiques dans les réactions chimiques.
3 MATHEMATIQUES
Des compétences en mathématiques sont nécessaires pour résoudre les équations thermodynamiques.
La maîtrise du calcul différentiel et intégral est importante.
4 NOTIONS DE SYSTEMES ET D'ÉQUILIBRE
Savoir identifier les variables d'état (pression, température, volume, etc.).
Comprendre ce qu'est un système (ouvert, fermé, isolé) et les notions d'équilibre thermodynamique.
5 NOTIONS DE TRAVAIL ET DE CHALEUR
Avoir des notions de travail mécanique et de transfert de chaleur (conduction, convection, rayonnement).
Comprendre comment ces échanges d'énergie affectent les systèmes.



les objectifs de l'enseignement dans le domaine de la thermodynamique classique sont les suivants
D
1 DONNER LES BASES NÉCESSAIRES
L'objectif est de fournir aux étudiants les connaissances fondamentales en thermodynamique classique.
Cela inclut la compréhension des concepts de chaleur, d'énergie, d'entropie et de travail.
A
2 APPLICATIONS À LA COMBUSTION ET AUX MACHINES THERMIQUES
Les étudiants doivent être capables d'appliquer ces concepts à des domaines spécifiques tels que la combustion (par exemple, dans les moteurs à combustion interne) et les machines thermiques (comme les turbines à vapeur).
H
3 HOMOGÉNÉISER LES CONNAISSANCES DES ÉTUDIANTS
L'enseignement vise à égaliser le niveau de compréhension des étudiants.
Tous les apprenants devraient avoir une base solide en thermodynamique.
C
4 COMPÉTENCES À APPRÉHENDER
Acquisition d'une base scientifique.
Les étudiants doivent maîtriser les principes fondamentaux de la thermodynamique classique
Application à des systèmes variés.
Ils doivent être capables d'appliquer ces principes à différents systèmes, qu'il s'agisse de machines, de processus industriels ou de phénomènes naturels
Énoncé, explication et compréhension des principes fondamentaux.
Les compétences comprennent la capacité à formuler, expliquer et comprendre les lois et les concepts de la thermodynamique

Disclaimer

The material presented in this document is not original work; it is a compiled summary and selection of concepts, figures, and explanations from well-established textbooks and academic sources in the field of thermodynamics. It is intended solely for educational and personal study purposes.

Every effort has been made to ensure accuracy and proper attribution. The sources used are acknowledged and listed in the references section. This compilation does not claim ownership or authorship of the underlying content, and all rights belong to the respective authors and publishers.

This document is designed to support learning and should not be used as a substitute for consulting the original textbooks. For educational use only — not for commercial distribution.

Foreword

This course handout on Thermodynamics has been thoughtfully designed for first-year undergraduate students in the Sciences and Technologies ST program. It serves as a concise, structured, and student-friendly guide to introduce you to one of the most fundamental and far-reaching branches of physical science-thermodynamics.

At the heart of this handout are the Three Laws of Thermodynamics, which form the conceptual backbone of energy transformations in nature.

The First Law introduces the principle of conservation of energy, emphasizing that energy can be transferred or converted from one form to another—but never created nor destroyed. This law enables us to analyze heat, work, and internal energy in physical and chemical systems.

The Second Law brings in the concept of entropy, guiding us to understand why certain processes occur spontaneously while others do not. It reveals the inherent directionality of natural processes and introduces key ideas such as irreversibility and efficiency-concepts that are vital in fields ranging from chemistry to engineering.

The Third Law completes the theoretical framework by defining the behavior of systems at the lowest possible temperatures. It states that the entropy of a perfect crystalline substance approaches zero as the temperature approaches absolute zero, providing a crucial reference point for thermodynamic calculations.

Building upon these foundational laws, this handout also focuses on enthalpy of reactions-a practical and widely used concept in chemistry and engineering. You will learn how to calculate and interpret enthalpy changes in chemical reactions, distinguish between exothermic and endothermic processes, and apply Hess's Law to determine reaction heats indirectly.

Throughout this handout, clarity, relevance, and accessibility are prioritized. Key definitions, illustrative examples, and guided explanations are included to support your learning. Diagrams and step-by-step reasoning are used to demystify abstract ideas and connect theory to observable phenomena.

As a 1^{st} year ST student, you are beginning a journey that will equip you with the tools to analyze, innovate, and solve complex scientific and technological challenges. A solid grasp of thermodynamics is not only essential for future courses in physics, chemistry, and engineering but also empowers you to think critically about energy use, sustainability, and the natural world.

We encourage you to use this handout actively-read it alongside lectures, refer to it when solving problems, and return to it as your understanding deepens. Thermodynamics may challenge your intuition at times, but with persistence, it will reward you with a powerful way of seeing how the universe operates.

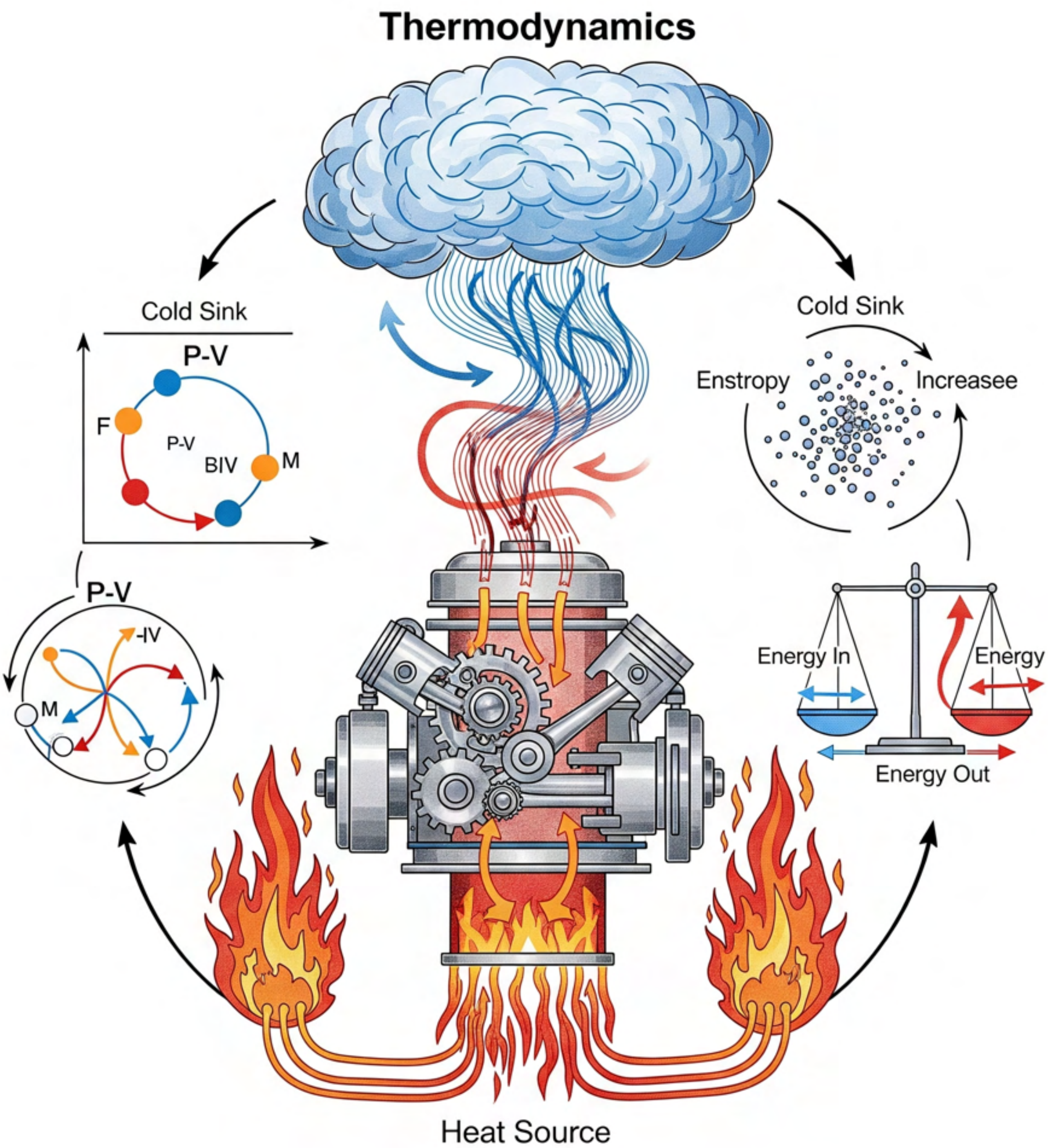
Welcome to the study of energy, change, and order. May this handout be a helpful companion on your academic journey.

Dr. ABDI Mohamed
Tissemsilt University – Ahmed Ben Yahia El-Wancharissi
Faculty of Sciences and Technologies
Department of Sciences and Technologies
abdi@univ-tissemsilt.dz
Academic Year 2025–2026

CONTENTS

FIRST CHAPTER

GENERALITIES ON THERMODYNAMICS



Handout Structure

This course handout has introduced the basic principles of energetic study of physical and chemical systems in six progressive and complementary chapters of thermodynamics. The chapters each have added a vital aspect to the complete knowledge of the laws of thermodynamics and their application.

First chapter, dedicates to the Generalities on Thermodynamics, provides the key concepts, which are thermodynamic systems and their states, states functions, transformations, exchanges of energy between a system and its surroundings. These concepts are the basis of the field.

Second chapter is the development of the First Law of Thermodynamics which states the conservation of energy and connects exchange of heat and work with the changes in internal energy. Extended to ideal gases and elementary transformations, this law formed the foundation of the computation of the balance of energy.

Third chapter extends the use of the first law to thermochemistry, and introduced the concept of reaction enthalpy, standard enthalpy, Hesss Law and Kirchoffs Law, thereby giving the methods by which the energetics of chemical reactions can be studied.

Fourth chapter presents the Second Law of Thermodynamics which was founded on the principle of entropy, the quantity by which the irreversibility of natural processes is measured and the natural direction of system evolution is determined. This law made it possible to identify the conditions of spontaneity and equilibrium criteria of isolated systems.

Five Chapter give the Third Law of Thermodynamics which provides a reference point of absolute entropy and the absolute entropy concept. It not only gave an idea of the behavior of systems at low temperatures, but also allowed to calculate absolute values of entropy, necessary to calculate thermodynamic quantities accurately.

Sixth chapter brings in the thermodynamic potentials including Gibbs free energy that would be used as convenient measures to assess spontaneity and equilibrium at constant temperature and pressure. These functions relate enthalpy, entropy, and free energy, and play a key role in the study of chemical equilibrium.

This systematic sequence of chapters enables the student to gain a complete and integrated view of classical thermodynamics, both in the simple concepts and in the sophisticated analysis of the instruments:

- Determine thermodynamic system energy balances;
- Study conditions of spontaneity and equilibrium;
- Know the relations of energy, entropy and temperature;
- Use thermodynamics on actual physical and chemical processes.

The course gives a good groundwork in the further examination of the applied fields of mixture thermodynamics, thermodynamic cycles, chemical kinetics, and energy and industrial processes. Uniting the notions of energy and transformation, thermodynamics has become an inseparable science to comprehend and master natural and artificial phenomenon.

Generalities on Thermodynamics

I

Thermodynamics is a subdivision of physics that examines the transformation of energy and matter that occurs between a system and the surrounding and the changes in the state of the system. The purpose of this first chapter is to present the fundamentals needed to be familiar with the concepts of thermodynamics and to find the ground work needed to analyze phenomena that have to do with energy.

We are going to start by presenting the functions of the state and their essence. These quantities (internal energy, enthalpy, entropy, temperature, pressure, volume etc.) characterize the state of a system without regard to the path used to reach the state. We are going to draw a line between extensive and intensive properties which are essential to a complete description of a thermodynamic state.

Next we will define what is a thermodynamic system and its surroundings. This difference is needed to create energy and mass balances. Depending on the type of the potential exchanges the systems are either isolated (no exchange), closed (exchange of energy only), or open (exchange of both energy and matter). The type of interactions between the system and the environment depends on the nature of the boundary which can be either adiabatic, diathermal, movable, or fixed.

The description of a thermodynamic system in terms of state variables, composition, and structure (homogeneous or heterogeneous systems) will be also provided in the chapter. This definition will result in the concept of thermodynamic equilibrium that can be described as some state where the macroscopic properties do not change with time.

Then we will examine how a system changes over time, and the different equilibrium points it can undergo. There will be the difference between reversible processes (theoretical, gradual, and controlled), and irreversible processes (real, spontaneous, and with dissipation of energy). These are some of the crucial concepts used in interpreting the nature and direction of thermodynamic transformations.

The potential interactions of the system and the environment will be considered in particular. Two primary energy transfer processes will be examined, heat transfer due to temperature differences and work, which is due to mechanical or other interactions. Mass transfer will also be taken into consideration in case of open systems. Combined with these exchanges, they constitute the first law of thermodynamics.

We will then consider the different changes in the state of a system, that is, changes in the state variables of the system subject to certain restrictions: isothermal (fixed temperature), isobaric (fixed pressure), isochoric (fixed volume), and adiabatic (no heat exchange). The ideas of operation (external action) and process (internal response of the system) will be also contrasted.

Lastly, the chapter ends with a summary of the basic laws of ideal gases, which depend on pressure, volume and temperature based on the equation $PV = nRT$. These perfect relationships also offer very powerful tools in the modeling of the behavior of gases in a wide range of practical applications.

At the conclusion of this chapter, the student must be able to define a thermodynamic system, define its interactions with the environment, comprehend the terms state and process, and can apply the laws of an ideal gas to simple cases.

What is thermodynamics?

The term Thermodynamics finds its origin in the Greek words therme (heat) and dynamis (force). It is both a branch of physics and of engineering. Scientists basically study thermodynamics to know the physical and chemical properties of a fixed amount of matter at rest through the application of its principles in interrelating various physical properties. Engineers, conversely, observe systems in terms of their interactions with the surrounding environment and often go beyond thermodynamic analyses restricted to closed systems to include open systems in which matter moves in and out [1].

The thermodynamics gained the status of an independent science during the early years of the 19th century, through studying basically those machines working by virtue of heat, especially steam engines recently invented. Thermodynamics was formed to give the fundamental principles of heat as input and useful work output as understood by motion (thermo-dynamics in Greek: heat-powered motion). From this point of practical application came two most famous principles of science that are known as the first and second laws of thermodynamics. In simple terms, these laws provide the foundation of the entire classical thermodynamics, and yet they bear very far-reaching implications [2] [3].

In the simplest description, thermodynamics is a tool that consists of a set of fundamental scientific laws to aid the engineer. Not all engineers necessarily engage in detailed thermodynamic calculations in their daily life, but many do regularly specify systems for design or analysis based on thermodynamic principles. Some will only occasionally apply thermodynamics; others will practically never work directly with these principles, but their work is probably underpinned by various thermodynamic concepts in a less obvious way. A good grasp of the fundamentals of thermodynamics will have to be possessed by all engineers. But before the principles themselves can be entered into, it is first necessary to clarify the elementary concepts on which the subject is based [4].

I.1 Fundamental Properties of State Functions

Thermodynamic properties can be classified as intensive or extensive. Intensive properties-representative examples being temperature, pressure, and density-do not depend on how much matter exists within the system. Extensive properties-doing the work of the total mass, volume, and momentum of a system-do scale according to size. One may adjudicate between the two types by splitting the system into half: the intensive property remains the same for each half while the extensive property scales down by half Figure I.1.

Historically speaking, extensive properties are customarily denoted using upper case alphabets (except for mass, m) while intensive properties use lower case alphabets (pressure P and temperature T are exceptions). When an extensive property is divided by mass it becomes the corresponding specific property, such as specific volume $(v = V/m)$ or specific total energy $(e = E/m)$ [5] [6] [7] [8].

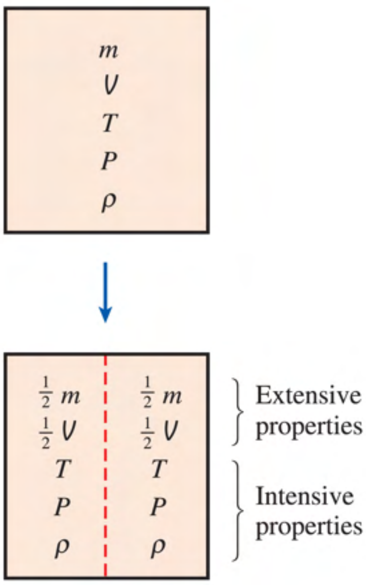


Figure I.1: Criterion to differentiate intensive and extensive properties [7].

I.2 Thermodynamic System and Surrounding

In thermodynamics, it is always one of the most important steps of any engineering analysis to clearly and specifically define what one is analyzing. In the same way that, in classical mechanics, engineers and physicists start with the (not always realistic) assumption of isolating a free body and determining all external forces on it before using the second law of motion to predict its behavior, a similar methodological stance is taken in thermodynamics. In this case, the study object is known as a thermodynamic system [2].

This system also needs to be clearly defined; the system should have its limits outlined and its nature outlined whether open or closed and whether isolated or open. After creating a proper system definition, the second thing to do is to define all the modes of interaction that the system has with its environment or with other systems. These interactions can be exchange of heat, work or mass across the system boundary. It is only once this prudent characterization has been made that appropriate laws and principles of thermodynamics, e.g., conservation of energy (the First Law) or the directionality of natural processes (the Second Law) can be used correctly to model, analyze, or predict the behavior of the system.

I.3 Description of the Thermodynamic System

A system, within the context of thermodynamics, is that amount of matter or volume of space that is being studied. This is a thermodynamic system and should be closely defined by an actual or fictive boundary [5]. The system is surrounded by this boundary—in this case, depicted by a dashed line—as can be seen in Figure I.2. The system contains anything within the boundary and anything below or above the boundary is the surroundings [4].

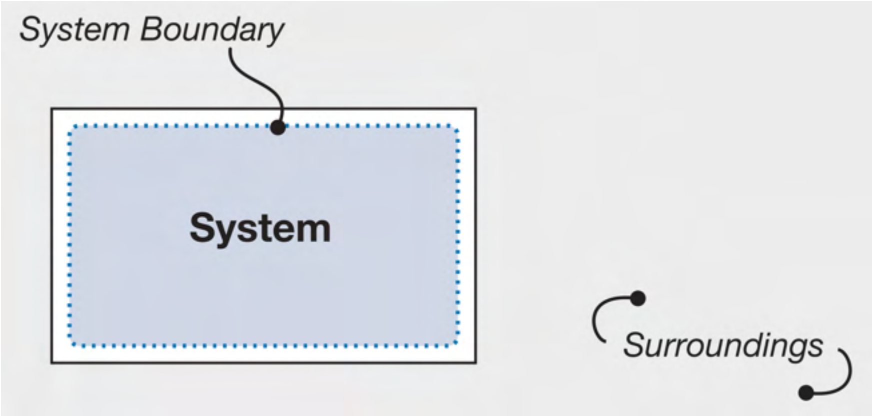


Figure I.2: Example of a thermodynamic system, the system boundary (represented by a dashed line), and the surroundings [4].

All matter outside the system of defined thermodynamics is referred to as surroundings. The system and the surroundings are divided by a boundary that can be real or fictive, fixed or movable. All the interactions between the system and surroundings, including mass or energy exchange, occur through this boundary and play a crucial part of the study of thermodynamics of engineering [2]. Together, the system and its surroundings constitute the universe [5].

$$\textbf{Universe} = \textbf{System} + \textbf{Surroundings}$$

A system is sometimes even termed a control system. The control boundary separates the system from its surroundings and is itself briefly designated by the control boundary. The system's volume that is enclosed by the system boundary is briefly termed the control volume. The control space is the space within the system boundary [5].

I.4 Evolution and Thermodynamic Equilibrium

Thermal equilibrium is reached when heat transfer is absent within a system or among systems, and this occurs when the temperatures will be the same—i.e., temperature differences that cause heat flow will be absent. Thermal equilibrium between two interacting systems will be reached when the two systems have equal temperatures Figure I.3 [5].

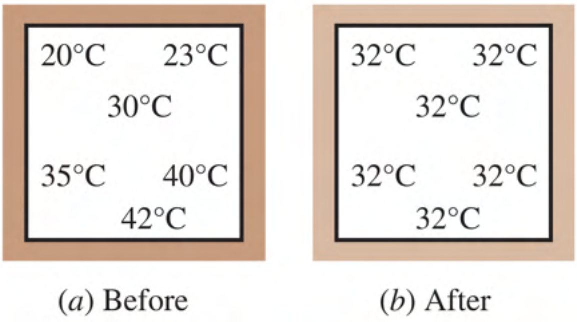


Figure I.3: A closed system reaching thermal equilibrium [7].

I.5 Possible Transfers

A thermodynamic system can be broken down into smaller sections known as subsystems, each of which can itself be regarded as a separate thermodynamic system.

The system can be considered to open, closed, and isolated thermodynamic systems are distinguished by the ability of mass and/or energy to flow past their boundaries and influence their environment. Characteristics of such exchanges across the system border are the sole basis for categorization [4] [5].

The way a system interacts with its surroundings depends on the nature of its boundary. Thermodynamic systems are commonly classified based on what can cross this boundary [9]:

- **Open systems** permit the transfer of matter (via convection) and energy with the environment.
- **Closed systems** do not allow matter to enter or leave, though energy exchange is still possible.

- **Diathermal systems** have boundaries that allow heat to flow through via conduction.
- **Adiabatic systems** are enclosed by boundaries that prevent any conductive heat transfer.
- **Isolated systems** have no interaction whatsoever with their surroundings—neither mass nor energy can be exchanged.

  These classifications help define how a system behaves and responds to its environment in thermodynamic analysis.

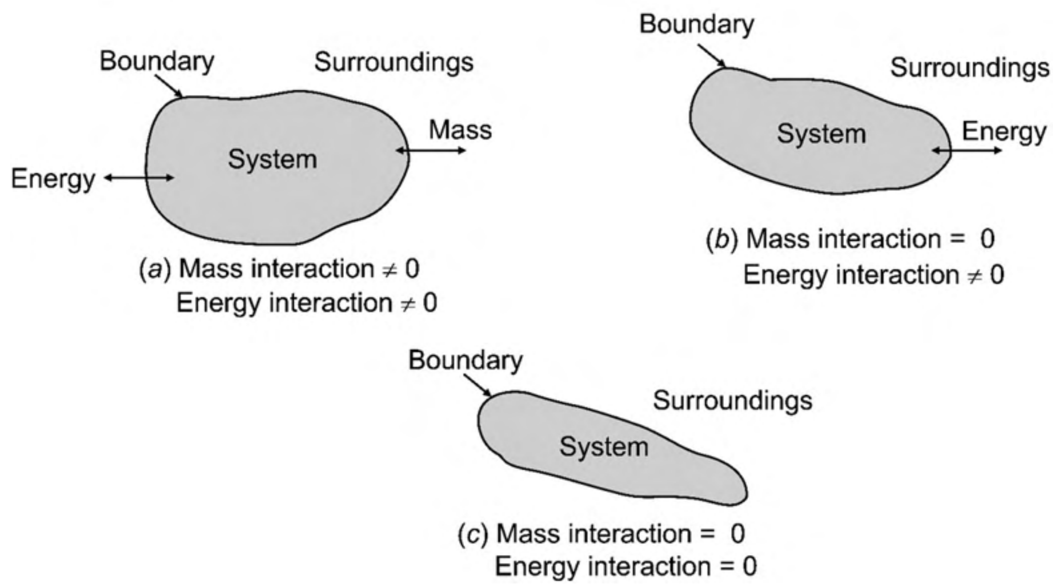


Figure I.4: (a) Open system, (b) Closed system, and (c) Isolated system [5].

On the other hand , boundary thermodynamic systems are often categorized as :

- **Fixed**, if it cannot move
- **Movable**, if it can move
- **Fermeable**, if it allows convective matter exchange with the environment.
- **Impermeable**, if it does not allow convective matter exchange with the environment.

- **Diathermal**, if it allows conductive heat exchange with the environment
- **Adiabatic**, if it does not allow conductive heat exchange with the environment.

I.5.1 Closed Systems

A closed system—in this case, referred to as a control mass or a system, with the understanding being that the context is appropriate—an amount of matter that is fixed will not have mass exit or enter (as depicted in Figure I.5). A closed system can, however, have energy, such as by way of work or heat, pass through its boundary, and its volume will not necessarily be fixed. The special case that will not see mass or energy pass through the boundary will be regarded as having an isolated system [7].

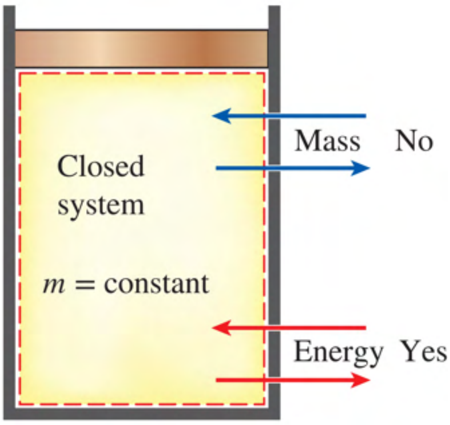


Figure I.5: Mass cannot cross the boundaries of a closed system, but energy can [7].

Figure I.6 depicts a simple illustration of a gas in a piston–cylinder device. Picture a cylinder with a piston that moves up and down on top and valves placed in such a way that you can open or close them [2].

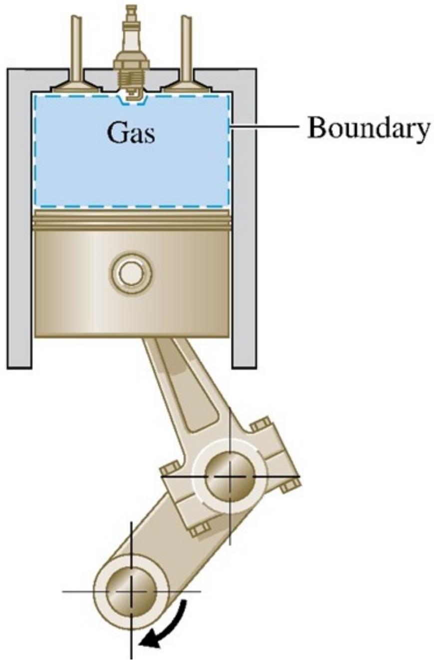


Figure I.6: Closed system: A gas in a piston–cylinder assembly [2].

I.5.2 Control Volumes

Most of the engineering problems—like the cases of the water heater, car radiator, turbines, and compressors—furnish mass coming into and out of the device and therefore best lend themselves to analysis using control volumes (i.e., open systems) instead of closed systems (control masses). A control volume is any portion of space we select (illustrated by Figure I.7), and here we can make very little choice. However, with a good choice of boundary, the problem can then be very substantially simplified [7].

I.6 Transformations of the State of a System

A process takes place when any or several of a system's qualities alter, and thus the system moves through one to another condition. If the qualities of a system are the same twice, that is, at two times, then the system is said to be in the same condition. A system is said to be at steady state if none of its qualities depend on time. To determine a process completely, we need to

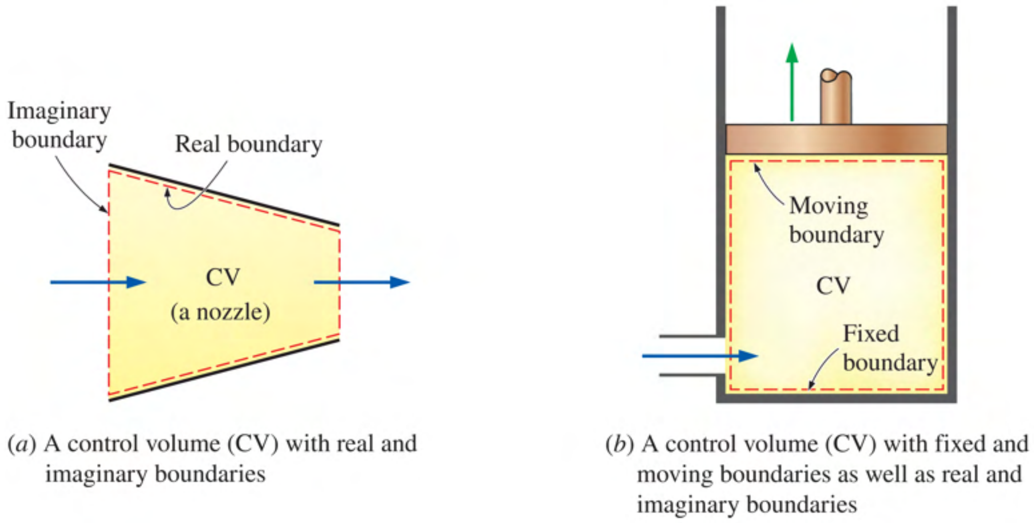


Figure I.7: A control volume can involve fixed, moving, real, and imaginary boundaries [7].

specify its initial and final conditions, together with the way through which the conditions intercede, and any system-surroundings interactions—as depicted below in Figure I.8 [7].

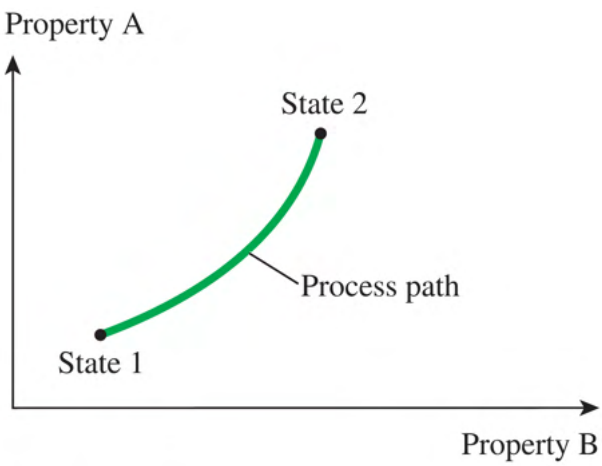


Figure I.8: A process between states 1 and 2 and the process path [7].

Figure I.9 illustrates the comparison between quasi-equilibrium and non-quasi-equilibrium processes of a gas compression process using a cylinder–piston setup [7].

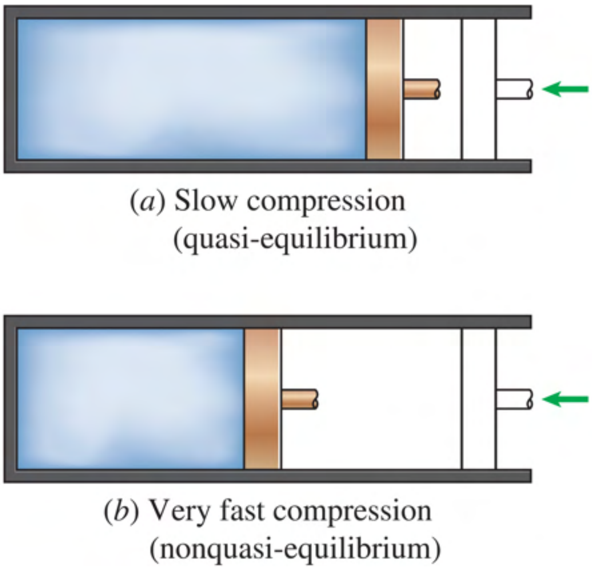


Figure I.9: Quasi-equilibrium and nonquasi-equilibrium compression processes [7].

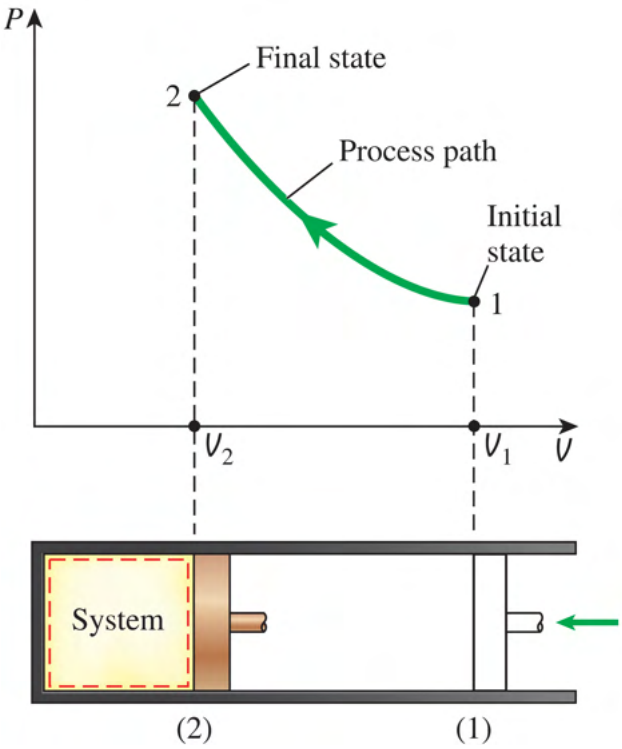


Figure I.10: The $P - V$ diagram of a compression process [7].

Depending on the constraint, it is common to consider and perform the following types of processes:

- **Isothermal**: the temperature of the system is constant (e.g. by placing it in thermal contact with a heat bath).

- **Isochoric** : the volume of the system is constant (e.g. by placing the system inside a closed rigid container).
- **Isobaric** : the pressure of the system is constant (e.g. by placing it in contact with a volume bath).
- **Adiabatic**: there is no transfer of thermal energy between system and surroundings.

I.7 Reminders of the Ideal Gas Laws

During the 19th century, scientists set up an experimental knowledge of the behavior of gases under conditions of moderate temperature and pressure and derived the ideal gas equation $PV = RT$, with the molar volume V and the universal gas constant R. The equation is applicable to many of the useful everyday applications close to ambient conditions [3].

An ideal gas is a theoretical ideal that assumed molecules or atoms of a gas have no intermolecular forces and experience no collisions other than perfectly elastic collisions (as depicted below in Figure I.11) [4].

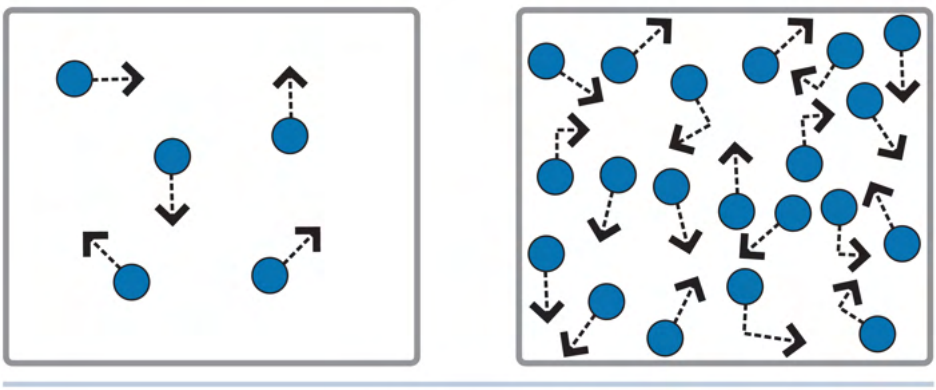


Figure I.11: On the left, a gas at low molecular density will behave like an ideal gas, with no interactions between molecules. On the right, a gas with a high density will have many interactions between molecules, resulting in nonideal gas behaviour [4].

The ideal gas law gives the connection between pressure, volume, and temperature of an ideal gas. It can be given in various forms, depending on whether the mass or molar amounts of analysis hold and whether specific (with respect to mass or mole) or total volume is involved. That way, the equation can be specialized to various contexts of engineering and science [4]:

$$PV = mRT \tag{I.1}$$

$$Pv = RT \tag{I.2}$$

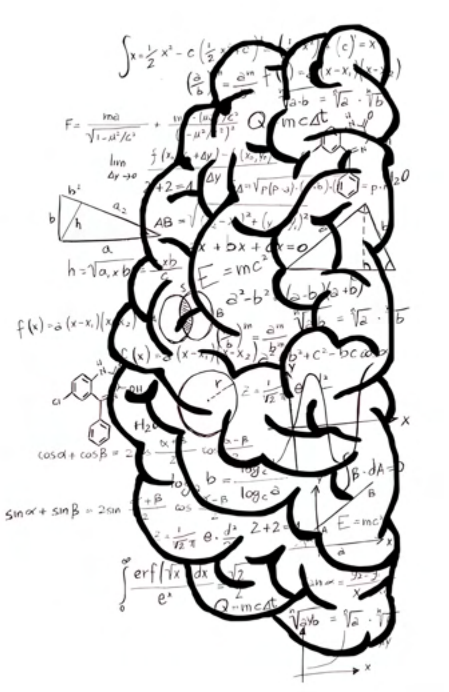
$$PV = n\bar{R}T \tag{I.3}$$

$$P\bar{v} = \bar{R}T \tag{I.4}$$

where $\bar{R}$ is the universal ideal gas constant $\left(\bar{R} = 8.314\,KJ/Kmol.K\right)$, R is the gas-specific ideal gas constant ($R = \bar{R}/M$, where M is the molecular mass of the gas), and $\bar{v}$ is the molar specific volume $(\bar{v} = V/n)$ [4].

PRACTICE

EXERCISES AND SOLUTIONS



I.8 Problem Solving

Problem 1 SKILLS PROBLEM-SOLVING

The temperature of a body is $50°F$. Find its temperature in $°C$, K, and $°R$ [10][11][12].

Solution 1

The relations between absolute and relative temperatures are:

$$T\,(°R) = T\,(°F) + \ 459.67T$$

$$T\,(K) \ \ = T\,(°C) + 273.15$$

$$T(C°) = \frac{5}{9}\,(50 - 32) = 10$$

$$T\,(K) = 10 + 273 = 283\ K$$

$$T(°R) = \ 50 + 460 = \ 510°R$$

Problem 2 SKILLS PROBLEM-SOLVING

Identify which of the following are extensive properties and which are intensive properties: (a) $10m^3$ volume, (b) $30J$ of kinetic energy, (c) a pressure of $90KPa$, (d) a stress of $1000KPa$, (e) a mass of $75Kg$, and (f) a velocity of $60m/s$. (g) Convert all extensive properties to intensive properties assuming $m = 75Kg$ [10].

Solution 2

(a) Extensive. If the mass is doubled, the volume doubles

(b) Extensive. If the mass doubles, the kinetic energy doubles.

(c) Intensive. Pressure is independent of mass.

(d) Intensive. Stress is independent of mass.

(e) Extensive. If the mass doubles, the mass doubles.

(f) Intensive. Velocity is independent of mass.

(g) $\frac{V}{m} = \frac{10}{75} = 0.1333\, m^3/Kg$ $\frac{E}{m} = \frac{30}{75} = 0.40\, J/Kg$ $\frac{m}{m} = \frac{75}{75} = 1.0\, Kg/Kg$

Problem 3 SKILLS PROBLEM-SOLVING

Convert the following readings of pressure to KPa assuming that barometer reads $760mm$ of Hg? (i) $80cm$ of Hg (ii) $30cm$ Hg vacuum (iii) $1.35m$ H_2O gauge (iv) $4.2bar$ [13][14] .

Solution 3

Assuming density of Hg, $\rho_{Hg} = 13.596 \times 1000 Kg/m^3$

Pressure of $760mm$ of Hg will be

$= \rho \times g \times h = 13.596 \times 1000 \times 9.806 \times (760/1000)$

$= 101325Pa = 101.325KPa.$

(i) Pressure of $80cm$ of Hg

$= (800/760) \times 101.325 = 106.65KPa$.

(ii) $30cm$ Hg vacuum $= 76 - 30 = 46cm$ of Hg absolute.

Pressure due to $46cm$ of Hg

$= (460/760) \times 101.325$

$= 61.328KPa$.

(iii) Pressure due to $1.35m$ H_2O gauge

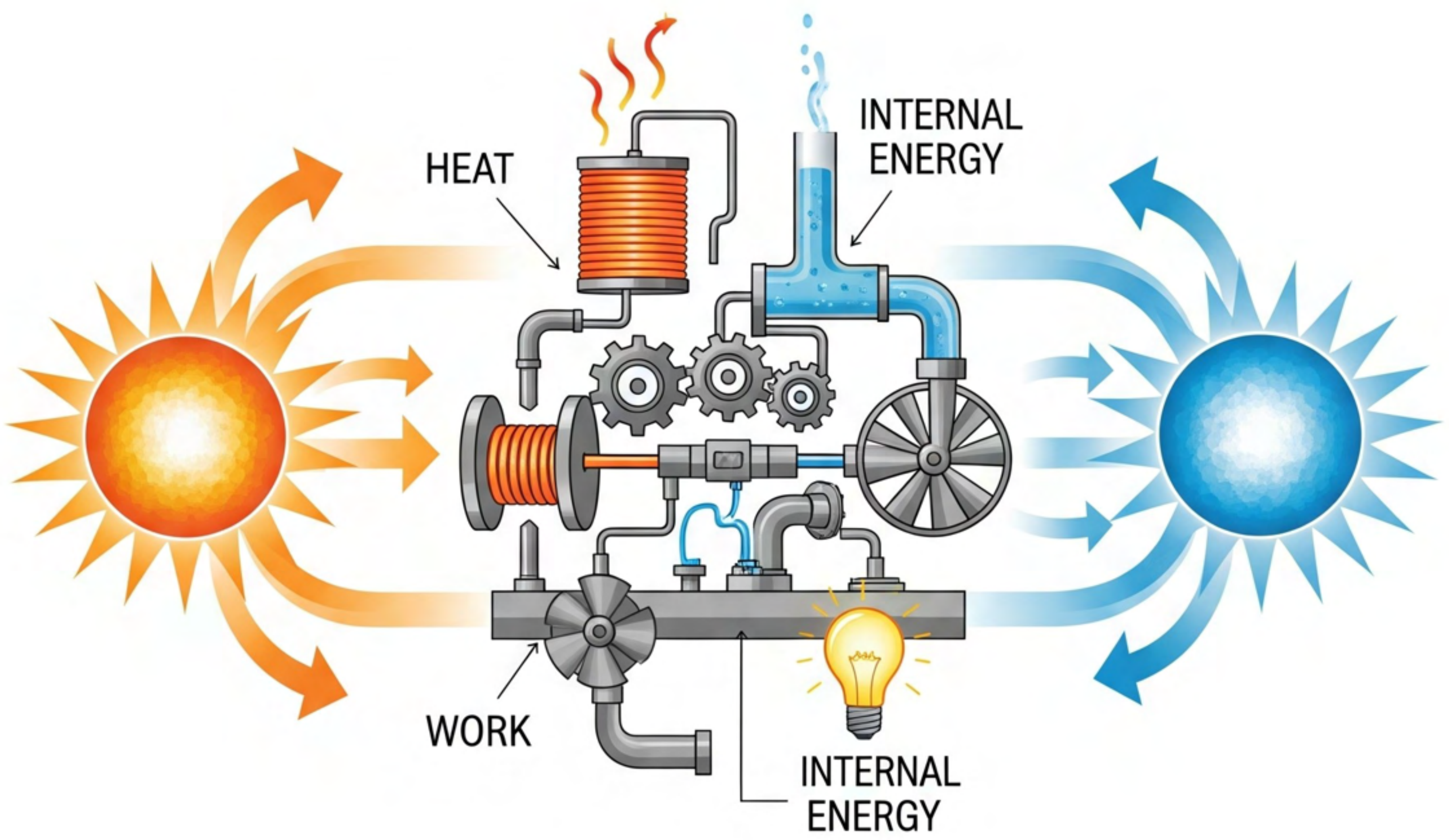
$= 1000 \times 9.806 \times 1.35 = 13238Pa$

$= 13.238KPa$.

(iv) 4.2 bar $= 4.2 \times 102$ $KPa = 420KPa$.

SECOND CHAPTER

FIRST LAW OF THERMODYNAMIC



First Law of Thermodynamic

II

The first law of thermodynamics is the principle of energy conservation that is applied to thermodynamic systems. According to it, the total energy of an isolated system is constant, but may transform between forms, for example heat or work. The chapter attempts to introduce the physical principles of this law, its mathematical expression, and its use in simple systems, especially ideal gases.

We start with the various types of exchanges of energy between a system and the world:

- Work (W): energy of a mechanical nature (compression, expansion, displacement);
- Heat (Q): the amount of energy exchanged by a temperature difference;
- Internal energy (U): a state function which is the amount of microscopic energy stored in the system (kinetic energy of the particles and potential energy of the particles).

The connecting equation between these quantities is the energy balance equation: $\Delta U = Q + W$. That any fluctuation of internal energy is the sum of the heat and of the work received and given out to the surroundings.

The second section of the chapter is devoted to the declaration of the first law of thermodynamics, its physical explanation and the use of internal energy as the state function. We shall differentiate between state quantities (such as U) and that which depends on paths (as in Q and W). A use of the first law to ideal gases will enable us to determine the connections between the changes in internal energy, temperature and the various forms of energy transfer in any given transformation.

We then discuss the notion of enthalpy H, which is defined as. $H = U + V$, which is especially convenient in processes that take place at constant pressure. We shall define and understand the heat capacities under constant volume C_V and constant pressure C_P, with the focus on their relations to the variations in inner energy and enthalpy.

The last section of the chapter is devoted to study of reversible thermodynamic transformations in an ideal gas:

- Isochoric process (V=constant): the transfer of heat only changes the internal energy;
- Isobaric process (P=constant): the amount of heat and the amount of work contribute to change in energy;
- Isothermal process (T=constant): then internal energy remains constant, and the entire exchange is in the nature of work;
- Adiabatic process ($Q = 0$): the change in the internal energy is completely transferred into mechanical work.

At the conclusion of this chapter, the student will have a good knowledge on the thermodynamic systems on energy conservation. They can study energy balances and differentiate between various types of energy exchange and use the first law of thermodynamics to apply to other processes, especially the one that involves ideal gases.

Definition

The First Law of Thermodynamics holds that energy is conserved—it cannot be made or destroyed. Although it's not offering a single accurate universal definition of energy, through its measurable forms, each of which is defined mathematically, in practice, among scientists and engineers, energy is comprehended: that is, kinetic energy, for instance, depends on velocity, and gravitational potential energy on height [3].

Net Energy Transfer In (or out) of a System Energy Change in the System

Notably, the First Law occurs within the combined system and surroundings, not solely within the system. For any process, this law sets down a basic requirement: the combined system plus its surroundings will always have to have its total energy remain unaffected [3]:

$$\Delta \text{ (Energy of the system)} + \Delta \text{ (Energy of surroundings)} = 0 \qquad \text{(II.1)}$$

where the difference operator Δ signifies finite changes in the quantities enclosed in pare theses. The system may change in its internal energy, in its potential or kinetic energy, and in the potential or kinetic energy of its finite parts (Figure II.1) [3].

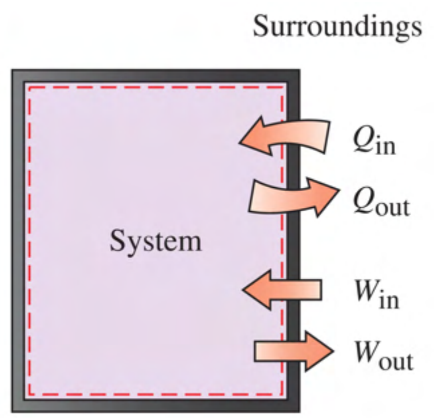


Figure II.1: Specifying the directions of heat and work.

II.1 Work, Heat, Internal Energy, and Conservation of Energy

II.1.1 Work

Work in thermodynamics refers to energy in transition that doesn't depend on a difference in temperature—whereas that aspect doesn't apply to heat transfer. Coversion instead happens by virtue of some macroscopically measurable change such as a change in the volume of a fluid and always constitutes bulk motion in the system boundary. At a microscopic scale, this bulk motion translates into a nett motion of molecules [9].

There are several methods to work on a system or by it. Boundary work, or the work created when a gas or liquid is compressed or expanded, is among the most significant. For example, a closed system like the gas inside a piston–cylinder setup (Figure II.2). As the gas expands, it applies pressure P to the piston, generating a force equal to $P \times A$ (with A being the piston's cross-sectional area). If the piston shifts by a small distance dx, the work done by the system is this force multiplied by the displacement. This relationship forms the basis for calculating work in thermodynamic processes that involve volume change.

$$\partial W = pAdx \tag{II.2}$$

The product Adx in Equation II.2 equals the change in volume of the system, dV. Thus, the work expression can be written as

$$\partial W = pdV \tag{II.3}$$

Since dV is positive when volume increases, the work at the moving boundary is positive when the gas expands. For a compression, dV is negative, and so is work found from Equation II.3. These signs are in agreement with the previously stated sign convention for work. For a change in volume from V_1

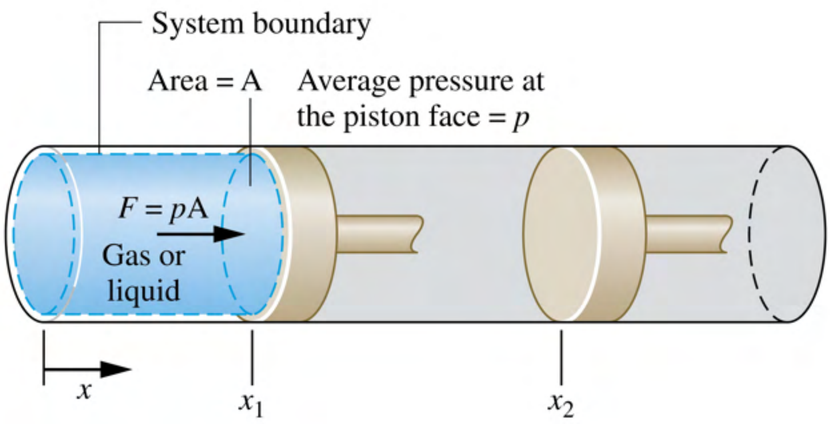


Figure II.2: Expansion or compression of a gas or liquid [2].

to V_2, the work is obtained by integrating Equation II.3:

$$W = \int_{V_1}^{V_2} PdV \tag{II.4}$$

Although Equation II.4 is derived for the case of a gas (or liquid) in a piston–cylinder assembly, it is applicable to systems of any shape provided the pressure is uniform with position over the moving boundary.

II.1.2 Heat

Heat is defined as energy transferred across a system's boundary purely because of a temperature difference [9]. It always flows naturally from a higher-temperature region to a lower-temperature one.

When heat is supplied to a system, its temperature increases; when heat is removed, the temperature decreases. This relationship is described by the heat capacity C, which measures how much heat energy dQ is needed to raise the system's temperature by a small increment dT [9], Mathematically,

$$dQ \equiv CdT \tag{II.5}$$

The amount of energy transferred as heat to a thermodynamic system that changes from an initial state i whose temperature is T_i, to a final state f, whose temperature is T_f, is [9]:

$$Q_{i \to f} = \int_{T_i}^{T_f} C(T)dT \tag{II.6}$$

When C is independent of temperature the equation above can be written as:

$$Q_{i \to f} = C\Delta T \tag{II.7}$$

With $\Delta T = T_f - T_i$

The value of a heat transfer depends on the details of a process and not just the end states. Thus, like work, heat is not a property, and its differential is written as δQ. The amount of energy transfer by heat for a process is given by the integral [2]:

$$Q = \int_{1}^{2} \delta Q \tag{II.8}$$

where the limits mean "from state 1 to state 2" and do not refer to the values of heat at those states. As for work, the notion of "heat" at a state has no meaning, and the integral should never be evaluated as $Q_2 - Q_1$ [2].

II.1.3 Internal Energy

Internal energy, kinetic energy, and potential energy are the three main components that make up a substance's total energy. All of them are important in different situations, but practically speaking, their contributions are not always equal. (Figure II.3) demonstrates unequivocally that in some situations, some energy sources could be insignificant. This allows the scientists and engineers to simplify the thermodynamic analysis while maintaining the necessary level of accuracy [4].

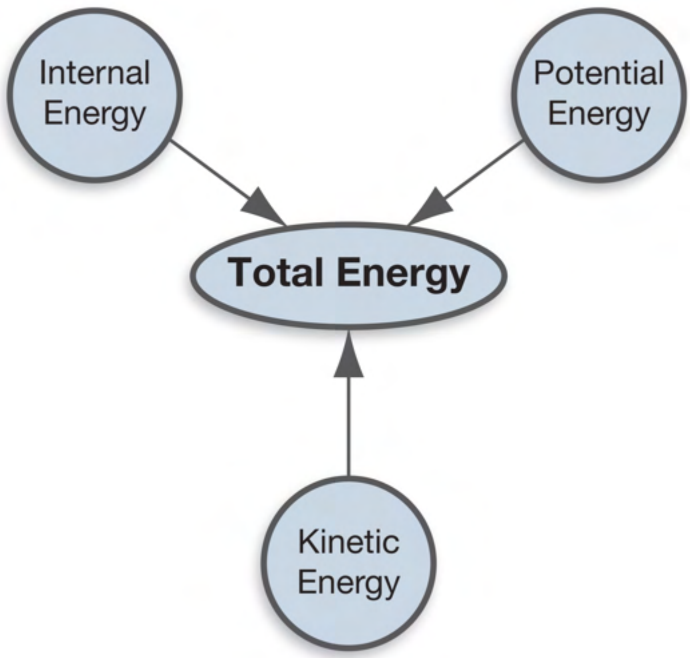


Figure II.3: The total energy of a system is the combination of the system's internal energy, kinetic energy, and potential energy [4].

II.1.4 Concept of conservation of energy

The total energy entering a system less the total energy exiting it is the net change in the system's total energy throughout a process [7]. That's

$$\begin{bmatrix}\text{Total energy entering}\\ \text{the system}\end{bmatrix} = \begin{bmatrix}\text{Total energy leaving}\\ \text{the system}\end{bmatrix} - \begin{bmatrix}\text{Change in the total energy}\\ \text{of the system}\end{bmatrix} \tag{II.9}$$

$$E_{in} - E_{out} = \Delta E_{system} \tag{II.10}$$

$$E_{in} - E_{out} = (Q_{in} - Q_{out}) + (W_{in} - W_{out}) + (E_{mass,in} - E_{mass,out}) = \Delta E_{system} \tag{II.11}$$

These net amounts are the result of both the process's work exchanges and total heat [2]. Symbols for the energy balance are as follows:

$$E_2 - E_1 = Q - W \tag{II.12}$$

For a closed system undergoing a cycle, the initial and final states are identical, and thus $\Delta E_{system} = E_2 - E_1 = 0$. Then the energy balance for a cycle simplifies to $E_{in} - E_{out} = 0$ or $E_{in} = E_{out}$. Noting that a closed system does not involve any mass flow across its boundaries, the energy balance for a cycle can be expressed in terms of heat and work interactions as [7]:

$$W_{net,out} = Q_{net,in} \text{ or } \dot{W}_{net,out} = \dot{Q}_{net,in} (\text{for a cycle}) \tag{II.13}$$

II.2 First law of Thermodynamic

II.2.1 Statement

A closed system does not allow mass to enter or exit, hence matter cannot carry energy beyond its border. Therefore, the only forms of energy that are exchanged with the surroundings are heat or work. The total amount of energy that changed in the environment was thus equal to the amount of energy that was transmitted back and forth on it as heat or work. This leads to a more practical and simpler version of the energy equation for closed systems, where the second component on the right side of Equation II.14, which we utilize for energy transfer, is replaced by explicit terms for work W and for heat Q [3].

$$\Delta\,(\text{Energy of surroundings}) = \pm Q \pm W \tag{II.14}$$

The system is always referred to by heat Q and work W, and the sign of the numerical values of these variables is determined by which direction of energy transfer related to the system is considered positive. For transfer from the surroundings into the system, we use the convention that renders both quantities' numerical values positive. Taking into account the surroundings, the comparable values, Q_{surr} and W_{surr}, have the opposite sign, meaning that $Q_{surr} = -Q$ and $W_{surr} = -W$. With this knowledge in mind [3]:

$$\Delta\,(\text{Energy of surroundings}) = Q_{surr} + W_{surr} = -QW \tag{II.15}$$

Equation II.15 now becomes:

$$\Delta\,(\text{Energy of the system}) = Q + W \tag{II.16}$$

II.2.2 Concept of internal energy of a system

An ideal gas, according to our definition, is one whose specific volume, temperature, and pressure are connected by

$$PV = nRT \tag{II.17}$$

It has been demonstrated mathematically and experimentally (Joule, 1843) that for an ideal gas the internal energy is a function of the temperature only [7]. That is,

$$u = u(T) \tag{II.18}$$

Equation II.16 energy balance for $1mole$ of a homogeneous fluid inside a closed system is expressed as [3]:

$$\Delta U = Q + W \tag{II.19}$$

The work for a mechanically reversible, closed-system process is given by Equation II.3, here written: $dW = \; -PdV$. Substitution into the preceding equation yields:

$$dU = dQ - PdV \tag{II.20}$$

This represents the overall energy balance for one mole or a unit mass of homogeneous fluid within a closed system undergoing a mechanically reversible operation [3].

For a constant-volume change of state :

$$dU = dQ \;\; (\text{const } V) \tag{II.21}$$

Integration yields:

$$\Delta U = Q \;\; (\text{const } V) \tag{II.22}$$

The internal energy change for a closed-system, mechanically reversible process with constant volume is equal to the heat input [3]:

$$dU + PdV = d(U + PV) = dQ \tag{II.23}$$

II.2.3 Application to ideal gas

Specific internal energy for a gas that follows the ideal gas model is only dependent on temperature. Therefore, the specific heat c_v, as determined by Equation II.24, is similarly only dependent on temperature. That's [2],

$$c_v(T) = \frac{du}{dT} \tag{II.24}$$

This is expressed as an ordinary derivative because u depends only on T [2].

Therefore, it is possible to express differential changes in internal energy as a function of temperature change alone [7]

$$du = c_v(T)dT \tag{II.25}$$

The change in internal energy for an ideal gas during a transition from state 1 to state 2 is obtained by integrating these equations [7]:

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T)dT \ \ (KJ/Kg) \tag{II.26}$$

The existence of constant-volume specific heat c_v in an equation does not restrict its use to processes with constant volumes. In fact, for an ideal gas, the formula $\Delta u = c_{v,avg}\Delta T$ applies to any process, whether or not there are volume changes, provided that the gas acts ideally (as seen in Figure II.4). This is because, for perfect gases, the internal energy depends solely on temperature and not on the nature or course of the process [7].

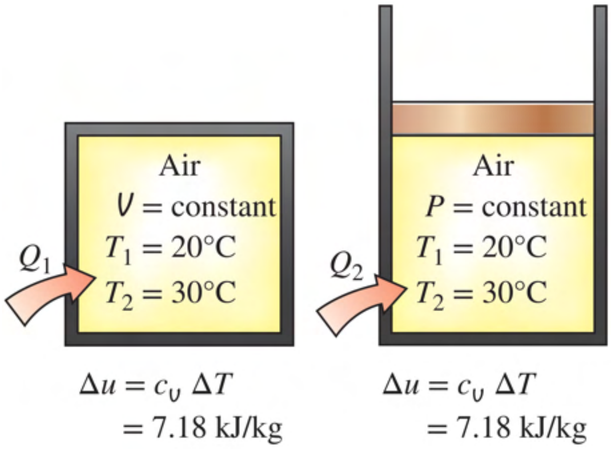


Figure II.4: The relation $\Delta u = c_{v,avg}\Delta T$ is valid for any kind of process, constant-volume or not [7].

II.2.4 Enthalpy function

In this case, the change in the amount $U + PV$ in going from an initial state to a final state may be used to express the transferred heat in a process. Since internal energy, pressure, and volume are state functions that only depend on the system's actual state, their total, $U + PV$, also turns out to be a state function. This total is presented by thermodynamics as a new expanding property called enthalpy H [6], which is useful for convenience.

$$H = U + PV \tag{II.27}$$

Since U, P, and V are all properties, this combination is also a property. Enthalpy can be expressed on a unit mass basis

$$h = u + pv \tag{II.28}$$

$$\bar{h} = \bar{u} + p\bar{v} \tag{II.29}$$

Enthalpy is expressed in the same units as internal energy [2]. where molar or unit-mass values are represented by H, U, and V. The prior energy balance becomes:

$$dH = dQ \;\; (\text{const } P) \tag{II.30}$$

Integration yields:

$$\Delta H = Q \;\; (\text{const } P) \tag{II.31}$$

The concept of two categories of processes is motivated by Equation Equation II.31:

- **Exothermal processes** are those for which $\Delta H < 0$ as a result of energy being transferred as heat from the system to the surroundings.
- **Endothermal processes** are those for which $\Delta H > 0$ as a result of energy being transferred as heat to the system from the surroundings.

Because U, P, and V are all state functions, H as defined by Equation II.27 is also a state function. Like U and V, H is an intensive property of matter. The differential form of Equation II.27 is:

$$dH = dU + d\left(PV\right) \tag{II.32}$$

This equation applies to any differential change of state. After integration, it becomes an equation for a finite change of state:

$$\Delta H = \Delta U + \Delta\left(PV\right) \tag{II.33}$$

Equations II.27, II.32, and II.33 apply to a unit mass or mole of a substance [3].

It is now possible to express the energy equation for a constant-pressure quasi-equilibrium process as [10]:

$$Q_{1-2} = H_2 - H_1 \tag{II.34}$$

II.2.5 Heat capacity

Specific heat is defined as the amount of energy needed to raise a substance's temperature by one degree per unit mass (Figure II.5). Since it depends on how the process is carried out, thermodynamics divides this energy requirement into two main categories [7]:

C_V : specific heat by constant volume,

C_P : specific heat at constant pressure.

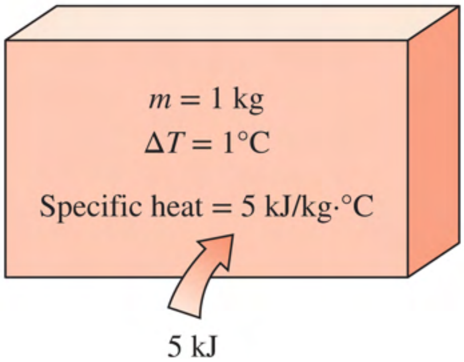


Figure II.5: Specific heat is the energy required to raise the temperature of a unit mass of a substance by one degree in a specified way [7].

When the volume remains constant, the specific heat needed to raise the temperature by one degree while keeping the volume constant is called C_V. Likewise, while the pressure remains constant, the specific heat C_P is the energy required to increase the same amount of temperature while keeping the pressure constant, as shown in Figure II.6.

In a simple system, the state may be determined by just two independent variables. The particular internal energy may this be thought of as [10], which depends on both temperature and specific volume.

$$u = u(T, v) \tag{II.35}$$

$$du = \left.\frac{\partial u}{\partial T}\right|_v dT + \left.\frac{\partial u}{\partial v}\right|_T dv \tag{II.36}$$

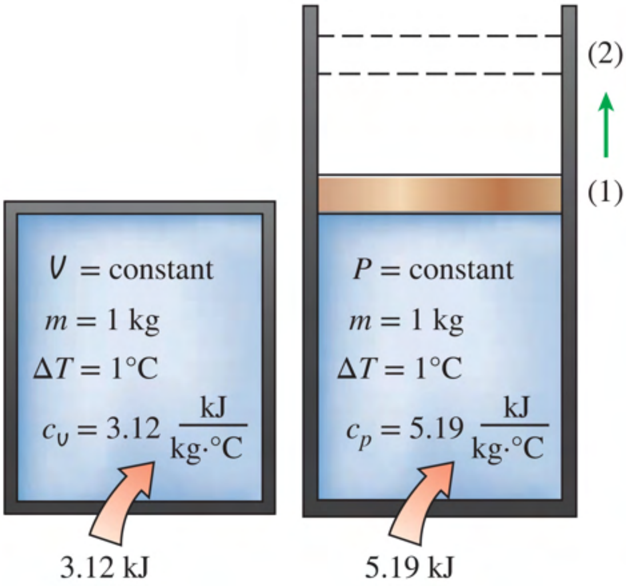


Figure II.6: Constant-volume and constant-pressure specific heats C_V and C_P (values given are for helium gas) [7].

Since u, v, and T are all properties, the partial derivative is also a property and is called the constant-volume specific heat C_V; that is,

$$C_v = \left.\frac{\partial u}{\partial T}\right|_v \qquad \text{(II.37)}$$

For a gas that exhibits ideal gas behavior, we have

$$\left.\frac{\partial u}{\partial T}\right|_v = 0 \qquad \text{(II.38)}$$

Combining Equations II.36, II.37, and II.38,

$$du = C_v dT \qquad \text{(II.39)}$$

They may be combined to provide

$$u_2 - u_1 = \int_{T_1}^{T_2} C_v dT \qquad \text{(II.40)}$$

For a known $C_V\,(T)$ this can be integrated to find the change in internal energy over any temperature interval for an ideal gas [10].

Similarly, assuming that specific enthalpy depends on the variables T and P, we obtain

$$dh = \left.\frac{\partial h}{\partial T}\right|_P dT + \left.\frac{\partial h}{\partial P}\right|_T dP \tag{II.41}$$

The constant-pressure specific heat C_p is defined as

$$C_P = \left.\frac{\partial h}{\partial T}\right|_P \tag{II.42}$$

Using the definition of enthalpy from (Equation II.27) for an ideal gas, we obtain

$$h = u + PV = u + RT \tag{II.43}$$

We can see that because u depends only on T, h for an ideal gas also depends only on T. Therefore, [10] for a ideal gas

$$\left.\frac{\partial h}{\partial T}\right|_T = 0 \tag{II.44}$$

and we have, from (Equation II.41),

$$dh = C_P dT \tag{II.45}$$

Over the temperature range T_1 to T_2 this is integrated to give for an ideal gas [10].

$$h_2 - h_1 = \int_{T_1}^{T_2} C_P dT \tag{II.46}$$

The molar specific temperatures $\bar{C}_V$ are and $\bar{C}_P$; it is frequently more easier to describe specific heats on a per-mole basis as opposed to a per-unit-mass basis. We obviously have the relations [10].

$$\bar{C}_v = MC_v \text{ and } \bar{C}_P = MC_P \tag{II.47}$$

where M is the molar mass. Thus values of $\bar{C}_V$ and $\bar{C}_P$ may be simply calculated from the values of C_V and C_P [10].

Using the enthalpy equation, the specific heats and the gas constant for an ideal gas may be related. The form of Equation II.27.27 in differential form is as follows:

$$dh = du + d(pv) \tag{II.48}$$

The ideal-gas equation and specific heat relations are introduced.

$$C_P dT = C_V dT + RdT \tag{II.49}$$

which, after dividing by dT, gives

$$C_P = C_V + R \tag{II.50}$$

This relationship or its molar equivalent $\bar{C}_P = \bar{C}_V + R$ allows C_V to be determined from tabulated values or expressions for C_P. Note that the difference between C_P and C_V for an ideal gas is always the gas constant R [10].

The specific heat ratio γ is also a property of particular interest; is the Laplace coefficient; it is defined as

$$\gamma = \frac{C_P}{C_V} \tag{II.51}$$

This can be substituted into Equation II.50 to give

or

$$C_V = \frac{R}{\gamma - 1} \tag{II.52}$$

Obviously, since R is a constant for an ideal gas, the specific heat ratio will depend only on temperature [10].

Ideal gas	γ
Monatomic Ar, He, Ne	1.66
Diatomic H_2, O_2, N_2	1.4
Others CO_2, H_2O	1.33

Table II.1: Laplace coefficients.

II.2.6 Reversible transformations

II.2.6.1 Reversible Constant pressure process or isobaric process

A constant-volume border during a constant-volume operation causes pressure to rise when heat is added, as seen in Figure II.7. However, in a process that operates at constant pressure, the system's boundary has to be moving, like a piston in a cylinder, in order for it to push against an external force when heat is added. The gas does work on the outside when it forces the piston outward. This motion maintains pressure as the volume grows, demonstrating why working is required for constant-pressure systems [14].

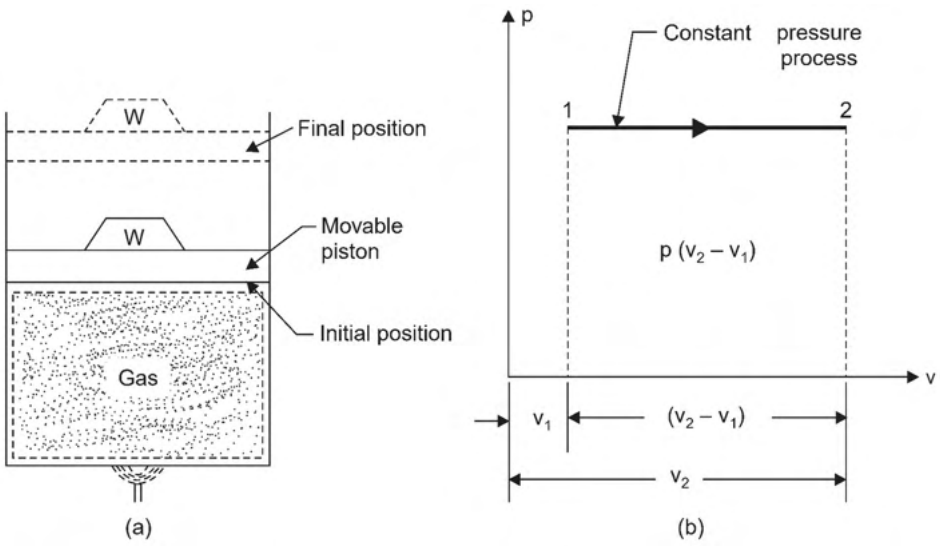


Figure II.7: Reversible constant pressure process [14].

The work involved in the raising of piston shall be given by [5],

$$W_{1-2} = \int_{V_1}^{V_2} P dV = P(V_2 - V_1) \tag{II.53}$$

According to the first law of thermodynamics, mathematically terms,

$$dQ = dU + dW \tag{II.54}$$

$$\int_1^2 dQ = \int_1^2 dU + \int_1^2 dW \tag{II.55}$$

$$Q_{12} = m\, c_v(T_2T_1) \; + P(V_2V_1) \; = m\, c_v(T_2T_1) \; + mR(T_2T_1) \tag{II.56}$$

Substituting for C_V, i.e

$$c_v = \frac{R}{\gamma - 1} \tag{II.57}$$

$$Q_{12} = m\ \mathrm{R}(T_2 T_1)\left\{\frac{1}{(\gamma - 1)} + 1\right\} \tag{II.58}$$

II.2.6.2 Reversible Constant volume process or isochoric process

A constant-volume (or isochoric) process occurs when a fluid is enclosed in a solid, immovable shell that prevents volume changes, for as when a gas is enclosed in a long-lasting container. The equation $P/T = const$ is maintained in an ideal gas, meaning that pressure will be directly proportional to temperature [5].

See the system before and after heating in constant-volume conditions as depicted by Figure II.8 [13] [14].

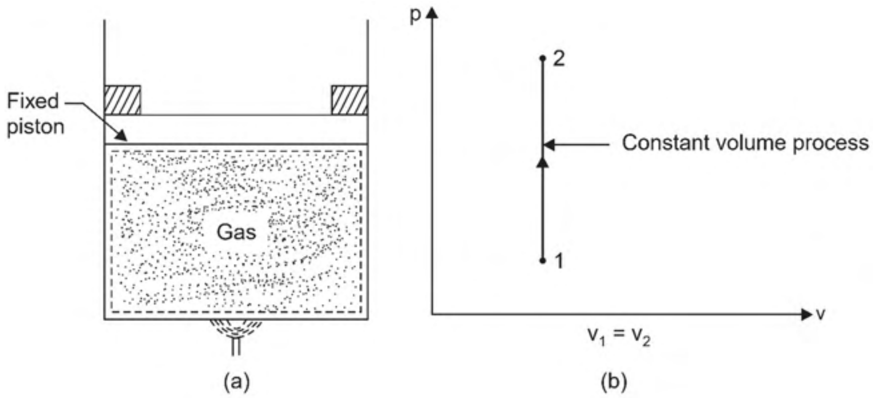


Figure II.8: Reversible constant volume process [14].

Work involved shall be [5],

$$W_{1-2} = \int_{V_1}^{V_2} PdV = 0 \tag{II.59}$$

From first law of thermodynamics,

$$dQ = dU + dW \tag{II.60}$$

$$\int_1^2 dQ = \int_1^2 dU + \int_1^2 dW = \int_1^2 dU + 0 \tag{II.61}$$

or

$$Q_{1-2} = U_2 - U_1 = mc_v(T_2 - T_1) \tag{II.62}$$

Thus, it indicates that the effect of heat addition in constant volume process is to increase the temperature and consequently the internal energy of system [5].

II.2.6.3 Reversible Constant temperature process or isothermal process

A process that takes place at a steady temperature is called an isothermal process [14]. Figure II.9 shows the system and states before and after the heat addition at constant temperature [14].

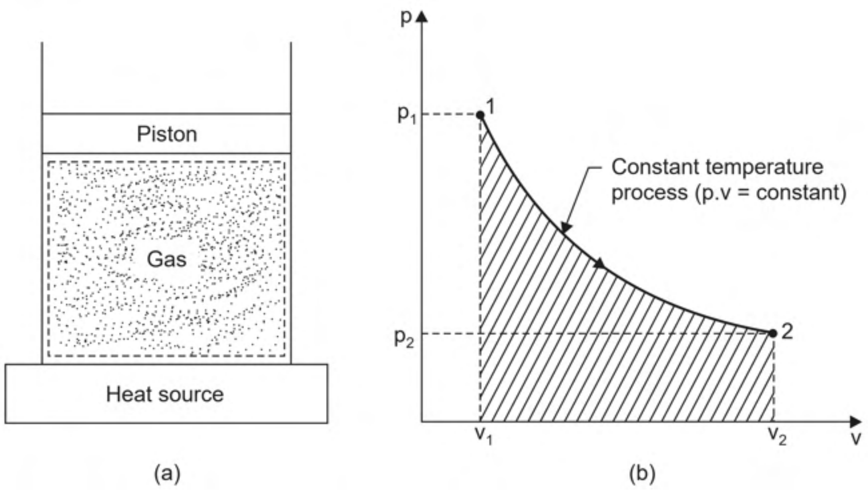


Figure II.9: Reversible isothermal process [5].

$$P_1V_1 = P_2V_2 = \text{ Constant, or, } P = \frac{P_1V_1}{V} \tag{II.63}$$

so work involved [5],

$$W_{1-2} = \int_{V_1}^{V_2} PdV \tag{II.64}$$

$$W_{1-2} = \int_{V_1}^{V_2} \frac{P_1V_1}{V}dV = P_1V_1 \ln\left(\frac{V_2}{V_1}\right) = P_1V_1 \ln\left(\frac{P_1}{P_2}\right) \tag{II.65}$$

By first law of thermodynamics [5]

$$\int_1^2 dQ = \int_1^2 dU + \int_1^2 dW \tag{II.66}$$

$$Q_{12} = W_{1-2} = (U_2 - U_1) = W_{1-2} + 0 \tag{II.67}$$

$$Q_{1-2} = \int_{V_1}^{V_2} \frac{P_1V_1}{V} dV = P_1V_1 \ln\left(\frac{V_2}{V_1}\right) = P_1V_1 \ln\left(\frac{P_1}{P_2}\right), \quad \left(\frac{V_2}{V_1}\right) = \left(\frac{P_1}{P_2}\right) \tag{II.68}$$

$$U_2 - U_1 = mc_v(T_2 - T_1), \text{ and } T_1 = T_2 \tag{II.69}$$

II.2.6.4 Reversible Adiabatic process

When the surrounding $Q = 0$, an adiabatic process indicates that no heat will be transported. This process obeys the relationship $PV^\gamma = \ constant$, where γ (the adiabatic index) is the ratio of specific heats. Adiabatic Expansion Process Figure II.10 [5]:

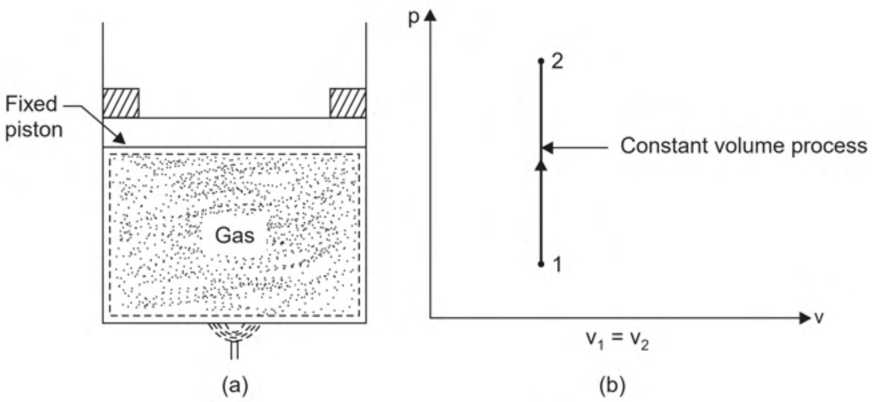


Figure II.10: Reversible adiabatic process [14].

Reversible adiabatic process [5]:

$$W_{1-2} = \int_{V_1}^{V_2} PdV \tag{II.70}$$

Considering unit mass of working substance and applying first law to the process

$$W = U_2 - U_1 \text{ for any adiabatic process} \tag{II.71}$$

To derive the law $PV^{\gamma} = \ constant$:

To obtain a law relating P and V for a reversible adiabatic process let us consider the nonflow energy equation in differential form,

$$dQ = du + dW \tag{II.72}$$

For a reversible process

$$dW = PdV \tag{II.73}$$

$$dQ = du + PdV = \ 0 \tag{II.74}$$

Also for a perfect gas

$$PV = RT \text{ or } P = \frac{RT}{V} \tag{II.75}$$

Hence substituting,

$$dU + \frac{RTdV}{V} = \ 0 \tag{II.76}$$

Also

$$U = C_V T \text{ or } dU = C_V dT \tag{II.77}$$

$$C_V dT + \frac{RTdV}{V} = 0 \tag{II.78}$$

Dividing both sides by T, we get [14]

$$C_V \frac{dT}{T} + \frac{RdV}{V} = 0 \tag{II.79}$$

Integrating

$$C_V \ln T \ + \ R \ln V = \ \text{constant} \tag{II.80}$$

Substituting $T = \frac{PV}{R}$

$$C_V \ln \frac{PV}{R} \ + \ R \ln V = \ \text{constant} \tag{II.81}$$

Dividing throughout both sides by C_V

$$\ln \frac{PV}{R} \ + \ \frac{R}{C_V} \ln V = \ \text{constant} \tag{II.82}$$

Again

$$C_V = \frac{R}{(\gamma - 1)} \text{ or } \frac{R}{C_V} = \gamma - 1 \tag{II.83}$$

Hence substituting

$$\ln \frac{PV}{R} + (\gamma - 1) \ln V = \text{constant} \tag{II.84}$$

$$\ln \frac{PV}{R} + \ln V^{(\gamma-1)} = \text{constant} \tag{II.85}$$

$$\ln \frac{PV.V^{(\gamma-1)}}{R} = \text{constant} \tag{II.86}$$

$$\frac{PV^{\gamma}}{R} = \mathrm{e}^{\text{constant}} = \text{constant} \tag{II.87}$$

$$PV^{\gamma} = \text{constant} \tag{II.88}$$

Expression for work W

A reversible adiabatic process for a perfect gas is shown on a $P - V$ diagram in Figure II.10 (b). The work done is given by the shaded area, and this area can be evaluated by integration [14].

$$W_{1-2} = \int_{V_1}^{V_2} PdV \tag{II.89}$$

Therefore, since $PV^{\gamma} = \ constant$, C, then

$$W_{1-2} = \int_{V_1}^{V_2} C \frac{dV}{V^{\gamma}} \tag{II.90}$$

$$W_{1-2} = C \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}} = C \left| \frac{V^{-\gamma+1}}{-\gamma+1} \right|_{V_1}^{V_2} \tag{II.91}$$

$$C = \left(\frac{V_2{}^{-\gamma+1} - V_1{}^{-\gamma+1}}{1-\gamma} \right) = C \left(\frac{V_1{}^{-\gamma+1} - V_2{}^{-\gamma+1}}{\gamma - 1} \right) \tag{II.92}$$

The constant in this equation can be written as $P_1 V_1{}^{\gamma}$ or as $P_2 V_2{}^{\gamma}$. Hence,

$$W = \frac{P_1 V_1{}^{\gamma} V_1{}^{-\gamma+1} - P_2 V_2{}^{\gamma} V_2{}^{-\gamma+1}}{\gamma - 1} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \tag{II.93}$$

$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \tag{II.94}$$

or

$$W = \frac{R(T_1 - T_2)}{\gamma - 1} \tag{II.95}$$

Relationship between T and V, and T and P

By using equation $PV = RT$, the relationship between T and V, and T and P, may by derived as follows:

$$PV = RT \tag{II.96}$$

$$P = \frac{RT}{V} \tag{II.97}$$

Putting this value in the equation $PV^\gamma = \ constant$

$$\frac{RT}{V}.V^\gamma = \text{constant} \tag{II.98}$$

$$T.V^{\gamma-1} = \text{constant} \tag{II.99}$$

Also $V = RT/P$; hence substituting in equation $PV^\gamma = \ constant$

$$P\left(\frac{RT}{P}\right)^\gamma = \text{constant} \tag{II.100}$$

$$\frac{T^\gamma}{P^{\gamma-1}} = \text{constant} \tag{II.101}$$

$$\frac{T}{(P)^{\frac{\gamma-1}{\gamma}}} = \text{constant} \tag{II.102}$$

Therefore, for a reversible adiabatic process for a perfect gas between states 1 and 2, we can write: From Equation II.88,

$$P_1V_1{}^\gamma = P_2V_2{}^\gamma \quad \text{or} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma \tag{II.103}$$

From Equation Equation II.99,

$$T_1V_1{}^{\gamma-1} = T_2V_2{}^{\gamma-1} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \tag{II.104}$$

From Equation Equation II.102,

$$\frac{T_1}{(P_1)^{\frac{\gamma-1}{\gamma}}} = \frac{T_2}{(P_2)^{\frac{\gamma-1}{\gamma}}} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{II.105}$$

From Equation II.71, the work done in an adiabatic process per kg of gas is given by $W = \ (U_1 - U_2)$. The gain in internal energy of a perfect gas is given by equation [14]:

$$U_2 - U_1 = C_V\,(T_2 - T_1) \tag{II.106}$$

$$W = C_V\,(T_1 - T_2) \tag{II.107}$$

Also, we know that

$$C_V = \frac{R}{\gamma - 1} \tag{II.108}$$

Hence substituting, we get

$$W = \frac{R\,(T_1 - T_2)}{\gamma - 1} \tag{II.109}$$

Using equation,

$$PV = RT \tag{II.110}$$

$$W = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \tag{II.111}$$

This is the same expression obtained before as Equation II.95 [14].

II.2.6.5 Polytropic process

The most popular thermodynamic process in real-world applications is the polytropic process. According to this, the formula $PV^n = \ constant$, where n is the index that can range from $-\infty$ to $+\infty$, governs the thermodynamic process [5],

We know that for any reversible process,

$$W = \int PdV \tag{II.112}$$

For a process in $PV^n = \ constant$, we have $P = \frac{C}{V^n}$, where C is a constant

$$W = C\int_{V_1}^{V_2} \frac{dV}{V^n} = C\left|\frac{V^{-n+1}}{-n+1}\right|_{V_1}^{V_2} = C\left(\frac{{V_2}^{-n+1} - {V_1}^{-n+1}}{-n+1}\right) \tag{II.113}$$

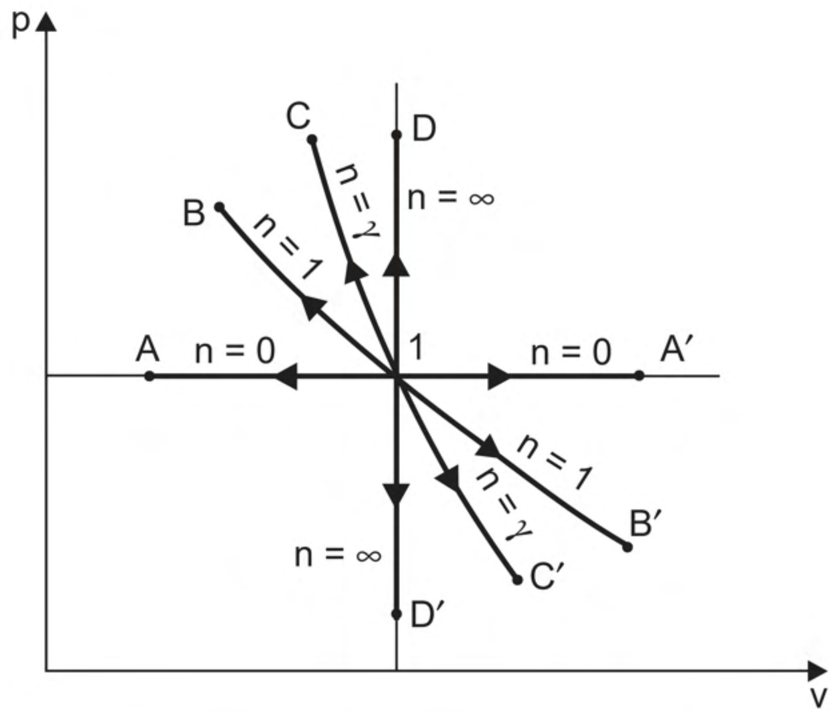


Figure II.11: Polytropic exponents for various processes [14].

$$W = C\left(\frac{V_1{}^{-n+1} - V_2{}^{-n+1}}{n-1}\right) = \frac{P_1V_1{}^nV_1{}^{-n+1} - P_2V_2{}^nV_2{}^{-n+1}}{n-1} \tag{II.114}$$

(since the constant C, can be written as $P_1V_1{}^n$ or as $P_2V_2{}^n$) Work done,

$$W = \frac{P_1V_1 - P_2V_2}{n-1} \tag{II.115}$$

or

$$W = \frac{R\left(T_1 - T_2\right)}{n-1} \tag{II.116}$$

For each working material going through a reversible polytropic process, Equation II.116 holds valid. Consequently, we may write for every polytropic process [14],

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^n \tag{II.117}$$

It is possible to obtain the following relations (using the same approach as under reversible adiabatic process).

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1} \tag{II.118}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} \tag{II.119}$$

Heat transfer during polytropic process (for perfect gas $PV = RT$)

Using non-flow energy equation, the heat flow/transfer during the process can be found,

$$Q = (U_2 - U_1) + W = C_V (T_2 - T_1) + \frac{R (T_1 - T_2)}{n-1} \tag{II.120}$$

$$= \frac{R (T_1 - T_2)}{n-1} - C_V (T_1 - T_2) \tag{II.121}$$

On substituting [14] ($C_V = \frac{R}{(\gamma-1)}$),

$$Q = \frac{R}{n-1} (T_1 - T_2) - \frac{R}{\gamma - 1} (T_1 - T_2) \tag{II.122}$$

$$Q = R (T_1 - T_2) \left(\frac{1}{n-1} - \frac{1}{\gamma - 1}\right) \tag{II.123}$$

$$Q = \frac{R (T_1 - T_2) (\gamma - 1 - n + 1)}{(\gamma - 1)(n-1)} = \frac{R (T_1 - T_2)(\gamma - n)}{(\gamma - 1)(n-1)} \tag{II.124}$$

$$Q = \frac{(\gamma - n)}{(\gamma - 1)} \frac{R (T_1 - T_2)}{(n-1)} \tag{II.125}$$

$$Q = \frac{(\gamma - n)}{(\gamma - 1)} W \tag{II.126}$$

In a polytropic process, the index n depends only on the heat and work quantities during the process. The various processes considered earlier are special cases of polytropic process for perfect gas (Figure II.11) [14].

- When $n = 0$, $PV^0 = constant$ i.e., $P = constant$
- When $n = \infty$, $PV^\infty = constant$ or $P^{1/\infty} V = constant$, i.e., $V = constant$
- When $n = 1$, $PV = constant$, i.e., $T = constant$ [since $(PV)/T = constant$ for a perfect gas]

- When $n = \gamma$, $PV^\gamma = \ constant$, i.e., reversible adiabatic.

This is illustrated on a $P - V$ diagram in Figure II.11.

- (i) State 1 to state A is constant pressure cooling ($n = 0$).
- (ii) State 1 to state B is isothermal compression ($n = 1$).
- (iii) State 1 to state C is reversible adiabatic compression ($n = \gamma$).
- (iv) State 1 to state D is constant volume heating ($n = \ \infty$).

Similarly,

- (i) State 1 to state A' is constant pressure heating ($n = 0$).
- (ii) State 1 to state B' is isothermal expansion ($n = 1$).
- (iii) State 1 to state C' is reversible adiabatic expansion ($n = \gamma$).
- (iv) State 1 to state D' is constant volume cooling ($n = \ \infty$).

It may be noted that, since γ is always greater than unity, than process 1 to C must lie between processes 1 to B and 1 to D; similarly, process 1 to C' must lie between processes 1 to B' and 1 to D' [14].

II.2.6.6 Hyperbolic process

A process is considered hyperbolic if the product of volume and pressure stays constant throughout. It is called hyperbolic expansion because the curve for this type of expansion process is a rectangular hyperbola [5].

For a perfect gas $PV/T = Constant$, if T is also constant then it means that for a perfect gas the hyperbolic process shall also be isothermal process. Figure II.12 shows hyperbolic expansion process between 1 and 2.

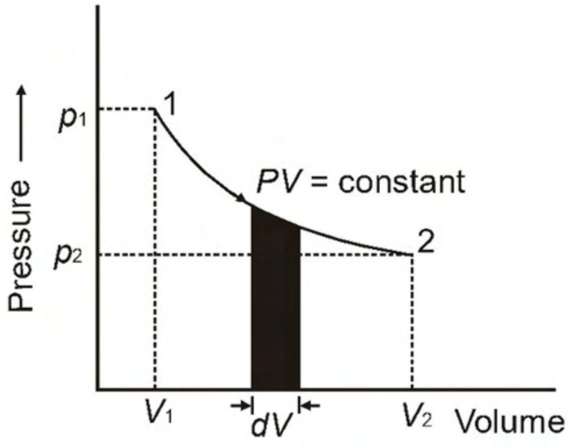


Figure II.12: Hyperbolic expansion [5].

Work done during process shall be [5]

$$W_{1-2} = \int_{V_1}^{V_2} PdV \text{ and } P_1V_1 = P_2V_2 = \text{constant} \quad \text{(II.127)}$$

$$W_{1-2} = \int_{V_1}^{V_2} \frac{P_1V_1}{V}\, dV = P_1V_1 \ln \frac{V_2}{V_1} \quad \text{(II.128)}$$

$$\int_1^2 dQ = \int_1^2 dU + \int_1^2 dW = (U_2 - U_1) + P_1V_1 \ln\left(\frac{V_2}{V_1}\right) \quad \text{(II.129)}$$

II.2.6.7 Free Expansion

Free expansion is the term used to describe the imbalanced expansion of a gas into a vacuum [5].

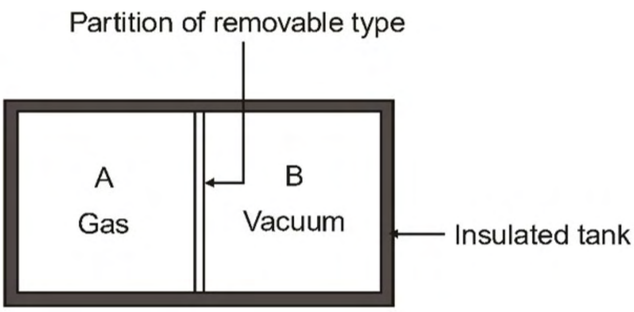


Figure II.13: Free expansion [5].

During free expansion no work shall be done by the gas or on the gas due to no boundary displacement in the system.

$$W_{free\ expansion} = 0 \quad \text{(II.130)}$$

Also in the above there shall be no heat interaction as tank is insulated. From first law of thermodynamics,

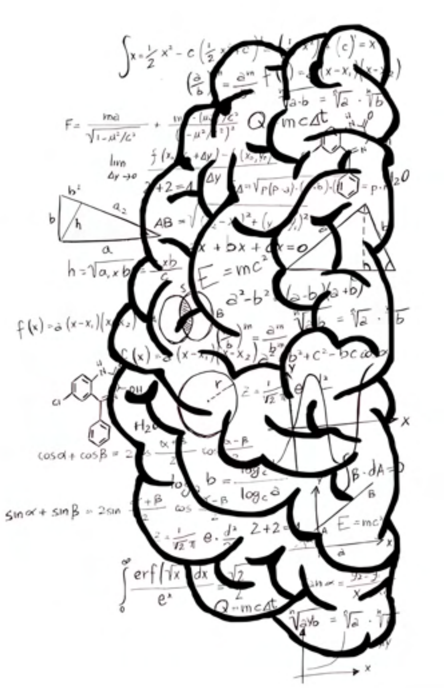
$$\Delta Q = \Delta U + \Delta W \quad \text{(II.131)}$$

$$0 = \Delta U + 0 \quad \text{(II.132)}$$

or, $U_{A+B} = U_A$, i.e. initial and final internal energies are same, which means for a perfect gas initial and final temperatures of gas are same.

PRACTICE

EXERCISES AND SOLUTIONS



II.3 Problem Solving

Problem 4 SKILLS PROBLEM-SOLVING

A completely evacuated cylinder of $0.78m^3$ volume is filled by opening its valve to atmosphere and air rushing into it. Determine the work done by the air and by surroundings on system [5].

Solution 4

Total work done by the air at atmospheric pressure of $101.325KPa$,

$$W = \int_{cylinder} PdV + \int_{air} PdV = 0 + P.\Delta V$$

Work done by air = − 101.325 × 0.78 = $-79.03KJ$

Work done by surroundings on system = $+79.03KJ$

Problem 5 SKILLS PROBLEM-SOLVING

A system comprising of a gas of $5Kg$ mass undergoes expansion process from $1MPa$ and $0.5m^3$ to $0.5MPa$. Expansion process is governed by, $PV^{1.3} = constant$. The internal energy of gas is given by, $U = 1.8PV + 85, KJ/kg$. Here u is specific internal energy, P is pressure in KPa, V is specific volume in m^3/Kg. Determine heat and work interaction and change in internal energy [5].

Solution 5

Given mass of gas, $m = 5Kg$, $PV^{1.3} = \ constant$. Assuming expansion to be quasi-static, the work may be given as,

$$W = m \int PdV$$

$$= \frac{(P_2V_2 - P_1V_1)}{(1-n)}$$

From internal energy relation, change in specific internal energy,

$$\Delta U = U_2U_1 = \ 1.8\ (P_2V_2P_1V_1),\ KJ/kg$$

Total change,

$$\Delta U = 1.8 \times m \times \ (P_2V_2P_1V_1),\ KJ$$

$$\Delta U = 1.8\ (P_2V_2P_1V_1),\ KJ$$

Between states 1 and 2,

$$P_1{V_1}^{1.3} = P_2{V_2}^{1.3}$$

$$V_2 = (0.5)\left(\frac{1}{0.5}\right)^{1/1.3}$$

$$V_2 = \ 0.852m^3$$

Total change in internal energy, $\Delta U = \ 133.2KJ$

Work

$$W = \frac{(0.5 \times 0.852 - 1 \times 0.5)\,10^3}{(1-1.3)}$$

$$W = 246.67KJ$$

From first law,

$$\Delta U = Q + W = -133.2 + 246.7$$

$$\Delta Q = \ 113.5KJ$$

Problem 6 SKILLS PROBLEM-SOLVING

The specific heat of superheated steam at approximately $150KPa$ can be determined by the equation

$$C_P \ = 2.07 + \frac{T-400}{1480} \ KJ/Kg°C$$

(a) What is the enthalpy change between $300°C$ and $700°C$ for $3Kg$ of steam?

(b) What is the average value of C_P between $300°C$ and $700°C$ based on the equation and based on the tabulated data [10]?

Solution 6

(a) The enthalpy change is found to be

$$\Delta H = m\int_{T_1}^{T_2} C_P dT = 3\int_{300}^{700}\left(2.07 + \frac{T-400}{1480}\right) dT = 2565KJ$$

From the tables we find, using $P = 150KPa$,

$$\Delta H = (3)\,(3928 - 3073) = 2565KJ$$

(b) The average value $C_{P,\ av}$ is found by using the relation

$$C_{P,av}\,\Delta T = m\int_{T_1}^{T_2} C_P dT$$

$$(3)\,(400C_{P,av}) \ = 3\int_{300}^{700}\left(2.07 + \frac{T-400}{1480}\right) \ dT$$

The integral was evaluated in part

(a); hence, we have

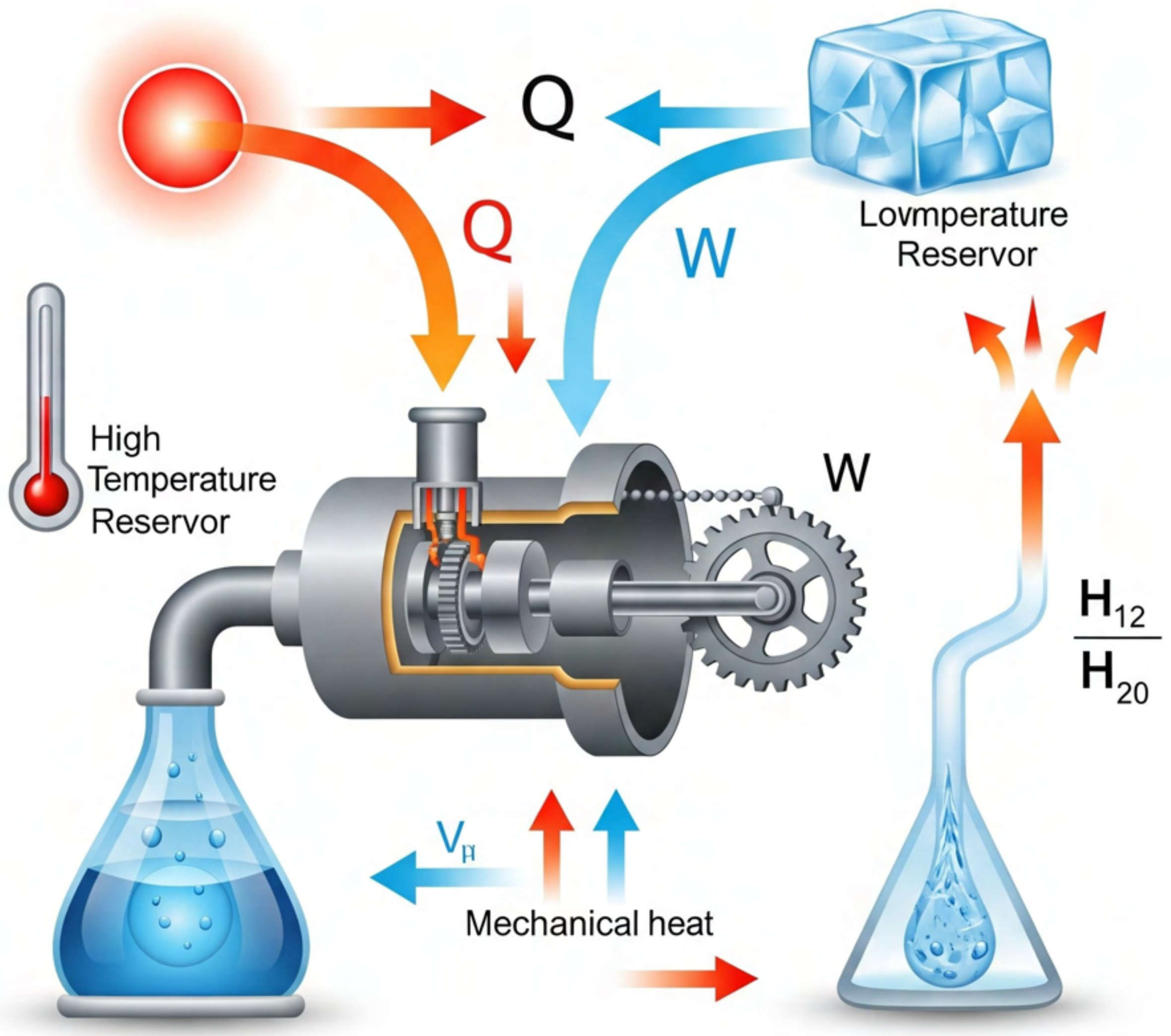
$$C_{P,av} = \frac{2565}{(3)\,(400)} = 2.14KJ/Kg°C$$

Using the values from the steam table, we have

$$C_{P,av} = \frac{\Delta h}{(\Delta T)} = (3928 - 3073)\,/400 = 2.14KJ/Kg°C$$

THIRD CHAPTER

APPLICATIONS OF THE FIRST PRINCIPLE OF THERMODYNAMICS TO THERMOCHEMISTRY



Applications of the First Principle to Thermochemistry III

This chapter will use the first law of thermodynamics in application to the chemical phenomenon by studying the relationship between heat exchanges and chemical reactions. This science is referred to as thermochemistry; it enables us to measure the changes of energy that take place during the process of chemical transformation and to comprehend that they are energetic.

Our starting point is to define the concept of heat of reaction, which is simply the thermal quantity of matter that a system changes during a chemical reaction process performed at constant pressure, or constant volume. These reaction heats are directly proportional to the changes in enthalpy energy or internal energy of the system.

Then we introduce the concept of the standard state that gives us a usual point of reference in which we can describe the value of enthalpy. The standard enthalpy of formation will be given as the enthalpy change which is related to the formation of one mole of a compound formed by its elements under standard conditions. We also present the enthalpy of dissociation and enthalpy of phase change (fusion, vaporization, sublimation, etc.), which characterize the amount of energy changes that are involved in physical changes.

The enthalpy change of a chemical reaction is to be examined as some characteristic amount, which will show whether the chemical reaction is an exothermic (releasing heat) or endothermic (absorbing heat) reaction. These principles are essential towards setting proper energy balances and thermal behaviour of chemical reactions.

Then two basic laws of thermochemistry will be discussed:

- The Law of Hess that states that enthalpy is additive: the overall change of enthalpy of a reaction is the same regardless of the path taken between the initial and final states, but not the path. This law is used to compute reaction enthalpies using mixtures of known reactions.
- The law of Kirchhoff, which is the variation of reaction enthalpy with temperature. Through it, the heats of reactions at non-standard-state temperatures may be estimated or corrected through the heat capacities of the reactants and products.

Throughout this chapter, students will learn how to:

- Calculate reaction enthalpies using tabulated data;
- Apply Hess's Law to determine enthalpies of complex reactions;
- Use Kirchhoff's Law to evaluate the effect of temperature on energy balances;
- Interpret the energetic direction and nature of chemical reactions.

This chapter is a key step toward understanding energy processes in chemistry and engineering, and it provides the foundation for more advanced studies in chemical thermodynamics and reaction kinetics.

III.1 Heats of Reaction

Similar to internal energy, a substance's enthalpy cannot be quantified or calculated exactly. Enthalpy changes alone may be measured. For the enthalpies of substances, a reference state must be established, since heights are measured with respect to a standard altitude [16].

It is possible to predict how much heat a chemical reaction will produce or use if the internal change in energy ΔU or enthalpy change ΔH is known.

A reaction that produces heat to the system is exothermic. At constant pressure, this means a lowering of the system's enthalpy, so $\Delta H < 0$ also termed as being exenthalpic. A reaction that takes up heat energy from the system is endothermic, so enthalpy increases, thus $\Delta H > 0$ called endenthalpic. Therefore, the sign of ΔH directly tells u if a reaction is endothermic or exothermic under constant-pressure situations endenthalpic [17].

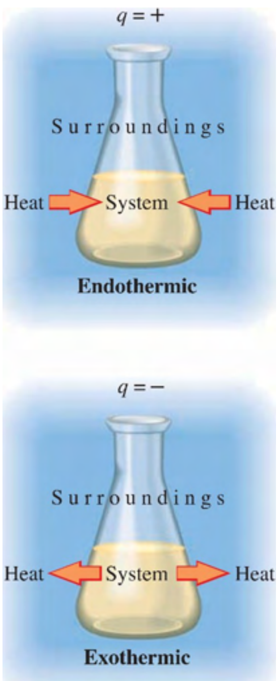


Figure III.1: Endothermic and Exothermic reactions [16].

III.2 Standard State

Like internal energy, a substance's enthalpy cannot be measured or computed in absolute terms. Measuring just enthalpy changes is possible. It is required to establish a reference state for the enthalpies of substances, just as elevations are measured in relation to a standard altitude [18].

Standard-state values of enthalpy and other quantities are designated by attaching a superscript $^\circ$ (pronounced "naught") to the symbol for the quantity and writing the specified temperature as a subscript. Any temperature may be chosen as the "specified temperature." The most common choice is $298.15K$ ($25°C$ exactly); if the temperature of a standard state is not explicitly indicated, $298.15K$ should be assumed to be the value [18].

III.3 Standard Enthalpy of Formation

The standard enthalpy change of a reaction, symbolized ΔH°, is the enthalpy change when reactants as well as products are in standard states—pure material at $100KPa$ ($1bar$) pressure as well as a specific temperature, normally $298K$ ($25°C$). This standardizing reference enables comparable comparison of energy change for various chemical reactions involving breaking as well as formation of chemical bonds.

The standard enthalpy of formation of a compound, ΔH_f°, is the change in enthalpy for the reaction that forms one mole of the compound from its elements with all substances in their standard states [15]:

$$\underset{\text{(in standard state)}}{\text{elements}} \longrightarrow \underset{\text{(1mol in standard state)}}{\text{compound}} \qquad \Delta H_{rxn} = \Delta H_f^\circ \tag{III.1}$$

To understand this definition, consider the standard enthalpy of formation of liquid water. Note that the stablest forms of hydrogen and oxygen at $1atm$ and $25°C$ are $H_2\,(g)$ and $O_2\,(g)$, respectively. These are therefore the reference forms of the elements. You write the formation reaction for $1mol$ of liquid water as follows [16]:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \text{(III.2)}$$

The standard enthalpy change for this reaction is $-285.8KJ$ per mole of H_2O. Therefore, the thermochemical equation is [16]:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\;\; \Delta H_f^{\circ} = -285.8KJ \qquad \text{(III.3)}$$

We usually report ΔH_f° values at $298K$. If an element exists in more than one form under standard conditions, the most stable form of the element is usually used for the formation reaction.

III.4 Enthalpy of Dissociation (Bond Enthalpies)

The intermediate species formed during bond breaking, such a hydrogen atom removed from methane, are short-lived and very reactive (typically lacking stable electron configurations), yet they may be studied experimentally. Because scientists have developed tools to examine and evaluate the features of bond energies and reaction processes during their short existence, it is now possible to fully understand them [18].

$$CH_4(g) \xrightarrow{\qquad\qquad} CH_3(g) + H(g) \qquad \text{(III.4)}$$

One such important measurable quantity is the enthalpy change when a bond is broken in the gas phase, called the bond enthalpy. This change is invariably positive because atoms bonded together have lower energy than when separated.

Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)	Substance or Ion	ΔH_f° (kJ/mol)
$e^-(g)$	0	$CH_3CHO(g)$	−166.1	$NO_2(g)$	33.10
Bromine		$CH_3CHO(l)$	−191.8	$HNO_3(aq)$	−207.4
$Br(g)$	111.9	**Chlorine**		**Oxygen**	
$Br^-(aq)$	−121.5	$Cl(g)$	121.3	$O(g)$	249.2
$Br^-(g)$	−219.0	$Cl^-(aq)$	−167.2	$O_2(g)$	0
$Br_2(g)$	30.91	$Cl^-(g)$	−234.0	$O_3(g)$	142.7
$Br_2(l)$	0	$Cl_2(g)$	0	$OH^-(aq)$	−230.0
$HBr(g)$	−36.44	$HCl(g)$	−92.31	$H_2O(g)$	−241.8
Calcium		**Fluorine**		$H_2O(l)$	−285.8
$Ca(s)$	0	$F(g)$	79.39	**Silicon**	
$Ca^{2+}(aq)$	−542.8	$F^-(g)$	−255.1	$Si(s)$	0
$CaCO_3(s$, calcite)	−1206.9	$F^-(aq)$	−332.6	$SiCl_4(l)$	−687.0
$CaO(s)$	−635.1	$F_2(g)$	0	$SiF_4(g)$	−1614.9
Carbon		$HF(g)$	−272.5	$SiO_2(s$, quartz)	−910.9
$C(g)$	716.7	**Hydrogen**		**Silver**	
$C(s$, diamond)	1.897	$H(g)$	218.0	$Ag(s)$	0
$C(s$, graphite)	0	$H^+(aq)$	0	$Ag^+(aq)$	105.6
$CCl_4(g)$	−95.98	$H^+(g)$	1536.2	$AgBr(s)$	−100.4
$CCl_4(l)$	−135.4	$H_2(g)$	0	$AgCl(s)$	−127.1
$CO(g)$	−110.5	**Iodine**		$AgF(s)$	−204.6
$CO_2(g)$	−393.5	$I(g)$	106.8	$AgI(s)$	−61.84
$CO_3^{2-}(aq)$	−677.1	$I^-(aq)$	−55.19	**Sodium**	
$CS_2(g)$	116.9	$I^-(g)$	−194.6	$Na(g)$	107.3
$CS_2(l)$	89.70	$I_2(s)$	0	$Na(s)$	0
$HCN(g)$	135.1	$HI(g)$	26.36	$Na^+(aq)$	−240.1
$HCN(l)$	108.9	**Lead**		$Na^+(g)$	609.3
$HCO_3^-(aq)$	−692.0	$Pb(s)$	0	$Na_2CO_3(s)$	−1130.8
Hydrocarbons		$Pb^{2+}(aq)$	−1.7	$NaCl(s)$	−411.1
$CH_4(g)$	−74.87	$PbO(s)$	−219.4	$NaHCO_3(s)$	−950.8
$C_2H_4(g)$	52.47	$PbS(s)$	−98.32	**Sulfur**	
$C_2H_6(g)$	−84.68	**Nitrogen**		$S(g)$	277.0
$C_6H_6(l)$	49.0	$N(g)$	472.7	$S(s$, monoclinic)	0.360
Alcohols		$N_2(g)$	0	$S(s$, rhombic)	0
$CH_3OH(l)$	−238.7	$NH_3(g)$	−45.90	$S_2(g)$	128.6
$C_2H_5OH(l)$	−277.7	$NH_4^+(aq)$	−132.5	$SO_2(g)$	−296.8
Aldehydes		$NO(g)$	90.29	$H_2S(g)$	−20.50
$HCHO(g)$	−117				

Table III.1: Standard Enthalpies of Formation, ΔH_f°, at 298 K [16].

Example

The bond enthalpy of a C-H bond in methane is $438 KJ\,mol^{-1}$, measured as the standard enthalpy change for the reaction in which $1 mol$ of C-H bonds is broken, one for each molecule of methane [18].

$$CH_4(g) \longrightarrow CH_3(g) + H(g) \qquad \Delta H^\circ = +438\ KJ \qquad \text{(III.5)}$$

Bond enthalpies are fairly constant from one compound to another. Each of the following gas-phase reactions involves the breaking of a C-H bond:

$$C_2H_6(g) \longrightarrow C_2H_5(g) + H(g) \qquad \Delta H^\circ = +410\ KJ \tag{III.6}$$

$$CHF_3(g) \longrightarrow CF_3(g) + H(g) \qquad \Delta H^\circ = +429\ KJ \tag{III.7}$$

$$CHCl_3(g) \longrightarrow CCl_3(g) + H(g) \qquad \Delta H^\circ = +380\ KJ \tag{III.8}$$

$$CHBr_3(g) \rightarrow CBr_3(g) + H(g) \qquad \Delta H^\circ = +377\ KJ \tag{III.9}$$

	Molar Enthalpy of Atomization (kJ mol^{-1})‡	Bond Enthalpy (kJ mol^{-1})†								
		H—	C—	C=	C≡	N—	N=	N≡	O—	O=
H	218.0	436	413			391			463	
C	716.7	413	348	615	812	292	615	891	351	728
N	472.7	391	292	615	891	161	418	945		
O	249.2	463	351	728					139	498
S	278.8	339	259	477						
F	79.0	563	441			270			185	
Cl	121.7	432	328			200			203	
Br	111.9	366	276							
I	106.8	299	240							

Table III.2: Average Bond Enthalpies [18].

III.5 Enthalpy of Change of Physical State

Energy changes in a system are known as phase changes. Atoms in a solid are tightly packed with the least amount of energy in particular locations. As the temperature rises, they will vibrate more intensely. They obtain enough energy at the melting point (fusion) to move about freely with a rise in average, and energy enters the system [15].

Enthalpy of fusion ΔH_{fus}: energy required to freeze a liquid ,

Enthalpy of vaporization ΔH_{vap}: energy expended on vaporizing a liquid.

These quantities give the absorbed heat during change of state under constant pressure and normal conditions, a measure of energy required for disruption of intermolecular forces and for enhancement in molecular liberty [15]:

$$H_2O\,(s) \longrightarrow H_2O\,(l) \qquad \Delta H_{fus} = 6.01\ KJ \tag{III.10}$$

Since a lot of energy is needed to break intermolecular interactions and transition from the liquid to the gaseous phase, it is equivalent to $40.7kJ/mol$ for water [15].

$$H_2O\,(l) \longrightarrow H_2O\,(g) \qquad \Delta H_{vap} = 40.7\ KJ \tag{III.11}$$

The particles of a solid can move directly into the gaseous state. The enthalpy change required for this transition is called the heat of sublimation, denoted ΔH_{sub} [15].

III.6 Enthalpy of a Chemical Reaction

The heat of combustion to be calculated directly from the heat absorbed by the cooling water. The setup ensures both accurate and practical measurement of reaction enthalpies under controlled conditions [3]

$$\Delta H = Q \tag{III.12}$$

The enthalpy of the system starts taking the value of the reactants in a chemical reaction and changes as the reaction goes on until it reaches the enthalpy of the product. For a given temperature and pressure, the enthalpy of reaction ΔH is the difference between the starting and final enthalpies [16]

$$\Delta H = H_{products} - H_{reactants} = \sum_{\text{Products}} \nu C^{\circ}_{P,m} - \sum_{\text{Reactants}} \nu C^{\circ}_{P,m} \tag{III.13}$$

Since enthalpy H is a state function, the enthalpy change ΔH in a chemical reaction is solely dependent on the reactants (the initial state) and the products (the final state), independent of the mechanism or path followed. Often expressed as ΔH_{rxn}, where "rxn" represents "reaction," this shift is known as the enthalpy of reaction or heat of reaction [15].

When we give a numerical value for ΔH_{rxn}, we must specify the reaction involved. For example, when $2mol\ H_2(g)$ burn to form $2mol\ H_2O\,(g)$ at a constant pressure, the system releases $483.6KJ$ of heat. We can summarize this information as [15]

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \qquad \Delta H \ = \ -483.6\ KJ \tag{III.14}$$

To illustrate the concepts we have introduced, consider the reaction at $25°C$ of sodium metal and water, carried out in a beaker open to the atmosphere at $1atm$ pressure [16].

$$2Na(s)+2H_2O(l) \longrightarrow 2NaOH(aq)+H_2(g) \qquad \Delta H \ = \ -368.6\ KJ \tag{III.15}$$

The reaction between sodium metal and water is extremely exothermic, generating $368.6kJ$ of heat for every mole of sodium (and water). The expression for heat transfer at constant pressure is $q_p = \ -368.6KJ$ because heat is released into the environment. This confirms that the process is exothermic, as the enthalpy change is $\Delta H = \ -368.6KJ$. A typical enthalpy diagram for this energy transition is Figure III.2, where the products show up at a lower enthalpy level than the reactants [16].

III.7 Hess's Law

This concept makes it possible to calculate ΔH for many reactions using tabular ΔH values from other known processes, eliminating the necessity for direct calorimetric measurements in every situation. This greatly increases the efficiency of thermochemical analysis by enabling the calculation of enthalpy changes for a variety of chemical processes using a very little quantity of experimental data [15].

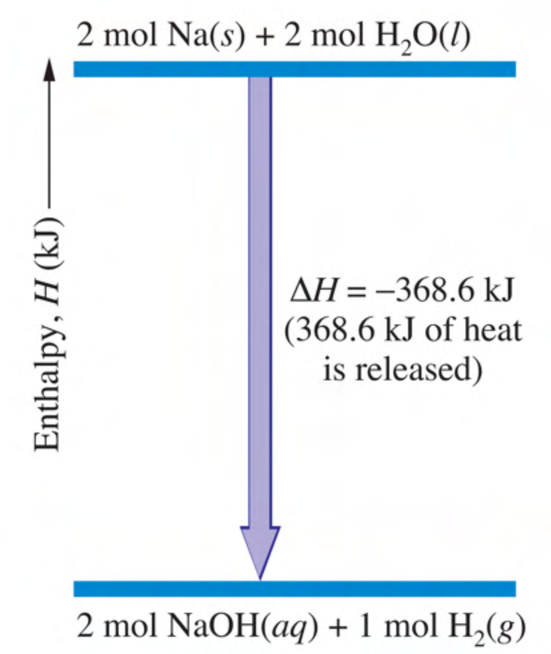


Figure III.2: Enthalpy reactions [16].

Hess's law states that the total enthalpy change for the desired equation, or the overall equation, is equal to the sum of the enthalpies for the two stages. The enthalpy changes for each of the individual processes must now be ascertained [16]. Just burning graphite in too much oxygen will give you the enthalpy change for the first phase. The outcome is $\Delta H = \ -393.5KJ$ per mole of CO_2. To calculate $2mol\ CO_2$, you multiply by two.

$$2C\,(graphite) + 2O_2(g) \rightarrow 2CO_2(g); \quad \Delta H = (-393.5KJ) \times (2) \tag{III.16}$$

You could determine the ΔH for that combustion by burning carbon monoxide in an excess of oxygen. The experiment is similar to the one for the combustion of graphite to carbon dioxide [16].

$$2CO\,(g) + O_2(g) \rightarrow 2CO_2(g); \quad \Delta H = (-566.0KJ) \tag{III.17}$$

The enthalpy change for the reverse reaction is just (-l) times the initial reaction, as you are aware from the characteristics of thermochemical equations.

$$2CO\,(g) + O_2(g) \rightarrow 2CO_2(g); \quad \Delta H = (-566.0KJ) \times (-1) \tag{III.18}$$

If you now add these two steps and add their enthalpy changes, you obtain the chemical equation and the enthalpy change for the combustion of carbon monoxide, which is what you wanted [16].

$$\begin{array}{lll} 2C\,(graphite) + 2O_2(g) & \rightarrow 2CO_2(g) & \Delta H_1 = (-393.5KJ) \times (2) \\ 2CO\,(g) & \rightarrow 2CO_2(g) + O_2(g) & \Delta H_2 = (-566.0KJ) \times (-1) \\ \hline 2C\,(graphite) + O_2(g) & \rightarrow 2CO_2(g) & \Delta H_3 = (-221.0KJ) \end{array} \quad \text{(III.19)}$$

You see that the combustion of $2mol$ of graphite to give $2mol$ of carbon monoxide has an enthalpy change of $-221.0KJ$. Figure III.3 gives an enthalpy diagram showing the relationship among the enthalpy changes for this calculation [16].

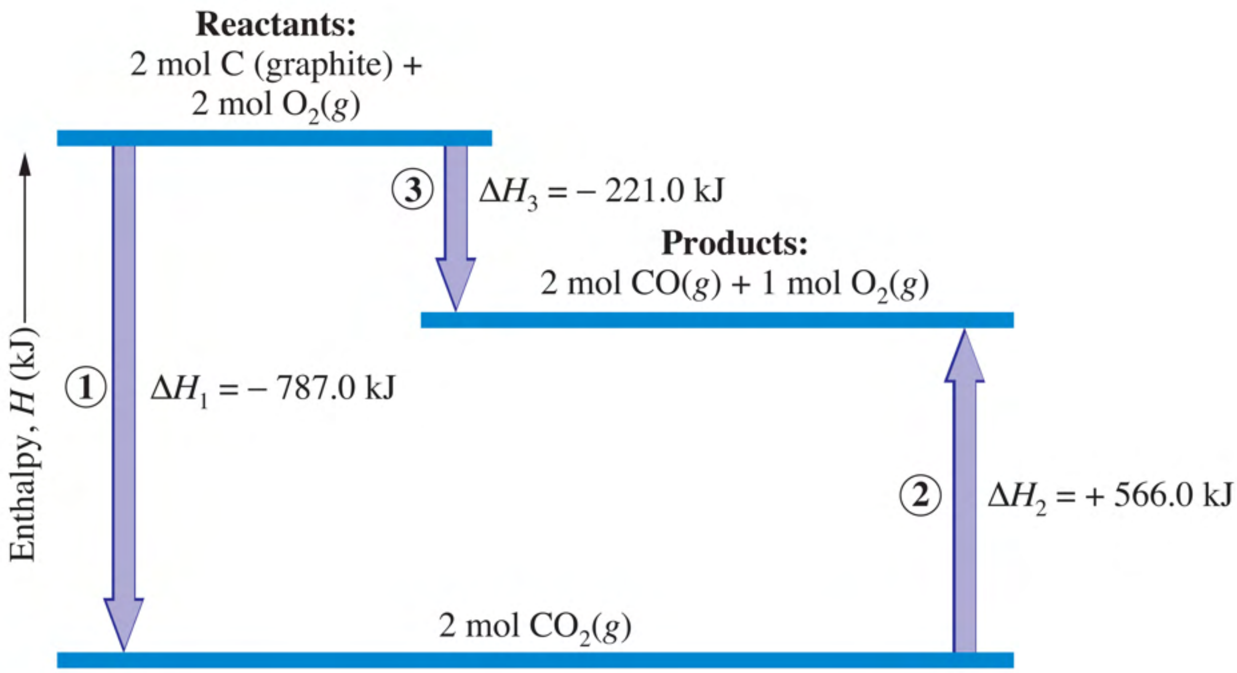


Figure III.3: Enthalpy diagram illustrating Hess's law [16].

III.8 Kirchoff's Law

Although standard enthalpies have been established at various temperatures for a number of significant reactions, these measurements are not always accessible. When they are absent, the enthalpy at a known reference temperature (see Figure III.4) [17] and heat capacity values can be used to determine the reaction enthalpy at a different temperature.

It follows from Equation III.20 that, when a substance is heated from T_1 to T_2, its enthalpy changes from $H\left(T_1\right)$ to

$$H\left(T_2\right) = H\left(T_1\right) + \int_{T_1}^{T_2} C_P dT \tag{III.20}$$

(We have assumed that no phase transition takes place in the temperature range of interest.) Because this equation applies to each substance in the reaction, the standard reaction enthalpy changes from $\Delta_r H^\circ\left(T_1\right)$ to [17]

$$\Delta_r H^\circ\left(T_2\right) = \Delta_r H^\circ\left(T_1\right) + \int_{T_1}^{T_2} \Delta_r C_P^\circ dT \tag{III.21}$$

Where $\Delta_r C_P^\circ$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation:

$$\Delta_r C_P^\circ = \sum_{\text{Products}} \nu C_{P,m}^\circ - \sum_{\text{Reactants}} \nu C_{P,m}^\circ \tag{III.22}$$

Kirchhoff's law is the name given to Equation III.21. Assuming that $\Delta_r C_P^\circ$ is independent of temperature, at least across relatively small ranges, is often an acceptable estimate. Even while each heat capacity may differ, the difference between them is not as great [17].

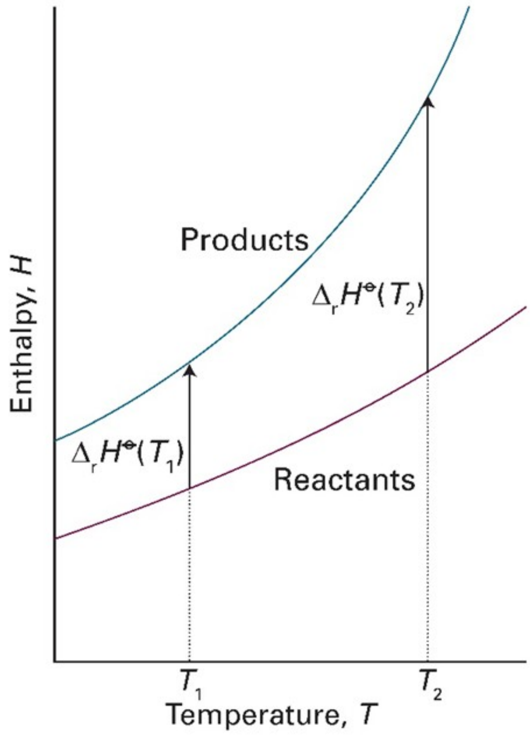


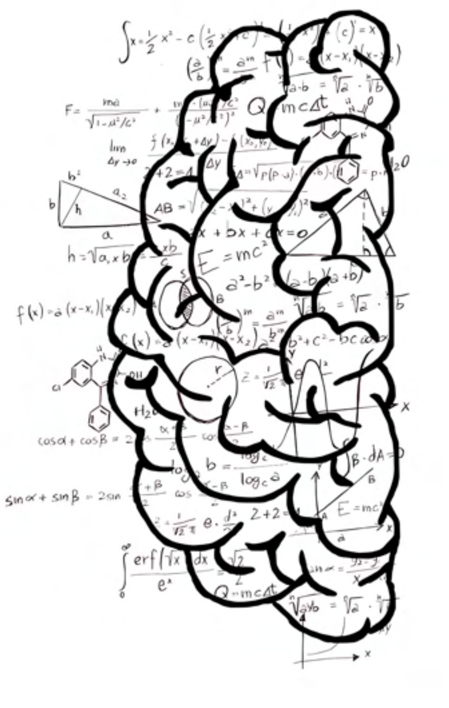
Figure III.4: An illustration of the content of Kirchhoff's law [17].

Property	Equation	Comment
First Law of thermodynamics	$\Delta U = q + w$	Acquisitive convention
Work of expansion	$dw = -p_{ex} dV$	
Work of expansion against a constant external pressure	$w = -p_{ex}\Delta V$	$p_{ex} = 0$ corresponds to free expansion
Work of isothermal reversible expansion of a perfect gas	$w = -nRT\ln(V_f/V_i)$	Isothermal, reversible, perfect gas
Heat capacity at constant volume	$C_V = (\partial U/\partial T)_V$	Definition
Heat capacity at constant pressure	$C_p = (\partial H/\partial T)_p$	Definition
Relation between heat capacities	$C_p - C_V = nR$	Perfect gas
Enthalpy	$H = U + pV$	Definition
The standard reaction enthalpy	$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus$	
Kirchhoff's law	$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$	
Internal pressure	$\pi_T = (\partial U/\partial V)_T$	For a perfect gas, $\pi_T = 0$
Joule–Thomson coefficient	$\mu = (\partial T/\partial p)_H$	For a perfect gas, $\mu = 0$

Table III.3: Laws [17].

PRACTICE

EXERCISES AND SOLUTIONS



III.9 Problem Solving

Problem 7 SKILLS PROBLEM-SOLVING

Water is heated to boiling under a pressure of $1.0atm$. When an electric current of $0.50A$ from a $12V$ supply is passed for $300s$ through a resistance in thermal contact with it, it is found that $0.798g$ of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point ($373.15K$) [17].

Solution 7

$$\Delta H = q_p = (0.50A) \times (12\ V) \times (300\ s) = 0.50 \times 12 \times 300\ J$$

Here we have used $1AVs = 1J$.

Because $0.798g$ of water

is $(0.798g)\,/\,(18.02g\,mol^{-1}) \;=\; (0.798/18.02)\,mol\;H_2O$,

the enthalpy of vaporization per $mole$ of H_2O is

$$\Delta H_m = \;+\frac{0.50 \times 12 \times 300J}{(0.798/18.02)\,mol} = +41\,KJ\,mol^{-1}$$

In the process $H_2O\,(l) \;\rightarrow H_2O\,(g)$ the change in the amount of gas molecules is $\Delta n_g = \;+1mol$, so

$$\Delta U_m = \;\Delta H_m - RT = +38\ KJ\ mol^{-1}$$

Notice that the internal energy change is smaller than the enthalpy change because energy has been used to drive back the surrounding atmosphere to make room for the vapour.

Problem 8 SKILLS PROBLEM-SOLVING

Calculate ΔU and ΔH for $1Kg$ of water when it is vaporized at the constant temperature of $100°C$ and the constant pressure of $101.33KPa$. The specific volumes of liquid and vapor water at these conditions are 0.00104 and $1.673m^3 \cdot Kg^{-1}$, respectively. For this change, heat in the amount of $2256.9KJ$ is added to the water [3].

Solution 8

We take the $1Kg$ of water as the system because it alone is of interest, and we imagine it contained in a cylinder by a frictionless piston that exerts a constant pressure of $101.33Kpa$. As heat is added, the water evaporates, expanding from its initial to its final volume.

$$\Delta H = Q = \ 2256.9\ KJ$$

$$\Delta U = \ \Delta H - \ \Delta(PV) = \ \Delta H - P\Delta V$$

For the final term:

$$P\Delta V = 101.33\ KPa\ \times\ (1.673 - 0.001)\ m^3$$

$$= \ 169.4\ KPa \cdot m^3 = \ 169.4\ kN \cdot m^{-2} \cdot m^3 = \ 169.4\ KJ$$

Then

$$\Delta U = 2256.9 - 169.4 = 2087.5\ KJ$$

Problem 9 SKILLS PROBLEM-SOLVING

The standard reaction enthalpy for the hydrogenation of propene [17] is $-124KJmol^{-1}$.

$$CH_2 = CHCH_3\,(g) + H_2\,(g) \rightarrow CH_3CH_2CH_3\,(g)$$

The standard reaction enthalpy for the combustion of propane is $-2220KJmol^{-1}$.

$$H_3CH_2CH_3\,(g) + 5\ O_2\,(g) \rightarrow 3\ CO_2\,(g) + 4\ H_2O\,(l)$$

Calculate the standard enthalpy of combustion of propene.

Solution 9

The combustion reaction we require is

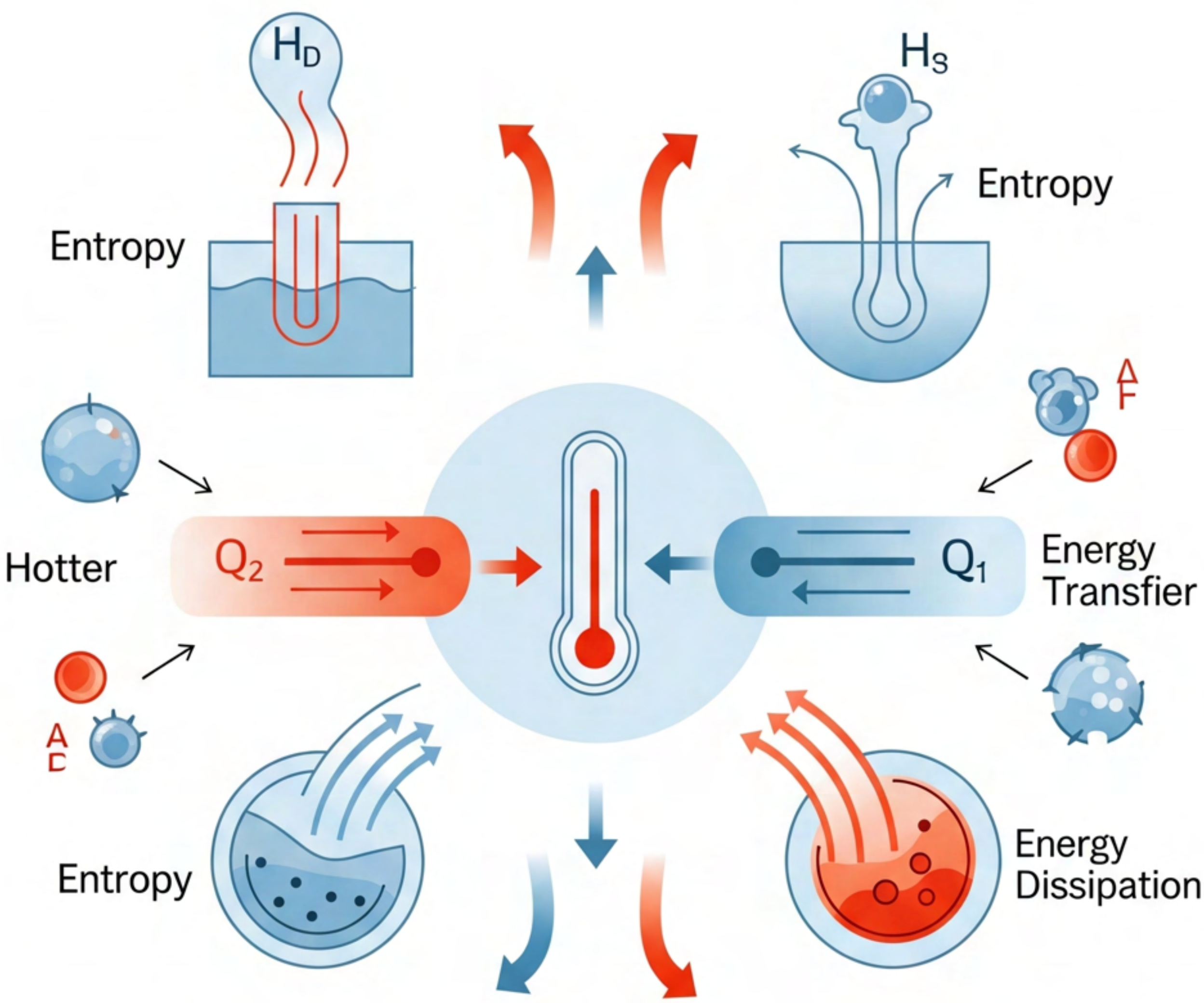
$$C_3H_6\,(g) + O_2\,(g) \rightarrow 3\ CO_2\,(g) + 3\ H_2O\,(l)$$

This reaction can be recreated from the following sum:

$C_3H_6\,(g) + H_2\,(g) \rightarrow C_3H_8\,(g)$	-124
$C_3H_8\,(g) + 5\ O_2\,(g) \rightarrow 3\ CO_2\,(g) + 4\ H_2O\,(l)$	-2220
$H_2O\,(l) \rightarrow H_2\,(g) + O_2\,(g)$	$+286$
$C_3H_6\,(g) + O_2\,(g) \rightarrow 3\ CO_2\,(g) + 3\ H_2O\,(l)$	$-\ 2058$

FOURTH CHAPTER

SECOND LAW OF THERMODYNAMICS



Second Law of Thermodynamics

IV

The second law of thermodynamics complements the first law by introducing the concept of the natural direction of transformations and establishing the conditions for spontaneous evolution of a system. While the first law expresses the conservation of energy, the second law determines the feasibility and direction of processes by introducing a new thermodynamic property: entropy.

This chapter first presents the second law applied to a closed system, highlighting the limitations imposed on real transformations. It distinguishes between possible (irreversible) transformations and ideal (reversible) ones, emphasizing that the second law introduces an additional constraint beyond the energy balance.

The statement of the second law will then be formulated in several ways, focusing particularly on the evolution of entropy. For an isolated closed system, it will be shown that entropy can only increase or remain constant in the case of a reversible process. This principle defines the thermodynamic arrow of time and reflects the irreversibility of natural phenomena.

Next, the chapter will focus on the calculation of entropy variation in different types of reversible transformations:

- **Isothermal reversible transformation:** entropy change related to heat exchange at constant temperature;

- **Isochoric reversible transformation:** entropy change associated with the heat capacity at constant volume;
- **Isobaric reversible transformation:** entropy change linked to the heat capacity at constant pressure;
- **Adiabatic reversible transformation:** constant entropy (isentropic process)

Special cases will also be studied:

- **Phase changes (fusion, vaporization, etc.):** calculation of entropy change from latent heat;
- **Chemical reactions:** determination of the overall entropy change from the standard molar entropies of reactants and products.

These analyses will allow students to relate entropy variation to heat exchanges and heat capacities, providing a deeper understanding of the behavior of systems during real processes.
By the end of this chapter, students should be able to:

- State and interpret the second law for a closed system;
- Calculate entropy variations for various reversible and irreversible transformations;
- Analyze the spontaneous direction of processes;
- Apply the concept of entropy to phase changes and chemical reactions.

This chapter is a key step toward understanding irreversible phenomena, entropy production, and thermodynamic equilibrium, and it lays the foundation for studying thermodynamic cycles and the efficiency of heat engines.

Definitions

The Second Law of Thermodynamics has its roots in the seminal book Reflections on the Motive Power of Fire by Sadi Carnot (1824). Carnot understood that understanding the underlying physical principles of heat engines was essential to their construction. He was the first to show that a heat engine can only generate work when heat moves through a working substance from a hot reservoir to a cold one. He came to the crucial conclusion that without this vital heat transfer between two bodies, no engine could produce work. Carnot presented the Carnot engine, an idealized model, to demonstrate his theories. This theoretical engine operates in a totally reversible cycle, achieving the highest efficiency achievable for any heat engine that operates between two temperatures. No actual engine can ever achieve the efficiency it sets as a basic upper limit [9].

IV.1 Clausius Inequality

The Clausius inequality states it was first stated by the German physicist R. J. E. Clausius (1822–1888), one of the founders of thermodynamics, and is expressed in 1865 [7] for any thermodynamic cycle as

$$\oint \left(\frac{\delta Q}{T}\right)_b \leq 0 \tag{IV.1}$$

where T is the absolute temperature at that system boundary and δQ is the heat transfer at that boundary for a portion of the cycle. Additionally, the subscript "b" reminds us that the integrand is assessed at the system's boundary while the cycle is running. The integral must be completed over the full cycle and over every portion of the boundary, as shown by the symbol [2].

The Clausius inequality can be expressed equivalently as

$$\oint \left(\frac{\delta Q}{T}\right)_b \leq -\sigma_{cycle} \tag{IV.2}$$

where σ_{cycle} can be interpreted as representing the "strength" of the inequality. The value of σ_{cycle} is positive when internal irreversibilities are present, zero when no internal irreversibilities are present, and can never be negative [2]. In summary, the nature of a cycle executed by a system is indicated by the value for σ cycle as follows:

$$\sigma_{cycle} = 0 \quad \text{no irreversibilities present within the system} \tag{IV.3}$$

$$\sigma_{cycle} > 0 \quad \text{irreversibilities present within the system} \tag{IV.4}$$

$$\sigma_{cycle} < 0 \quad \text{impossible} \tag{IV.5}$$

IV.2 Entropy

The only factor affecting a perfect gas's internal energy is temperature, which remains constant in this case. The work that the gas does W is equal to the heat that is absorbed H according to the First Law. The basis for quantitatively characterizing entropy is this reversible heat transfer at a given temperature [19].

$$dQ = dW = pdV = \frac{nRT}{V}\,dV \quad \text{so} \quad \frac{dV}{V} = \frac{dQ}{nRT} \tag{IV.6}$$

We introduce the symbol S for the entropy of the system, and we define the infinitesimal entropy change dS during an infinitesimal reversible process at absolute temperature T as [19]

$$dS = \frac{dQ}{T} \,\text{(infinitesimal reversible process)} \tag{IV.7}$$

If a total amount of heat Q is added during a reversible isothermal process at absolute temperature T, the total entropy change $\Delta S = S_2 - S_1$ is given by

$$\Delta S = S_2 - S_1 = \frac{Q}{T} \quad \text{(reversible isothermal process)} \tag{IV.8}$$

Entropy has units of energy divided by temperature; the SI unit of entropy is $1J/K$.

IV.2.1 Entropy Generation

Consider an irreversible thermodynamic cycle involving two processes. Process l-2 includes the cycle's irreversibilities, but process 2-l is reversible. The Clausius inequality may now be extended to [4]

$$\oint \left(\frac{\delta Q}{T}\right) = \int_1^2 \left(\frac{\delta Q}{T}\right) + \int_1^2 \left(\frac{\delta Q}{T}\right)_{rev} \leq 0 \tag{IV.9}$$

$$dS = \left(\frac{\delta Q}{T}\right)_{rev} \tag{IV.10}$$

When the two processes are both reversible, Equation IV.9 is equal to 0 (i.e., there are no irreversibilities in process 1-2).

Substituting with Equation IV.10,

$$\int_1^2 \left(\frac{\delta Q}{T}\right) + \int_1^2 dS \leq 0 \tag{IV.11}$$

and

$$\int_1^2 \left(\frac{\delta Q}{T}\right) + S_1 - S_2 \leq 0 \tag{IV.12}$$

Rearranging,

$$\int_1^2 \left(\frac{\delta Q}{T}\right) \leq S_1 - S_2 \tag{IV.13}$$

The irreversibility of a process is determined by the difference between the actual entropy change and the entropy change from heat transfer in a reversible process. This is because the entropy change for a reversible process is equal to the entropy transmitted by heat. This difference could be called the entropy that is created during a process, or simply the entropy generation S_{gen}. Incorporating this concept into Equation IV.13 and rewriting produces

[4].

$$S_{gen} = S_2 - S_1 - \int_1^2 \left(\frac{\delta Q}{T}\right) \tag{IV.14}$$

Using Equation IV.14, the amount of entropy that is generated during a process can be calculated. Note that for irreversible processes, which all real processes should be considered, entropy is always generated [4].

According to an entropy generation perspective, the following rules apply with respect to a process [4]:

$$S_{gen} > 0 \quad \text{Process is possible and irreversible} \tag{IV.15}$$

$$S_{gen} = 0 \quad \text{Process is possible and reversible} \tag{IV.16}$$

$$S_{gen} < 0 \quad \text{Process is impossible} \tag{IV.17}$$

IV.2.2 Evaluating Changes in the Entropy of a System

Practical formulas for entropy changes can be obtained by integrating the First Law of Thermodynamics with equations of state and property relations [4]

$$dQ - dW = dU \tag{IV.18}$$

For a simple compressible process,

$$\delta W = PdV \tag{IV.19}$$

For a reversible process, from Equation IV.10,

$$dQ = TdS \tag{IV.20}$$

Combining Equations IV.19 and IV.20 into IV.18 yields

$$TdS = dU + PdV \tag{IV.21}$$

Considering that $H = U + PV$,

$$dH = dU + PdV + VdP \tag{IV.22}$$

Substituting Equation IV.22 into Equation IV.21,

$$TdS = dH - VdP \tag{IV.23}$$

These equations can be divided by the system's mass, yielding relationships based on intensive properties [4]:

$$TdS = dU + PdV \tag{IV.24}$$

$$TdS = dH - VdP \tag{IV.25}$$

IV.2.3 Change in Entropy for Ideal Gases

As you can see in Equations IV.24 and IV.25, the change in specific entropy will depend on a change in either the specific internal energy or the specific enthalpy. These changes, for an ideal gas, are related to the change in temperature through [4]

$$dU = C_V dT \tag{IV.26}$$

and

$$dH = C_P dT \tag{IV.27}$$

These expressions can be substituted into the Gibbs equations, and the resulting equations are easily integrated if the specific heats are assumed to be constant. Incorporating in the ideal gas law ($P = RT/V$ or $V = RT/P$) allows Equations IV.24 and IV.25 to become [4]

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V} \tag{IV.28}$$

and

$$dS = C_P \frac{dT}{T} - R\frac{dP}{P} \tag{IV.29}$$

With the assumption of constant specific heats, integration yields

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \tag{IV.30}$$

and

$$S_2 - S_1 = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \tag{IV.31}$$

IV.2.4 Ideal Gases Considering Variable Specific Heats

When the variability of the specific heats for the ideal gas is taken into account, it is required to evaluate the effect of the changing specific heat on the change in specific enthalpy in Equation IV.25 or the change in specific internal energy in Equation IV.24. Typically, this just requires the usage of Equation IV.25. Including Equation IV.27, the ideal gas law, and then integrating Equation IV.25 gets [4].

$$S_2 - S_1 = \int_1^2 C_P \frac{dT}{T} - R \ln \frac{P_2}{P_1} \tag{IV.32}$$

Because the enthalpy change portion of Equations IV.32 is only a function of temperature for ideal gases, an entropy function based on the temperature of the ideal gas, so T, is often used to aid in completing the calculation [4]:

$$S_T^\circ = \int_1^2 C_P \frac{dT}{T} \tag{IV.33}$$

The values for S_T° are typically evaluated at a pressure of $101.325KPa$. Using Equations IV.32 and IV.33 can be rewritten to provide an expression that can be used to determine the change in specific entropy of an ideal gas with the variability of the specific heats taken into account [4]:

$$S_2 - S_1 = S_{T_2}^\circ - S_{T_1}^\circ - R \ln \frac{P_2}{P_1} \tag{IV.34}$$

IV.2.5 Change in Entropy for Incompressible Substances

A simple expression for the entropy change for incompressible substances can also be developed. We normally assume solids and liquids to be incompressible, unless the substance experiences a very large pressure change during a process. If $V = constant$, $dV = 0$, and for incompressible substances, Equation IV.24 reduces to [4]

$$TdS = C_V dT \tag{IV.35}$$

Considering that $C_P = C_V = C$ for an incompressible substance, Equation IV.35 becomes

$$dS = C\frac{dT}{T} \tag{IV.36}$$

If the specific heat of the incompressible substance is assumed to be constant, Equation IV.36 can be integrated to yield [4].

$$S_2 - S_1 = C \ln \frac{T_2}{T_1} \tag{IV.37}$$

IV.3 Entropy Change During Different Processes

IV.3.1 Isothermal Process

An isothermal expansion 1-2 at constant temperature T is shown in Figure IV.1. Entropy changes from S_1 to S_2 when gas absorbs heat during expansion [14]. The heat taken by the gas is given by the area under the line 1-2 which also represents the work done during expansion. In other words, $Q = W$ [14].

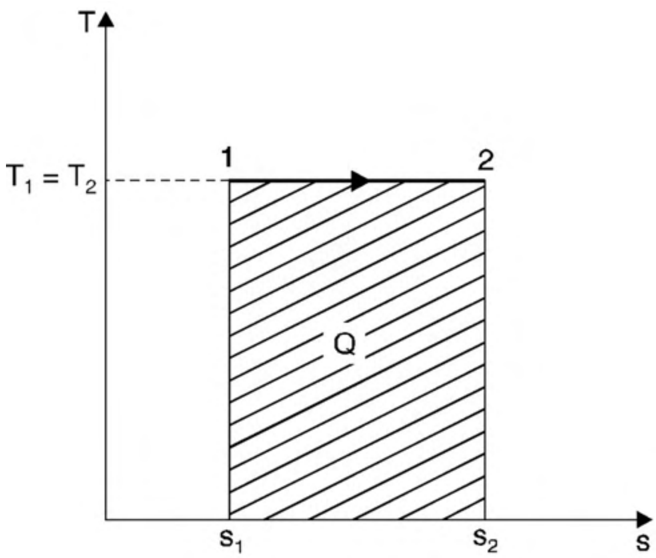


Figure IV.1: $T - S$ diagram: Isothermal process [14].

Therefore, entropy change shall be;

$$Q = \int_{S_1}^{S_2} T dS = T (S_2 - S_1) \quad \text{(IV.38)}$$

and

$$W = P_1 V_1 \ln \frac{V_2}{V_1} = RT_1 \ln \frac{V_2}{V_1} \; per\, Kg\, of\, gas \quad \text{(IV.39)}$$

$$T (S_2 - S_1) = RT_1 \ln \frac{V_2}{V_1} \quad \text{(IV.40)}$$

Or

$$(S_2 - S_1) = R_1 \ln \frac{V_2}{V_1} \quad \text{(IV.41)}$$

IV.3.2 Heating a Gas at Constant Volume

Refer Figure IV.2. Let $1Kg$ of gas be heated at constant volume and let the change in entropy and absolute temperature be from S_1 to S_2 and T_1 to T_2 respectively [14].

Then

$$Q = C_V (T_2 - T_1) \quad \text{(IV.42)}$$

Differentiating to find small increment of heat dQ corresponding to small rise in temperature dT.

$$dQ = C_V dT \quad \text{(IV.43)}$$

Dividing both sides by T, we get

$$\frac{dQ}{T} = C_V \frac{dT}{T} \quad \text{(IV.44)}$$

$$dS = C_V \frac{dT}{T} \quad \text{(IV.45)}$$

When we combine the two, we obtain

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} \quad \text{(IV.46)}$$

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} \quad \text{(IV.47)}$$

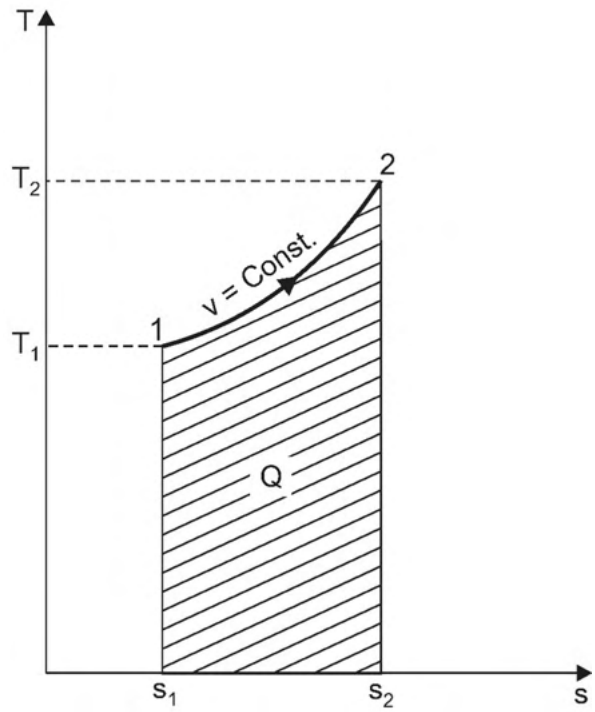


Figure IV.2: $T - S$ diagram: Constant volume process [14]

IV.3.3 Heating a Gas at Constant Pressure

Refer Figure IV.3. Let $1Kg$ of gas be heated at constant pressure, so that its absolute temperature changes from T_1 to T_2 and entropy S_1 to S_2 [14].

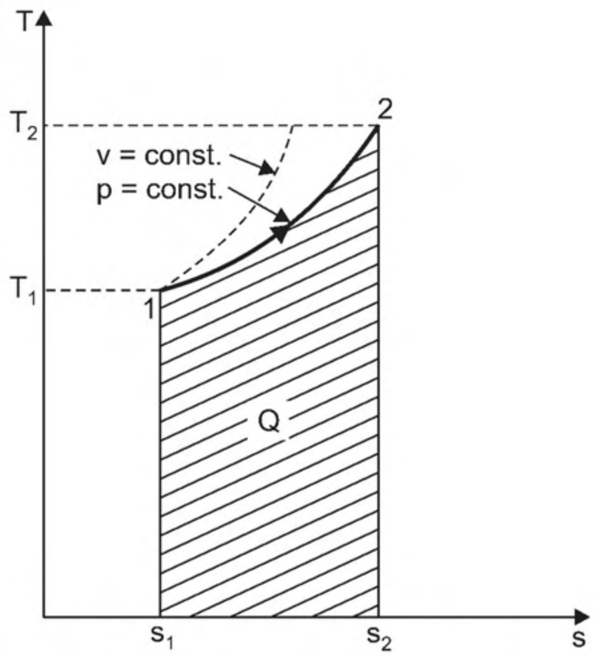


Figure IV.3: $T - S$ diagram: Constant pressure process [14].

Then

$$Q = C_P (T_2 - T_1) \tag{IV.48}$$

Differentiating to find small increase in heat, dQ of this gas when the temperature rise is dT.

$$dQ = C_P dT \tag{IV.49}$$

Dividing both sides by T, we get

$$\frac{dQ}{T} = C_P \frac{dT}{T} \tag{IV.50}$$

$$dS = C_P \frac{dT}{T} \tag{IV.51}$$

Integrating both sides, we get

$$\int_{S_1}^{S_2} dS = C_P \int_{T_1}^{T_2} \frac{dT}{T} \tag{IV.52}$$

$$S_2 - S_1 = C_P \ln \frac{T_2}{T_1} \tag{IV.53}$$

IV.3.4 Adiabatic Process (Reversible)

During an adiabatic process as heat is neither supplied nor rejected [14],

$$dQ = 0 \tag{IV.54}$$

$$\frac{dQ}{dT} = 0 \tag{IV.55}$$

$$dS = 0 \tag{IV.56}$$

This indicates that there is no change in entropy, making it an isentropic process. Figure IV.4 illustrates an adiabatic process. Because it is a vertical line (l-2), the area under it is 0; hence, heat provided or removed, as well as entropy change, are zero.

For any such case, Equations IV.30 and IV.31 reduce to the equations [2]

$$0 = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \tag{IV.57}$$

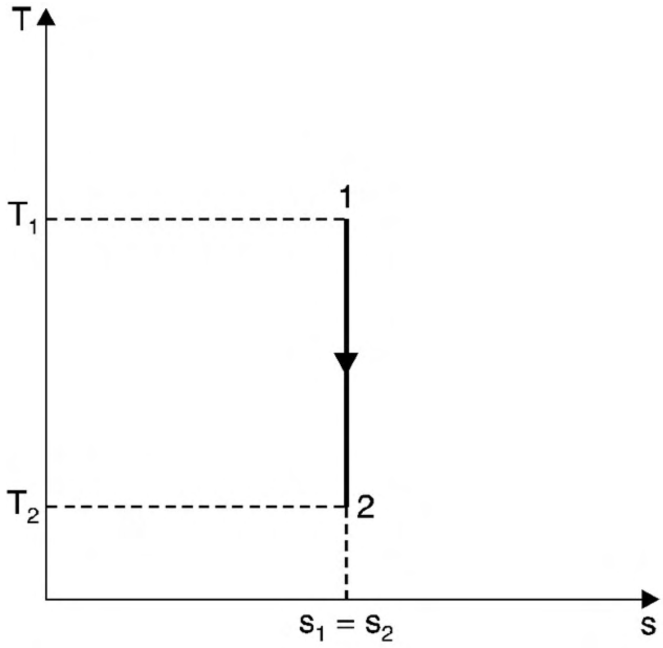


Figure IV.4: $T - S$ diagram: Adiabatic process [14].

$$0 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \tag{IV.58}$$

Introducing the ideal gas relations

$$C_P = \frac{\gamma R}{\gamma - 1}, \quad C_V = \frac{R}{\gamma - 1} \tag{IV.59}$$

where γ is the specific heat ratio and R is the gas constant, these equations can be solved, respectively, to give [2]

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} \qquad S_1 = S_2, \text{constant}\,\gamma \tag{IV.60}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad S_1 = S_2, \text{constant}\,\gamma \tag{IV.61}$$

The following relation can be obtained by eliminating the temperature ratio from Equations IV.60 and IV.61 [2]:

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} \qquad S_1 = S_2, \text{constant}\,\gamma \tag{IV.62}$$

IV.3.5 Polytropic Process

The expression for "entropy change" in polytropic process ($PV^n = constant$) can be obtained from Equation IV.30

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \tag{IV.63}$$

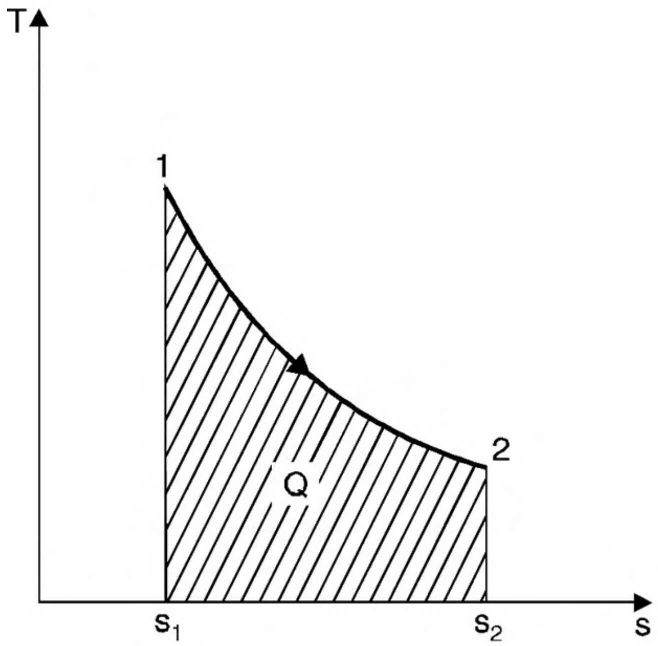


Figure IV.5: $T - S$ diagram: Polytropic process [14].

$$P_1 {V_1}^n = P_2 {V_2}^n \tag{IV.64}$$

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^n \tag{IV.65}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{IV.66}$$

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}\frac{T_1}{T_2} \tag{IV.67}$$

From Equations IV.65 and IV.67, we get [14]

$$\left(\frac{V_2}{V_1}\right)^n = \frac{V_2}{V_1}\frac{T_1}{T_2} \tag{IV.68}$$

$$\left(\frac{V_2}{V_1}\right)^{n-1} = \frac{T_1}{T_2} \tag{IV.69}$$

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{T_1}{T_2}\right)^{\frac{1}{n-1}} \tag{IV.70}$$

Substituting the value of $\frac{V_2}{V_1}$ in Equation IV.30, we get [14]:

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \left(\frac{T_1}{T_2}\right)^{\frac{1}{n-1}} = C_V \ln \frac{T_2}{T_1} + R\left(\frac{1}{n-1}\right) \ln \left(\frac{T_1}{T_2}\right) \quad \text{(IV.71)}$$

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} - R\left(\frac{1}{n-1}\right) \ln \left(\frac{T_2}{T_1}\right) \quad \text{(IV.72)}$$

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} - (C_V - C_P)\left(\frac{1}{n-1}\right) \ln \left(\frac{T_2}{T_1}\right) \quad \text{(IV.73)}$$

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} - (\gamma.C_V - C_P)\left(\frac{1}{n-1}\right) \ln \left(\frac{T_2}{T_1}\right) \quad \text{(IV.74)}$$

$$S_2 - S_1 = C_V \left[1 - \left(\frac{\gamma - 1}{n-1}\right)\right] \ln \left(\frac{T_2}{T_1}\right) = C_V \left[\left(\frac{(n-1)-(\gamma-1)}{(n-1)}\right)\right] \ln \left(\frac{T_2}{T_1}\right) \quad \text{(IV.75)}$$

$$S_2 - S_1 = \left[\left(\frac{(n-1-\gamma+1)}{(n-1)}\right)\right] \ln \left(\frac{T_2}{T_1}\right) \quad \text{(IV.76)}$$

$$S_2 - S_1 = \left[\left(\frac{(n-\gamma)}{(n-1)}\right)\right] \ln \left(\frac{T_2}{T_1}\right) \text{ per Kg of gas} \quad \text{(IV.77)}$$

IV.4 Entropy for Phase Changes

In the same way as internal energy U and enthalpy H are state functions, so is entropy S. Only the system's current state determines its worth; how the system got there is not. Consequently, the beginning and ending circumstances alone define the change in entropy ΔS between two states, regardless of the procedure or route followed. One essential characteristic of entropy that contributes to its potency in thermodynamic analysis is its route independence [15]:

$$\Delta S = S_{final} - S_{initial} \quad \text{(IV.78)}$$

For the special case of an isothermal process, ΔS is equal to the heat that would be transferred if the process were reversible, q_{rev}, divided by the absolute temperature at which the process occurs [15]:

$$\Delta S = \frac{q_{rev}}{T} \text{ (constant T)} \tag{IV.79}$$

There are several ways to move the system from one state to another, but only one of those ways is associated with a reversible process. Thus, the value of q_{rev} is uniquely defined for any two states of the system. Because S is a state function, we can use Equation IV.79 to calculate ΔS for any isothermal process between states, not just the reversible one [15].

The enthalpy of fusion for H_2O is $\Delta H_{fusion} = 6.01KJ/mol$ (a positive value because melting is an endothermic process). Thus, we can use Equation IV.79 to calculate ΔS_{fusion} for melting $1mol$ of ice at $273K$ [15]:

$$\Delta S_{fusion} = \frac{q_{rev}}{T} = \frac{\Delta H_{fusion}}{T} = \frac{(1\,mol)\,(6.01 \times 10^3\ J/mol\ )}{273K} = 22.0J/K \tag{IV.80}$$

Notice that (1) we must use the absolute temperature in Equation IV.79, and (2) the units for ΔS, J/K, are energy divided by absolute temperature, as we expect from Equation IV.79.

IV.5 Entropy for Chemical Reaction

The change in entropy, ΔS°, for a reaction may be computed when the standard entropies of each participant in the process have been established. It is occasionally possible to anticipate the sign of ΔS° for a reaction even in the absence of values for the entropies of substances.

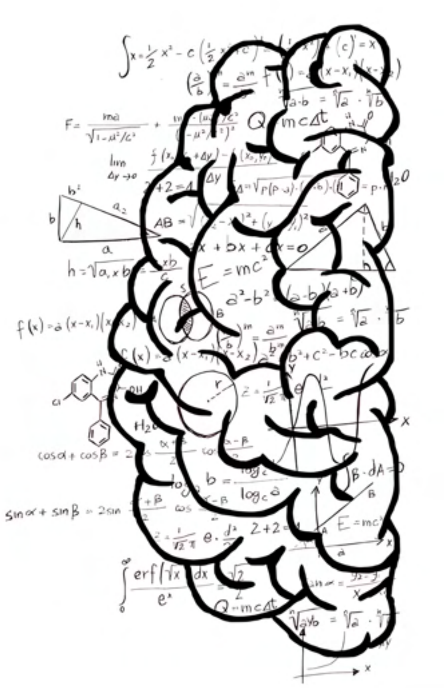
Predicting the sign of ΔS° is important. The reaction becomes somewhat clearer to you, and you might utilize the prediction in qualitative research. You must, however, determine the value of ΔS° for quantitative work. As with ΔH, you may deduct the standard entropies of reactants from the standard entropies of products to find the standard change of entropy, ΔS°, for a process [16].

$$\Delta S^{\circ} = \sum nS^{\circ}\,(\text{products}) - \sum mS^{\circ}\,(\text{reactants}) \tag{IV.81}$$

The coefficients n and m are the coefficients in the balanced chemical equation for the reaction [17].

PRACTICE

EXERCISES AND SOLUTIONS



IV.6 Problem Solving

Problem 10 SKILLS PROBLEM-SOLVING

Now, let's consider the previous example, but make the heat transfer irreversible by having the object have a temperature of $300K$ Determine the change in entropy of the thermal reservoir, the object, and the universe. Given: $T_{b,res} = 500K$, $T_{b,obj} = 300K$, $Q_{res} = -1000KJ$, $Q_{obj} = +1000KJ$ (where "res" is the thermal reservoir, and "obj" is the object). The heat transfer is irreversible [4].
Find: $\Delta S_{res}, \Delta S_{obj}, \Delta S_{universe}$.

Solution 10

The relations between absolute and relative temperatures are

For the reservoir,

$$Q_{res} = -1000\ KJ, \text{ and } T_{b,res} = 500\ K, \text{ so}$$

$$\Delta S_{res} = Q_{res}/T_{b,res} = (-1000\ KJ)/500\ K = -2\ KJ/K$$

For the object,

$$Q_{obj} = +1000\ KJ, \text{ and } T_{b,obj} = 300\ K, \text{ so}$$

$$\Delta S_{obj} = Q_{obj}/T_{b,obj} = (+1000\ KJ)/300\ K = +3.33\ KJ/K$$

Because these are the only two items in consideration for the "universe",

$$S_{universe} = \Delta S_{res} + \Delta S_{obj} = 1.33\ KJ/K$$

Problem 11 SKILLS PROBLEM-SOLVING

A $40Kg$ steel casting $(C_P = 0.5KJ \cdot Kg^{-1} \cdot K^{-1})$ at a temperature of $450°C$ is quenched in $150Kg$ of oil $(C_P = 2.5KJ \cdot Kg^{-1} \cdot K^{-1})$ at$25°C$. If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together [3]?

Solution 11

The final temperature t of the oil and the steel casting is found by an energy balance. Because the change in energy of the oil and steel together must be zero,

$$(40)\,(0.5)\,(t - \ 450) + (150)\,(2.5)\,(t \ - \ 25) = 0$$

Solution yields $t = 46.52°C$.

(a) Change in entropy of the casting:

$$\Delta S^t = m\int \frac{C_P dT}{T} = mC_P \ln\frac{T_2}{T_1}$$

$$= \ (40)\,(0.5)\ \ ln\frac{273.15 + 46.52}{273.15 + 450} = -16.33\ kJ \cdot K^{-1}$$

(b) Change in entropy of the oil:

$$\Delta S^t = \ (150)\,(2.5)\ \ ln\frac{273.15 + 46.52}{273.15 + 25} = 26.13\ kJ \cdot K^{-1}$$

(c) Total entropy change:

$$\Delta S_{total} = -16.33 + 26.13 \ = 9.80\ KJ \cdot K^{-1}$$

Note that although the total entropy change is positive, the entropy of the casting has decreased.

Problem 12 SKILLS PROBLEM-SOLVING

A $2.0Kg$ block of iron at $20°C$ is dropped into a large bucket of boiling water at $100°C$. The iron is heated until its temperature is $100°C$. Determine the increase in entropy of the iron during this process [4].

Given: $m = 2.0Kg$, $T_1 = 20°C$= $293K$, $T_2 = 100°C$= $373K$

Find: ΔS (the change in total entropy for the iron)

Solution 12

Assume: The iron behaves as an incompressible substance with constant specific heats. For the change in total entropy:

$$S_2 - S_1 - m\,(s_2 - s_1)$$

Assuming that the iron behaves as an incompressible substance with constant specific heats, can be used for the change in specific entropy. For iron, $C = 0.45KJ/Kg.K$.

$$S_2 - S_1 = m\left(C\ln\frac{T_2}{T_1}\right) = \left(2\,(0.45)\ln\frac{373}{293}\right)$$

$$S_2 - S_1 = 0.217\,KJ/K$$

FIFTH CHAPTER

THIRD LAW OF THERMODYNAMICS

Third Law of Thermodynamics

V

The third law of thermodynamics completes the fundamental framework of classical thermodynamics. After the first law, which expresses the conservation of energy, and the second law, which establishes the direction of spontaneous processes, the third law introduces an absolute reference for the thermodynamic quantity known as entropy, allowing it to be expressed with an absolute value, not only as a variation.

This law, often stated as the Nernst principle, affirms that the entropy of a pure, perfectly crystalline substance tends toward zero as the temperature approaches absolute zero . At this limit, the system reaches a state of perfect order, with no thermal agitation and no possible internal transformations.

The chapter begins by presenting the physical foundations and formulations of the third law, followed by its consequences on the behavior of thermodynamic systems at very low temperatures. A key implication, the principle of the inaccessibility of absolute zero, will be discussed — it states that absolute zero cannot be reached through any finite number of operations.

Next, the chapter explains how to calculate the absolute entropy of a system from absolute zero by integrating the heat exchanged in reversible transformations:
This approach makes it possible to determine the absolute entropy values of pure substances at any given temperature — essential data for

thermochemistry, phase equilibria, and chemical reaction analysis.

The applications of the third law also include:

- Understanding the behavior of heat capacities at low temperatures;
- Explaining the concept of residual entropy;
- Ensuring consistency in entropy balances for physical and chemical transformations.

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

- State and interpret the Third Law of Thermodynamics;
- Explain the concept of absolute entropy;
- Calculate absolute entropy values from $0K$;
- Discuss the thermodynamic implications of the third law at low temperatures.

This chapter concludes the study of the fundamental laws of thermodynamics, providing the essential foundation for a quantitative and predictive understanding of energy and entropy in physical and chemical processes.

V.1 The Nernst Heat Theorem

The experimental observation that turns out to be consistent with the view that the entropy of a regular array of molecules is zero at $T = 0$ is summarized by the Nernst heat theorem:

Theorem

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly ordered.

Theorem

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropies of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline co pounds also have zero entropy at $T = 0$ (because the change in entropy that accompanies the formation of the compounds, like the entropy of all transformations at that temperature, is zero).

Theorem

This conclusion is summarized by the Third Law of thermodynamics [17]: The entropy of all perfect crystalline substances is zero at $T = 0$.

V.2 Third Law Entropies

Entropies reported on the basis that $S(0) = 0$ are called Third-Law entropies (and often just 'entropies'). When the substance is in its standard state at the temperature T, the standard (Third-Law) entropy is denoted $S^\circ(T)$. A list of values at $298K$ is given in Table V.1.

The standard reaction entropy, $S^\circ(T)$, is defined, like the standard reaction enthalpy, as the difference between the molar entropies of the pure, separated products and the pure, separated reactants, all substances being in their standard states at the specified temperature [17]:

$$\Delta_r S^\circ = \sum n S_m^\circ\,(\text{products}) - \sum m S_m^\circ\,(\text{reactants}) \tag{V.1}$$

The coefficients n and m are the coefficients in the balanced chemical equation for the reaction [17].

$$\Delta_r S^\circ = \sum_J \nu_J S_m^\circ \tag{V.2}$$

The entropy at the same temperature but a different pressure P can be computed using the proper thermodynamic relation for entropy change with pressure, for instance, if the absolute entropy is known at temperature T and pressure P_{ref}. This technique eliminates the requirement for direct measurement and allows scientists and engineers to assess absolute entropy under a variety of circumstances [2].

We can use Equation IV.77 to calculate the entropy of a system at a temperature T_f from a knowledge of its entropy at another temperature T_i and the heat supplied to change its temperature from one value to the other [17]:

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{dq_{rev}}{T} \tag{V.3}$$

From the definition of constant-pressure heat capacity $(dq_{rev} = C_P dT)$. Consequently, at constant pressure [17]:

Substance or Ion	S_f° J/(mol·K)	Substance or Ion	S_f° J/(mol·K)	Substance or Ion	S_f° J/(mol·K)
$e^-(g)$	20.87	*Aldehydes (continued)*		**Nitrogen** *(continued)*	
Bromine		$CH_3CHO(g)$	246.4	$NO_2(g)$	239.9
$Br(g)$	174.9	$CH_3CHO(l)$	160.4	$HNO_3(aq)$	146.4
$Br^-(aq)$	82.4	**Chlorine**		**Oxygen**	
$Br^-(g)$	163.4	$Cl(g)$	165.1	$O(g)$	160.9
$Br_2(g)$	245.3	$Cl^-(aq)$	56.5	$O_2(g)$	205.0
$Br_2(l)$	152.2	$Cl^-(g)$	153.2	$O_3(g)$	238.8
$HBr(g)$	198.6	$Cl_2(g)$	223.0	$OH^-(aq)$	−10.75
Calcium		$HCl(g)$	186.8	$H_2O(g)$	188.7
$Ca(s)$	41.59	**Fluorine**		$H_2O(l)$	69.95
$Ca^{2+}(aq)$	−53.1	$F(g)$	158.6	**Silicon**	
$CaCO_3(s$, calcite)	92.9	$F^-(g)$	145.5	$Si(s)$	18.82
$CaO(s)$	38.21	$F^-(aq)$	−13.8	$SiCl_4(l)$	239.7
Carbon		$F_2(g)$	202.7	$SiF_4(g)$	282.7
$C(g)$	158.0	$HF(g)$	173.7	$SiO_2(s$, quartz)	41.46
$C(s$, diamond)	2.377	**Hydrogen**		**Silver**	
$C(s$, graphite)	5.740	$H(g)$	114.6	$Ag(s)$	42.55
$CCl_4(g)$	309.7	$H^+(aq)$	0	$Ag^+(aq)$	72.68
$CCl_4(l)$	216.4	$H^+(g)$	108.8	$AgBr(s)$	107.1
$CO(g)$	197.5	$H_2(g)$	130.6	$AgCl(s)$	96.2
$CO_2(g)$	213.7	**Iodine**		$AgF(s)$	83.7
$CO_3^{2-}(aq)$	−56.9	$I(g)$	180.7	$AgI(s)$	115.5
$CS_2(g)$	237.9	$I^-(aq)$	109.6	**Sodium**	
$CS_2(l)$	151.3	$I^-(g)$	169.2	$Na(g)$	153.6
$HCN(g)$	201.7	$I_2(s)$	116.1	$Na(s)$	51.46
$HCN(l)$	112.8	$HI(g)$	206.5	$Na^+(aq)$	59.1
$HCO_3^-(aq)$	91.2	**Lead**		$Na^+(g)$	147.8
Hydrocarbons		$Pb(s)$	64.78	$Na_2CO_3(s)$	138.8
$CH_4(g)$	186.1	$Pb^{2+}(aq)$	10.5	$NaCl(s)$	72.12
$C_2H_4(g)$	219.2	$PbO(s)$	66.32	$NaHCO_3(s)$	101.7
$C_2H_6(g)$	229.5	$PbS(s)$	91.34	**Sulfur**	
$C_6H_6(l)$	173.4	**Nitrogen**		$S(g)$	167.7
Alcohols		$N(g)$	153.2	$S(s$, monoclinic)	33.03
$CH_3OH(l)$	126.8	$N_2(g)$	191.6	$S(s$, rhombic)	32.06
$C_2H_5OH(l)$	160.7	$NH_3(g)$	192.7	$S_2(g)$	228.1
Aldehydes		$NH_4^+(aq)$	113.4	$SO_2(g)$	248.1
$HCHO(g)$	219.0	$NO(g)$	210.6	$H_2S(g)$	205.6

Table V.1: Standard Entropies $(at\ 25°C)$ [16].

$$S\left(T_f\right) = S\left(T_i\right) + \int_{T_i}^{T_f} \frac{C_P dT}{T} \tag{V.4}$$

The same formula is correct at constant volume, but C_V is used in instead of C_P . In the temperature range of interest, C_P may be taken outside the integral and we get [17] when it is temperature independent.

$$S\left(T_f\right) = S\left(T_i\right) + \int_{T_i}^{T_f} \frac{C_P dT}{T} = S\left(T_i\right) + C_P \ln \frac{T_f}{T_i} \tag{V.5}$$

The entropy of a system at a temperature T is related to its entropy at $T = 0$ by measuring its heat capacity C_P at different temperatures and evaluating the integral in Equation IV.81, taking care to add the entropy of transition $(\Delta_{trs}H/T_{trs})$ for each phase transition between $T = 0$ and the temperature of interest [17].

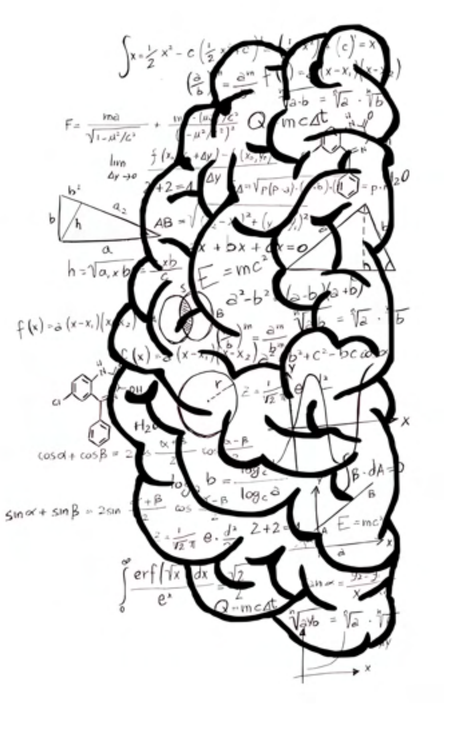
For example, if a substance melts at T_f and boils at T_b, then its molar entropy above its boiling temperature is given by [17]

$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{P,m}(S,T)}{T} dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{P,m}(1,T)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_{P,m}(g,T)}{T} dT \tag{V.6}$$

As the entropy of a perfect crystal is zero at $0K$, the Third Law of Thermodynamics allows absolute entropy values to be given. However, in reality, a lot of thermodynamic issues only deal with entropy variations rather than absolute quantities. As a result, easy reference states are often employed.

PRACTICE

EXERCISES AND SOLUTIONS



V.3 Problem Solving

Problem 13 SKILLS PROBLEM-SOLVING

An iron cube at a temperature of $400°C$ is dropped into an insulated bath containing $10Kg$ water at $25°C$. The water finally reaches a temperature of $50°C$ at steady state. Given that the specific heat of water is equal to $4186J/KgK$. Find the entropy changes for the iron cube and the water. Is the process reversible ? If so why [14]?

Solution 13

Entropy changes for the iron cube and the water: Is the process reversible?

Now, Heat lost by iron cube = Heat gained by water

$$m_i C_{Pi}\,(673 - 323) \;= m_w C_{Pw}\,(323 - 298) \;= 10 \times 4186 \;(323 - 298)$$

$$m_i C_{Pi} = \frac{10\,(4186)\,(323 - 298)}{623 - 323} = 2990$$

Entropy of iron at

$$673K = m_i C_{Pi} \ln\left(\frac{673}{273}\right)$$

$$= 2990 \ln\left(\frac{673}{273}\right) = 2697.8 \; J/K$$

$$298K = m_w C_{Pw} \ln\left(\frac{298}{273}\right)$$

$$= 10\,(4186) \ln\left(\frac{673}{273}\right) = 3667.8\, J/K$$

Entropy of iron at

$$323K = 2990 \ln\left(\frac{323}{273}\right) = 502.8\, J/K$$

Entropy water at

$$323K = 10\,(4186) \ln\left(\frac{323}{273}\right) = 7040.04\, J/K$$

Changes in entropy of iron $= 502.8 – 2697.8 = –2195 J/K$

Change in entropy of water $= 7040.04 – 3667.8 = 3372.24 J/K$

Net change in entropy $= 3372.24 – 2195 = 1177.24 J/K$

Problem 14 SKILLS PROBLEM-SOLVING

An ideal gas is heated from temperature T_1 to T_2 by keeping its volume constant. The gas is expanded back to its initial temperature according to the law $PV^n = constant$. If the entropy change in the two processes are equal, find the value of n in terms of the adiabatic index γ [5].

Solution 14

Change in entropy during constant volume process

$$= mC_V \ln\left(\frac{T_2}{T_1}\right)$$

Change in entropy during polytropic process $(PV^n = constant)$

$$= mC_V \left(\frac{\gamma - 1}{n - 1}\right) \ln\left(\frac{T_2}{T_1}\right)$$

For the same entropy, equating (i) and (ii), we have
$\left(\frac{\gamma-1}{n-1}\right)$, or $(\gamma n) = (n\ 1)$ or $2n = \gamma +\ 1$

$$\left(\frac{\gamma + 1}{2}\right)$$

Problem 15 SKILLS PROBLEM-SOLVING

Oxygen is compressed reversibly and isothermally from $125KPa$ and 27^oC to a final pressure of $375KPa$. Determine change in entropy of gas [5]? .

Solution 15

Gas constant for oxygen:

$$R = \frac{8.314}{32} = 0.259\, KJ/Kg.K$$

For reversible process the change in entropy may be given as;

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

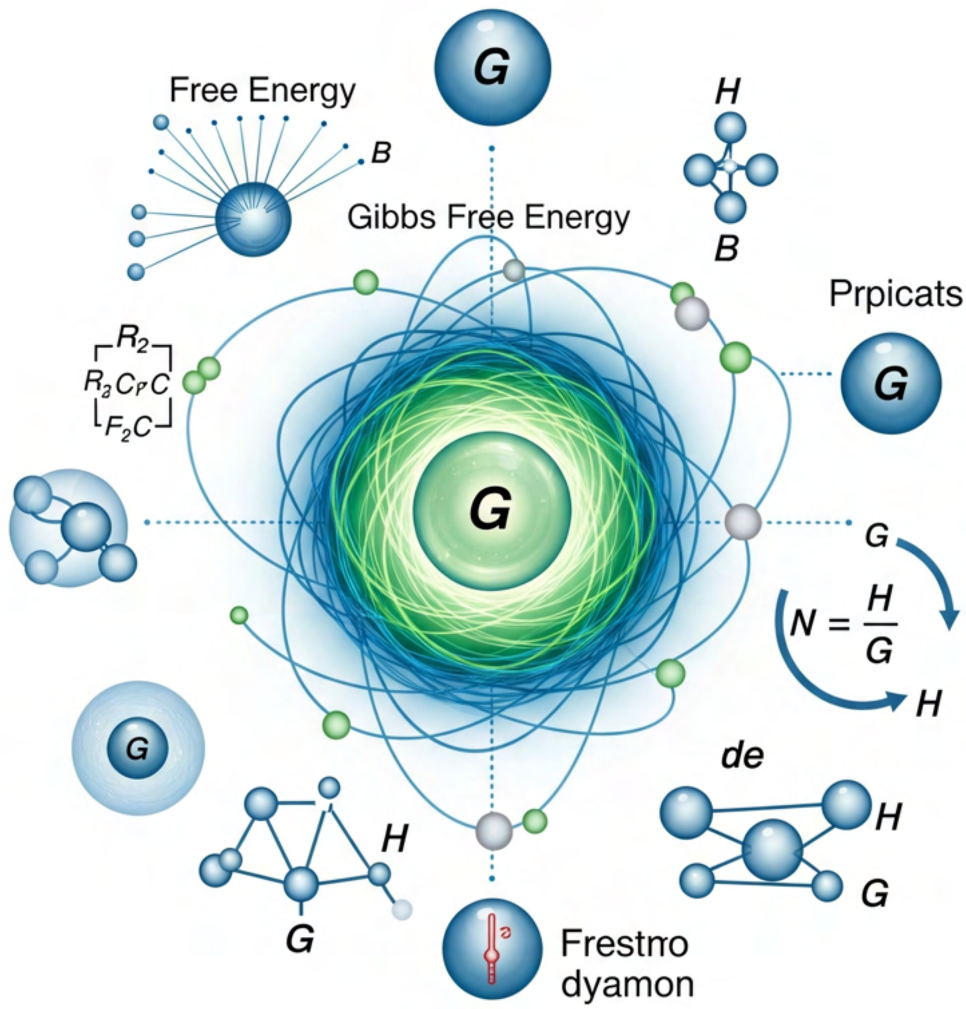
Substituting values of initial and final states

$$\Delta S = 6R \ln \frac{375}{125} = -0.285\, KJ/Kg.K$$

Entropy change $= -0.285 KJ/Kg.K$

SIXTH CHAPTER

FREE ENERGY AND ENTHALPY – CRITERIA FOR THE EVOLUTION OF A SYSTEM



Free Energy and Enthalpy–Criteria for the Evolution of a System

VI

After studying the three fundamental laws of thermodynamics, this chapter introduces the essential tools for predicting the direction of spontaneous processes and establishing the conditions of equilibrium in a thermodynamic system. While the second law provides a theoretical basis through the concept of entropy, its direct application can be complex when the system exchanges heat or work with its surroundings. To overcome this limitation, new state functions, known as thermodynamic potentials, are introduced to provide practical and simple criteria for determining spontaneity and equilibrium.

The third part applies these concepts to chemical equilibria. The chapter will show how the variation of Gibbs free energy determines the spontaneous direction of a reaction, the composition of the equilibrium mixture, and the relationship between Gibbs free energy and the equilibrium constant.

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

- Use thermodynamic potentials to describe system evolution;
- Determine criteria of spontaneity and equilibrium under various conditions;
- Apply these concepts to the study of chemical reactions and equilibrium states.

This chapter provides a crucial foundation for understanding the thermodynamic behavior of physical and chemical systems, the spontaneity of reactions, and the conditions governing equilibrium.

This Gibbs free energy is defined as:

$$G = H - TS \tag{VI.1}$$

where T is the absolute temperature. For an isothermal process, the change in the free energy of the system, ΔG, is [15]:

$$\Delta\ G = \Delta H - T\Delta S \tag{VI.2}$$

To see how the state function G relates to reaction spontaneity, recall that for a reaction occurring at constant temperature and pressure [15]:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \left(\frac{-\Delta H_{sys}}{T}\right) \tag{VI.3}$$

where Equation IV.79 substitutes for ΔS_{surr}. Multiplying both sides by T gives [15]:

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys} \tag{VI.4}$$

Comparing Equations IV.2 and IV.4, we see that in a process occurring at constant temperature and pressure, the free-energy change, ΔG, is equal to $-T\Delta S_{univ}$. We know that for spontaneous processes, ΔS_{univ} is always positive and, therefore, $-T\Delta S_{univ}$ is always negative. Thus, the sign of ΔG provides us with extremely valuable information about the spontaneity of processes that occur at constant temperature and pressure. If both T and P are constant, the relationship between the sign of ΔG and the spontaneity of a reaction is [15]:

- If $\Delta G < 0$, the reaction is spontaneous in the forward direction.
- If $\Delta G = 0$, the reaction is at equilibrium.
- If $\Delta G > 0$, the reaction in the forward direction is nonspontaneous (work must be done to make it occur) but the reverse reaction is spontaneous.

It is more convenient to use ΔG as a criterion for spontaneity than to use ΔS_{univ} because ΔG relates to the system alone and avoids the complication of having to examine the surroundings [15].

VI.1 ΔG° as a Criterion for Spontaneity

The Gibbs free energy, defined as $G = H - TS$, serves as a key criterion for determining whether a chemical reaction will occur spontaneously under given conditions. The relevant quantity is the change in Gibbs free energy ΔG for the actual conditions of the reaction [16]:

- When ΔG° is a large negative number (more negative than about $-10KJ$), the reaction is spontaneous as written, and reactants transform almost entirely to products when equilibrium is reached.
- When ΔG° is a large positive number (larger than about $10KJ$), the reaction is nonspontaneous as written, and reactants do not give significant amounts of products at equilibrium.
- When ΔG° has a small negative or positive value (less than about $10KJ$), the reaction gives an equilibrium mixture with significant amounts of both reactants and products.

VI.2 Standard Free-Energy Change

Keep in mind that specific standard states are selected for the sake of tabulating thermodynamic data; these are denoted by a superscript degree sign on the quantity's symbol. The following are the standard states: $1atm$ pressure for pure liquids and solids, $1atm$ partial pressure for gases, and one $1M$ concentration for solutions. The temperature is the temperature of interest, usually $25°C$ $(298K)$.

The standard free-energy change, ΔG°, is the free-energy change that occurs when reactants in their standard states are converted to products in their standard states [16].

$$\Delta\ G^{\circ} = \Delta H^{\circ} - T\Delta S\ ^{\circ} \tag{VI.5}$$

VI.3 Standard Free Energies of Formation

Standard enthalpies of formation, or ΔH_f°, are defined as the enthalpy change that occurs when a material is produced from its individual components under specific standard circumstances. Similarly, we may define standard free energies of formation, ΔG_f°: The free-energy change required for a material to develop from its constituent elements under normal circumstances is denoted by ΔG_f°. According to Table VI.1, standard state refers to the pure solid for solids, the pure liquid for liquids, and $101.3KPa$ for gases. A concentration of $1M$ is often the reference state for compounds in solution [15].

Example

The standard free energy of formation of $NH_3\,(g)$ is the free-energy change for the reaction [16]:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \tag{VI.6}$$

The reactants, N_2 and H_2, each at $1atm$, are converted to the product, NH_3, at $1atm$ pressure. You found ΔG° for the formation of $2mol\ NH_3$ from its elements to be $-32.8KJ$.

Hence,

$$\Delta G_f^{\circ}\,(NH_3) = 32.8\ KJ/2\ mol = 16.4\ KJ/1\ mol \tag{VI.7}$$

As in the case of standard enthalpies of formation, the standard free energies of formation of elements in their stablest states are assigned the value zero. By tabulating ΔG_f° for substances, as in Table VI.1, you can easily calculate ΔG° for any reaction involving those substances. You simply subtract the standard free energies of reactants from the standard free energies of products [16]:

$$\Delta G^\circ = \sum n\Delta G_f^\circ\,(\text{products}) - \sum m\Delta G_f^\circ\,(\text{reactants}) \qquad \text{(VI.8)}$$

Substance or Ion	ΔG_f° (kJ/mol)
$e^-(g)$	0
Bromine	
$Br(g)$	82.40
$Br^-(aq)$	−104.0
$Br^-(g)$	−238.8
$Br_2(g)$	3.159
$Br_2(l)$	0
$HBr(g)$	−53.50
Calcium	
$Ca(s)$	0
$Ca^{2+}(aq)$	−553.5
$CaCO_3(s, \text{calcite})$	−1128.8
$CaO(s)$	−603.5
Carbon	
$C(g)$	671.3
$C(s, \text{diamond})$	2.900
$C(s, \text{graphite})$	0
$CCl_4(g)$	−53.65
$CCl_4(l)$	−65.27
$CO(g)$	−137.2
$CO_2(g)$	−394.4
$CO_3^{2-}(aq)$	−527.9
$CS_2(g)$	66.85
$CS_2(l)$	65.27
$HCN(g)$	124.7
$HCN(l)$	124.9
$HCO_3^-(aq)$	−586.8
Hydrocarbons	
$CH_4(g)$	−50.80
$C_2H_4(g)$	68.39
$C_2H_6(g)$	−32.89
$C_6H_6(l)$	124.4
Alcohols	
$CH_3OH(l)$	−166.4
$C_2H_5OH(l)$	−174.9
Aldehydes	
$HCHO(g)$	−113
$CH_3CHO(g)$	−133.4

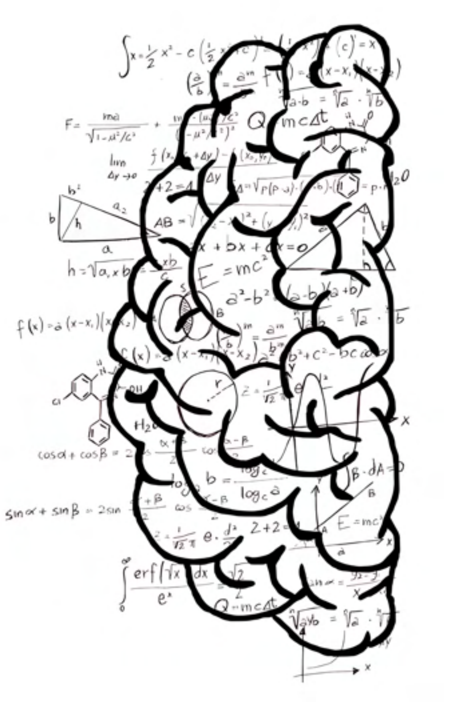
Substance or Ion	ΔG_f° (kJ/mol)
Aldehydes (continued)	
$CH_3CHO(l)$	−128.3
Chlorine	
$Cl(g)$	105.3
$Cl^-(aq)$	−131.3
$Cl^-(g)$	−240.2
$Cl_2(g)$	0
$HCl(g)$	−95.30
Fluorine	
$F(g)$	62.31
$F^-(g)$	−262.0
$F^-(aq)$	−278.8
$F_2(g)$	0
$HF(g)$	−274.6
Hydrogen	
$H(g)$	203.3
$H^+(aq)$	0
$H^+(g)$	1517.0
$H_2(g)$	0
Iodine	
$I(g)$	70.21
$I^-(aq)$	−51.59
$I^-(g)$	−221.5
$I_2(s)$	0
$HI(g)$	1.576
Lead	
$Pb(s)$	0
$Pb^{2+}(aq)$	−24.39
$PbO(s)$	−189.3
$PbS(s)$	−96.68
Nitrogen	
$N(g)$	455.6
$N_2(g)$	0
$NH_3(g)$	−16.40
$NH_4^+(aq)$	−79.37
$NO(g)$	86.60
$NO_2(g)$	51.24

Substance or Ion	ΔG_f° (kJ/mol)
Nitrogen *(continued)*	
$HNO_3(aq)$	−111.3
Oxygen	
$O(g)$	231.8
$O_2(g)$	0
$O_3(g)$	163.2
$OH^-(aq)$	−157.3
$H_2O(g)$	−228.6
$H_2O(l)$	−237.1
Silicon	
$Si(s)$	0
$SiCl_4(l)$	−619.9
$SiF_4(g)$	−1572.7
$SiO_2(s, \text{quartz})$	−856.4
Silver	
$Ag(s)$	0
$Ag^+(aq)$	77.12
$AgBr(s)$	−96.90
$AgCl(s)$	−109.8
$AgF(s)$	—
$AgI(s)$	−66.19
Sodium	
$Na(g)$	76.86
$Na(s)$	0
$Na^+(aq)$	−261.9
$Na^+(g)$	574.4
$Na_2CO_3(s)$	−1048.0
$NaCl(s)$	−384.0
$NaHCO_3(s)$	−851.0
Sulfur	
$S(g)$	236.5
$S(s, \text{monoclinic})$	0.070
$S(s, \text{rhombic})$	0
$S_2(g)$	79.7
$SO_2(g)$	−300.1
$H_2S(g)$	−33.33

Table VI.1: Standard Free Energies of Formation (at $25°C$) [16].

PRACTICE

EXERCISES AND SOLUTIONS



VI.4 Problem Solving

Problem 16 SKILLS PROBLEM-SOLVING

500 KJ of heat is removed from a constant temperature heat reservoir maintained at $835K$. Heat is received by a system at constant temperature of $720K$. Temperature of the surroundings, the lowest available temperature is $280K$. Determine the net loss of available energy as a result of this irreversible heat transfer [5].

Solution 16

Here, $T_0 = 280K$, i.e surrounding temperature.

Availability for heat reservoir

$$= T_0 \cdot S_{reservoir}$$
$$= 280 \left(\frac{500}{835}\right)$$
$$= 167.67\ KJ/Kg\ K$$

Availability for system

$$= T_0 \cdot S_{system}$$
$$= 280 \left(\frac{500}{720}\right)$$
$$= 194.44\ KJ/Kg\ K$$

Net loss of available energy = (167.67 − 194.44) = $26.77KJ/KgK$

Loss of available energy = $26.77KJ/KgK$

Problem 17 SKILLS PROBLEM-SOLVING

What is the standard free-energy change, ΔG, for the following reaction at $25°C$? [16]

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Calculate ΔH and ΔS then substitute these values into $\Delta H° - TDS°$ to obtain $\Delta G°$.

Solution 17

Write the balanced equation and place below each formula the values of ΔH_f° and S° multiplied by stoichiometric coefficients.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3\,(g)$$
$$H_f^\circ: \quad 0 \qquad 0 \qquad 2\times(-45.9)\ KJ$$
$$S^\circ: \quad 191.6 \quad 3\times 130.6 \quad 2\times 192.7\ J/K$$

You calculate H° and S° by taking values for products and subtracting values for reactants.

$$\Delta H^\circ = \sum n\Delta H_f^\circ\,(products) - \sum m\Delta H_f^\circ\,(reactants)$$
$$= [2\times(-45.9) - 0]\ KJ = \ -91.8\ KJ$$

$$\Delta S^\circ = \sum nS^\circ\,(products) - \sum mS^\circ\,(reactants)$$
$$= [2\times 192.7 - (191.6 + 3\times 130.6)]\ J/K = \ -198.0\ J/K$$

You now substitute into the equation for ΔG° in terms of ΔH° and ΔS°. Note that you substitute ΔS° in units of KJ/K.

$$\Delta G^\circ = \ \Delta H^\circ - T\Delta S^\circ \ = -91.8\ KJ - (298\ K)\,(-0.1980\ \mathrm{KJ}/K) = 32.8\ \mathrm{KJ}$$

Problem 18 SKILLS PROBLEM-SOLVING

Calculate ΔG° for the combustion of $1mol$ of ethanol, C_2H_5OH, at $25°C$ [16].

Calculate ΔG° from ΔG_f° values, similar to the way you calculate ΔH° from ΔH_f°.

Solution 18

Write the balanced equation with values of ΔG_f° multiplied by stoichiometric coefficients below each formula.

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO2(g) + 3H2O(g)$$

$$\Delta G_f^\circ : \quad -174.9 \qquad 0 \qquad 2(-394.4)\ 3(-228.6)\ KJ$$

The calculation is

$$\begin{aligned}\Delta G^\circ &= \sum n\Delta G_f^\circ(products) - \sum m\Delta G_f^\circ(reactants)\\ &= [2(-394.4) + 3(-228.6) - (-174.9)]\ \ KJ\\ &= 1299.7\ KJ\end{aligned}$$

BIBLIOGRAPHY

Bibliography

[1] Michael J. Moran and Howard N. Shapiro. *Fundamentals of Engineering Thermodynamics: SI Version*. John Wiley & Sons, 5th edition, 2006.

[2] Michael J. Moran, Howard N. Shapiro, Daisie D. Boettner, and Margaret B. Bailey. *Fundamentals of Engineering Thermodynamics*. John Wiley & Sons, 9th edition, 2018.

[3] J. M. Smith, H. C. Van Ness, M. B. Abbott, and M. T. Swihart. *Introduction to Chemical Engineering Thermodynamics*. McGraw-Hill Education, 8th edition, 2018.

[4] John R. Reisel. *Principles of Engineering Thermodynamics*. Cengage Learning, 2nd, si units edition, 2015.

[5] Onkar Singh. *Applied Thermodynamics*. New Age International Publishers, 3rd edition, 2007.

[6] Claus Borgnakke and Richard E. Sonntag. *Fundamentals of Thermodynamics*. John Wiley & Sons, 10th edition, 2019.

[7] Yunus A. Çengel, Michael A. Boles, and Mehmet Kanoğlu. *Thermodynamics: An Engineering Approach*. McGraw-Hill Education, 9th edition, 2023.

[8] Antonio Saggion, Roberto Faraldo, and Massimo Pierno. *Thermodynamics: Fundamental Principles and Applications*. Springer International Publishing, 2019.

[9] Pedro Faísca. *A Concise Introduction to Thermodynamics for Physicists.* CRC Press, 2023.

[10] Merle C. Potter and Craig W. Somerton. *Thermodynamics for Engineers.* McGraw-Hill Education, 4th edition, 2021.

[11] Jean-Philippe Ansermet and Sylvain D. Bréchet. *Principles of Thermodynamics.* Cambridge University Press, 2022.

[12] Stephen R. Turns and Laura L. Pauley. *Thermodynamics: Concepts and Applications.* Cambridge University Press, 2nd edition, 2020.

[13] N. D. Hari Dass. *The Principles of Thermodynamics.* CRC Press, 2018.

[14] R. K. Rajput. *Engineering Thermodynamics.* Laxmi Publications, 3rd edition, 2007.

[15] Theodore L. Brown, H. Eugene LeMay, Bruce E. Bursten, Catherine J. Murphy, Patrick M. Woodward, and Matthew W. Stoltzfus. *Chemistry: The Central Science.* Pearson, 14th, si units edition, 2018.

[16] Darrell D. Ebbing and Steven D. Gammon. *General Chemistry.* Houghton Mifflin, 9th edition, 2007.

[17] Peter Atkins and Julio de Paula. *Physical Chemistry.* Oxford University Press, 9th edition, 2010.

[18] David W. Oxtoby, H. P. Gillis, and Laurie J. Butler. *Principles of Modern Chemistry.* Cengage Learning, 8th edition, 2016.

[19] Hugh D. Young and Roger A. Freedman. *University Physics with Modern Physics.* Pearson, 15th, si units edition, 2020.