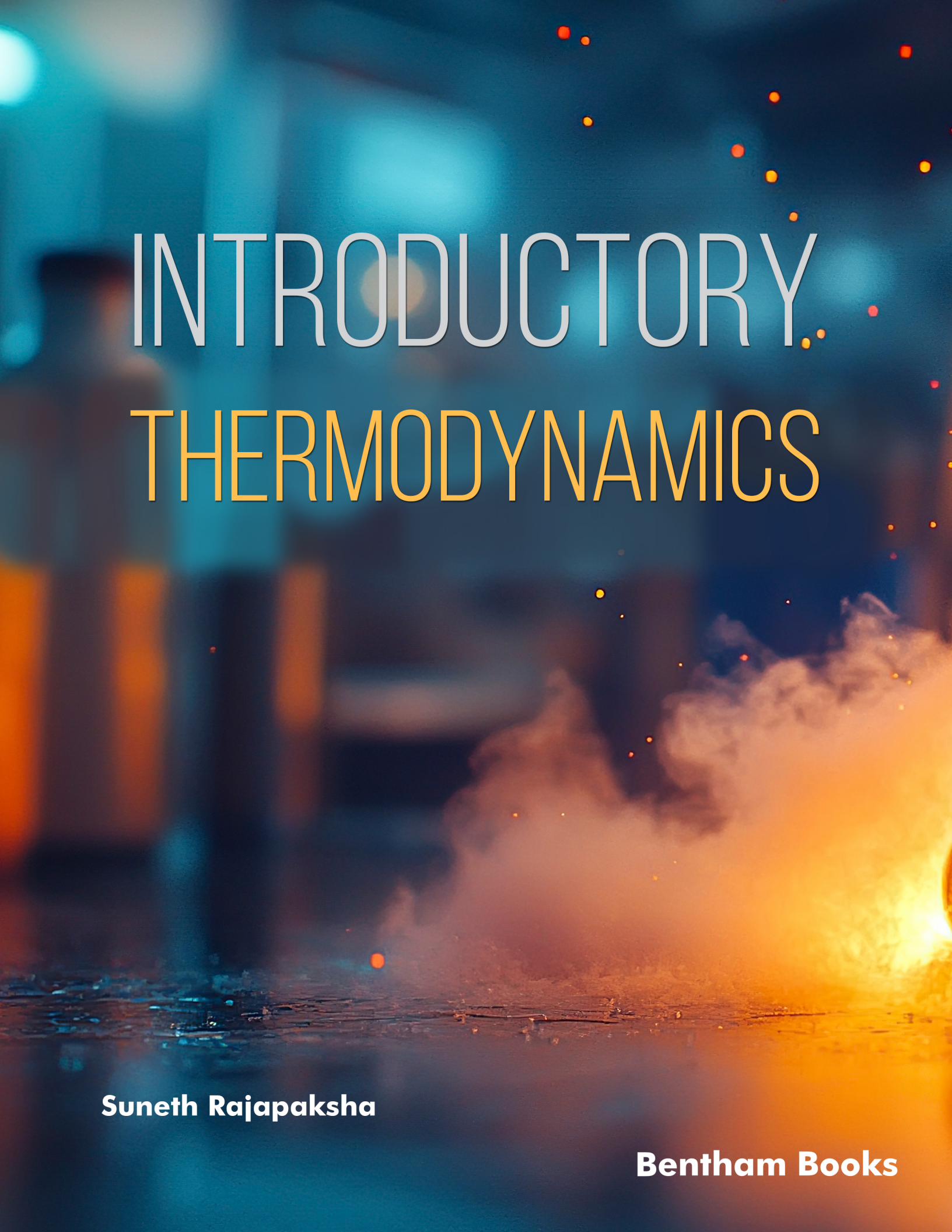




# INTRODUCTORY THERMODYNAMICS

**Suneth Rajapaksha**

**Bentham Books**

# **Introductory Thermodynamics**

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## **Introductory Thermodynamics**

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## PREFACE

This book is intended primarily for undergraduate students in science and engineering who seek a clear and conceptual understanding of thermodynamic principles. Thermodynamics stands as one of the foundational subjects in the physical sciences, linking the microscopic behavior of atoms and molecules to macroscopic observations. A clear understanding of thermodynamics is essential for students in physics, chemistry, biology, and engineering, as it provides the logical support for understanding how energy is transformed, transferred, and conserved in all natural and engineered systems.

Despite its importance, many students initially find thermodynamics abstract and challenging. Introductory Thermodynamics has been written to make this subject accessible for students coming from different disciplines and meaningful to learners encountering it for the first time. The book progresses from fundamental concepts, such as gas laws, systems, surroundings, and states, to the laws of thermodynamics and the nature of energy transformations. My approach in writing this book has been to explain concepts as simply as possible at first, then carefully build toward the corresponding mathematical formulations and relationships. Readers will find concise explanations and step-by-step derivations throughout the book, along with end-of-book exercises that include conceptual questions and numerical problems designed to reinforce understanding and stimulate analytical thinking. Answers to all exercises are provided to enable students to assess their progress and verify their solutions.

I hope this book will inspire students to appreciate the elegance and universality of thermodynamic principles and to apply them creatively within their respective disciplines. I am deeply grateful to my students, whose curiosity and feedback have continually shaped my approach to teaching thermodynamics. Their questions and insights have been invaluable in refining the explanations presented here. I am sincerely grateful to everyone who encouraged and supported me in writing this book. Finally, I owe my deepest gratitude to my loving family for their patience, love, and understanding during the long and irregular hours of writing.

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## **DEDICATION**

To all who believe that courage is where growth is born.

**CHAPTER 1****Introduction to Thermodynamics**

**Abstract:** Thermodynamics is the discipline concerned with the quantitative relationships among heat, work, energy, temperature, and pressure, as well as their roles in physical and chemical processes. Any transformation of matter involves an interplay between at least two of these fundamental variables. Over the past several centuries, systematic empirical observations and theoretical developments have established the modern understanding of thermodynamics, providing a structure for describing and predicting natural phenomena. The gas laws describe the quantitative relationships among pressure, volume, temperature, and the amount of gas, forming the basis of classical thermodynamics. Early empirical formulations, such as Boyle's law, Charles's law, and Avogadro's law, were later unified into the ideal gas law, which integrates these relationships into a single comprehensive expression. However, real gases do not always behave ideally. Deviations from ideality arise due to intermolecular interactions and the finite volume occupied by gas molecules. These effects are captured by more advanced models, most notably the Van der Waals equation.

**Keywords:** Avogadro's law, Boyle's law, Charles's law, Compressibility factor, Ideal gas law, Real gases, Van der Waals equation, Virial expansion.

**INTRODUCTION**

The development of thermodynamics was a cumulative process rather than the result of a single discovery, with contributions spanning several centuries. In 1656, Robert Boyle, in collaboration with Robert Hooke, established what is now known as Boyle's law, demonstrating that for a gas at constant temperature, the product of pressure and volume remains constant. This provided one of the earliest quantitative descriptions of gas behavior. In the 1780s, Jacques Charles formulated Charles's law, which states that the volume of a gas at constant pressure is directly proportional to its absolute temperature, thereby relating thermal effects to molecular motion. Subsequently, in 1808, Joseph Gay-Lussac showed that, for a fixed mass of gas at constant volume, the pressure is directly proportional to temperature, further advancing the quantitative understanding of gas behavior. These discoveries provided essential groundwork for the birth of classical thermodynamics, which emerged in the early 19<sup>th</sup> century in response to practical challenges, most notably, the quest to improve the efficiency of steam engines during the Industrial Revolution. A major leap forward came in 1824 when French engineer Nicolas Léonard Sadi Carnot published *Réflexions sur la puissance*

*motrice du feu* (Reflections on the Motive Power of Fire), which introduced the conceptual framework for the second law of thermodynamics. Decades later, physicists Rudolf Clausius and Lord Kelvin expanded upon Carnot's ideas, giving them a formal mathematical foundation. Carnot's pioneering vision eventually earned him the title 'Father of Thermodynamics'.

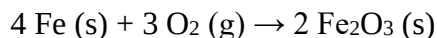
In 1834, French physicist Benoît Paul Émile Clapeyron synthesized earlier gas laws into a unified mathematical expression which is now known as the ideal gas law, providing a powerful tool for describing gas behavior under a range of conditions. A decade later, in 1845, English physicist James Prescott Joule conducted his famous paddle-wheel experiment, in which he experimented with the conversion of mechanical work into heat. His precise measurements established the mechanical equivalence of heat, a principle that supported the formulation of the first law of thermodynamics. In thermodynamics, energy transformations and the average properties of macroscopic matter in equilibrium are described. The fundamental principles of heat engines quickly spread to other fields due to their versatility in explaining various scientific concepts. One of the earliest disciplines to adopt thermodynamics was chemistry, leading to the development of chemical thermodynamics. This branch focuses on the roles of heat and work in chemical reactions, particularly in determining the spontaneity of reactions.

Natural processes exhibit distinct differences in their tendency to occur spontaneously. For example, sodium chloride dissolves readily in water, whereas sand remains undissolved under the same conditions. A sheet of paper will ignite in the presence of a flame but will not combust spontaneously at ambient temperature. Similarly, a cup of hot coffee cools to the surrounding room temperature but does not continue cooling below it. Such observations, which have long intrigued scientists, are explained within the framework of thermodynamics. Thermodynamics provides the theoretical basis for analyzing spontaneous processes, energy transfer, and equilibrium, allowing one to determine not only whether a process can occur but also the direction in which it will proceed and the fundamental limitations on its efficiency. Thermodynamics establishes that spontaneous processes are governed not only by energy changes, such as heat release or absorption, but also by the extent to which energy and matter become more dispersed or randomly distributed within a system. The combined consideration of energy and randomness provides a predictive framework for understanding natural processes, and the occurrence of certain chemical reactions without external input, while others require a continuous energy supply. When baking soda (sodium bicarbonate,  $\text{NaHCO}_3$ ) and vinegar (acetic acid,  $\text{CH}_3\text{COOH}$ )

are mixed, bubbles form due to the production of carbon dioxide (CO<sub>2</sub>), confirming a spontaneous chemical reaction.



Another naturally occurring spontaneous reaction is rusting. Iron (Fe) forms Fe (III) oxide by reacting with oxygen, which is the reason for rusting.



Alongside spontaneous reactions, numerous natural processes are non-spontaneous and proceed only with the continuous input of external energy. A central example is photosynthesis, which is among the most significant and widely studied processes in nature. In photosynthesis, green plants, algae, and certain bacteria convert carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) into glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>) and oxygen (O<sub>2</sub>) through a series of light-driven reactions.



This transformation requires a substantial input of energy under standard conditions and does not occur spontaneously. The required energy is supplied by sunlight, which is absorbed by pigments such as chlorophyll. These pigments capture photons and initiate a cascade of photochemical and redox events that ultimately drive the fixation of carbon. Without the continuous input of solar energy, the reaction cannot proceed, illustrating the fundamental principle that non-spontaneous processes depend on external energy sources to overcome thermodynamic constraints.

## THE BASIS OF THERMODYNAMICS

Thermodynamics is the study of macroscopic properties of matter and energy, focusing on how they behave when a system reaches equilibrium. Unlike microscopic approaches that deal with individual particles, thermodynamics emphasizes average, bulk properties, making it a powerful tool for describing and predicting the behavior of gases, liquids, and solids under various conditions. In thermodynamics, the variables  $n$ ,  $p$ ,  $V$ , and  $T$  commonly represent the amount of substance, pressure, volume, and absolute temperature of a system, respectively. The amount of substance  $n$  is measured in moles (mol), where one mole contains  $6.022 \times 10^{23}$  elementary particles. Pressure  $p$  is measured in pascals (Pa) in the SI system, where  $1 \text{ Pa} = 1 \text{ N m}^{-2}$ . Volume  $V$  is measured in cubic meters (m<sup>3</sup>), although liters (L) are also frequently used in practical applications. Temperature

**CHAPTER 2****Thermodynamic Essentials**

**Abstract:** This chapter introduces several fundamental thermodynamic concepts and terms that form the essential foundation of the subject. A clear understanding of these basic ideas is crucial before progressing to more advanced principles and applications presented in later chapters. By becoming familiar with core properties, system classifications, and thermodynamic variables at the outset, the reader will be better equipped to comprehend the laws of thermodynamics and their wide-ranging implications. This foundational knowledge ensures a smooth transition into deeper theoretical discussions and practical analyses that follow throughout the text.

**Keywords:** Path variables, Properties of systems, PV diagrams, State variables, Thermodynamic paths, Thermodynamic processes, Thermodynamic systems.

**INTRODUCTION**

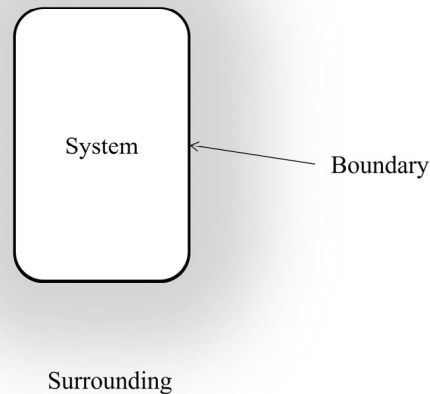
Thermodynamics employs a well-defined set of terminology that must be understood by beginners in order to follow the subject effectively. The term system is defined broadly but always with well-specified characteristics. In its widest sense, a system may refer to the entire universe or any portion of it chosen for study. More commonly, however, the thermodynamic system is the specific object or region under investigation, and its selection depends on the purpose of the study. For example, an iron cube can be treated as a system with clear physical boundaries, while the human body may also be considered a system, with the skin serving as its boundary.

In general, a system in thermodynamics can be defined as a specified quantity of matter or a region of space selected for analysis. Importantly, the boundaries of a system need not always be physical; they may also be imaginary or hypothetical. For instance, a certain volume of air in a room can be designated as a system, even though its boundaries exist only conceptually. The boundary is the surface that separates the system from its surroundings. Everything external to the system, that is, everything not included within its boundaries, is referred to as the surroundings. For example, if a cardboard box is chosen as the system, then the surroundings would include everything else: outside air, people, animals, vehicles, buildings, and even distant planets. Fig. (2.1) illustrates a system, its boundaries, and its surroundings.

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**Fig. (2.1).** A system, its boundary, and its surroundings.

Thermodynamic systems can be classified into three main types depending on whether and how they interact with their surroundings through their boundary walls. The nature of this interaction determines the exchange of energy and matter between the system and its environment.

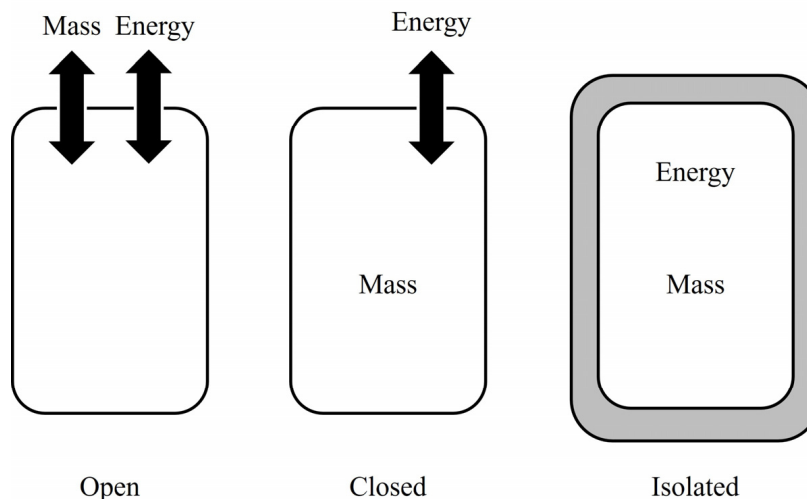
- Open systems
- Closed systems
- Isolated systems

In an open system, both mass and energy can cross the boundary. A boiling pot of water without a lid is a simple example: heat enters from the stove, and water vapor escapes into the air. In a closed system, only energy is exchanged while the mass within it remains fixed. A sealed container of gas may absorb or release heat, but no particles enter or leave the container. Finally, in an isolated system, neither mass nor energy is exchanged with the surroundings. An idealized example is a perfectly insulated thermos flask, which, in theory, prevents both heat loss and material transfer (Fig. 2.2).

## PROPERTIES OF THERMODYNAMIC SYSTEMS

To fully describe any thermodynamic system, it is essential to know its fundamental characteristics. The first step is to identify its macroscopic properties, such as

pressure, volume, temperature, and composition, which collectively define the state of the system. These properties are measurable and provide a bridge between the theoretical framework of thermodynamics and real-world observations. Another important consideration is whether the system is homogeneous or heterogeneous. A homogeneous system has a uniform composition and properties throughout, such as pure water or air. In contrast, a heterogeneous system contains distinct phases or regions with different properties, such as ice floating in water or an oil-water mixture.



**Fig. (2.2).** Open system, closed system and isolated system.

Further, the equilibrium state of the system must be specified to properly describe it. A system is said to be in equilibrium when its macroscopic properties remain constant over time, and there are no unbalanced driving forces causing spontaneous changes. Equilibrium itself can be mechanical, thermal, phase, or chemical, and complete equilibrium requires all of these to be satisfied simultaneously. Finally, the number of components present in the system must be determined. Components are the minimum number of chemically independent species needed to describe the composition of all phases in the system. For example, liquid water and steam together form a two-phase system but consist of only one component,  $\text{H}_2\text{O}$ . Together, macroscopic properties, homogeneity or heterogeneity, the equilibrium state, and the number of components provide the complete framework necessary for describing, classifying, and analyzing any thermodynamic system.

**CHAPTER 3****Zeroth Law of Thermodynamics**

**Abstract:** The zeroth law of thermodynamics establishes the foundational concept of thermal equilibrium and provides the logical basis for defining temperature as a measurable and comparable physical quantity. According to this law, if two systems are each in thermal equilibrium with a third system, they are in equilibrium with one another. Essential characteristics of an effective thermometer include a reproducible thermometric property, sensitivity to small temperature changes, a monotonic and stable response, and ease of calibration. Building upon these principles, several temperature scales have been developed, including the Celsius, Fahrenheit, and Kelvin scales, each reflecting distinct reference points and conventions. The ability to convert between these scales is critical for scientific communication and practical applications. Among all thermometer types, the ideal gas thermometer holds special significance because its readings closely approximate the thermodynamic temperature, particularly at low gas densities where real-gas effects are minimized. Together, the zeroth law, thermometer design principles, temperature scales, and the ideal gas thermometer form the conceptual foundation for quantitative thermal measurement in physics and chemistry.

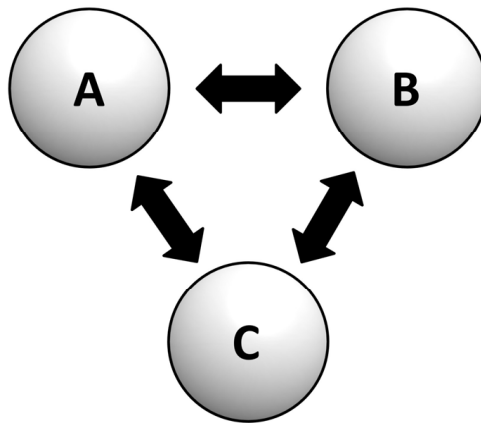
**Keywords:** Absolute zero, Celsius scale, Fahrenheit scale, Ideal gas thermometer Kelvin scale, Temperature scales, Zeroth Law.

**INTRODUCTION**

In science, laws are commonly formulated to explain or predict natural phenomena. These laws are developed within a scientific or mathematical framework and are valid under specific conditions. The idea of the ‘zeroth law’ is unusual in science, yet it plays a crucial role in thermodynamics. Historically, the first, second, and third laws of thermodynamics were introduced before the zeroth law was formally recognized. Later, scientists realized that a consistent and precise way of defining and measuring temperature was essential, since temperature appears in all the other three laws. To address this, a new foundational law was proposed. Naming it the ‘fourth law’ would have been misleading, as it needed to precede the others in logical order. Therefore, scientists designated it as the ‘zeroth law of thermodynamics,’ emphasizing that it provides the basis for discussing the other three laws.

## THE ZEROth LAW

The zeroth law of thermodynamics provides the basis for the concept of temperature and thermal equilibrium. It states that if two bodies are each in thermal equilibrium with a third body, then they are also in thermal equilibrium with each other. This principle may sound simple, but it is extremely powerful because it establishes temperature as a measurable and transitive property. When two systems are said to be in thermal equilibrium, it means that no net heat flows between them when they are placed in contact. If body *A* is in equilibrium with body *C*, and body *B* is also in equilibrium with body *C*, then logically, *A* and *B* must share the same temperature, and thus no heat will flow between them either. The equivalent mathematical statement is that ‘if  $A = B$  and  $B = C$ , then  $A = C$ ’ (Fig. 3.1).



**Fig. (3.1).** A, B and C are in thermal equilibrium if they all are at the same temperature.

By introducing a thermometer as the third body, one can assign numerical values to temperature. For example, if a thermometer shows the same reading when in contact with body *A* and body *B*, both *A* and *B* are at the same temperature and are therefore in thermal equilibrium with each other. This law might appear less fundamental than the first, second, or third laws of thermodynamics, which deal with energy conservation, entropy, and absolute zero, respectively. However, the zeroth law underpins them because it establishes the concept of temperature, which is central to thermodynamics. Without it, temperature measurement would lack meaning and consistency. However, the zeroth law of thermodynamics establishes the existence of a measurable quantity ‘temperature’; it does not specify how to construct a temperature scale for precise measurement. To achieve this, a thermometer must be calibrated by defining at least two fixed reference points and establishing a quantitative relationship between them (*e.g.*, linear, exponential,

quadratic) to ensure consistency and accuracy. Though several temperature scales are in use, the most common ones in daily life are the Celsius and the Fahrenheit scales. The Celsius scale is adopted by most countries around the world, while a few continue to rely primarily on the Fahrenheit scale. In scientific work, however, the universally accepted standard is the Kelvin scale, which is based on absolute zero and is used almost exclusively in research and academic contexts. Absolute zero, defined as 0 K on the Kelvin scale, represents the lower limit of temperature. In classical thermodynamics, it is often described as the state at which all molecular motion ceases. From a quantum mechanical perspective, particles can never be completely at rest. Even at absolute zero, a system retains a finite amount of energy known as zero-point energy. This arises from the constraints imposed by the Heisenberg Uncertainty Principle, which states that the position and momentum of a particle cannot both be known with arbitrary precision. If a particle were completely motionless with precisely defined position and zero momentum, this principle would be violated. Consequently, some residual motion must persist even at 0 K.

A thermometer is an instrument designed to measure temperature by relating it to a physical property of the instrument, known as a thermometric property. Each thermometer assigns numerical values to temperature using one of the accepted scales. For instance, in a mercury-in-glass thermometer, the length of the mercury column serves as the thermometric property, while in a constant-volume gas thermometer, it is the pressure of the enclosed gas. To construct a reliable thermometer, four essential factors must be carefully determined: the substance, the property, the reference points, and the interpolation scale. In mercury-in-glass thermometers, the working substance is mercury. The thermometric property in this case is the volume of mercury, which changes with temperature. Since the mercury is confined within a narrow capillary tube, a change in volume is observed as a change in the length of the mercury column. To calibrate such a thermometer, two fixed reference points are commonly used: the freezing point and the boiling point of water under standard atmospheric pressure. The scale between these two points is divided linearly, since the change in the length of the mercury column is, to a good approximation, directly proportional to temperature within this range.

Temperature is a fundamental physical quantity that measures the degree of hotness or coldness of a body and reflects the average kinetic energy of its particles. To quantify temperature, various temperature scales have been developed, each defined by specific reference points and units. The most commonly used scales are Celsius, Fahrenheit, and Kelvin. Understanding these scales and their interconversion is crucial in both experimental and theoretical thermodynamics.

**CHAPTER 4****First Law of Thermodynamics**

**Abstract:** The first law of thermodynamics establishes the fundamental principle of energy conservation in physical and chemical processes, stating that energy can neither be created nor destroyed, only transformed between different forms or transferred between a system and its surroundings. This law quantitatively relates heat  $q$ , work  $w$ , and the change in internal energy  $\Delta U$ , forming the basis for all thermodynamic analyses. Historical insights from James Prescott Joule's paddle-wheel experiment provided the first rigorous demonstration that mechanical work and heat are equivalent and interchangeable forms of energy, thereby laying the foundation for the first law. For cyclic processes, where the system returns to its initial state, the net change in internal energy over one complete cycle is zero, implying that the net heat absorbed equals the net work done by the system. In contrast, for non-cyclic processes, the internal energy change depends solely on the initial and final states, independent of the path taken, allowing the first law to be applied to a broad range of physical transformations.

**Keywords:** Energy transformation, First law, Heat, Internal energy, Joule's paddle-wheel experiment Work.

**INTRODUCTION**

This chapter mainly discusses the development of the first law of thermodynamics and the conversion of energy between its most prominent forms, work to heat. The total Energy ( $E$ ) of a system can be divided into two sub-groups, macroscopic energy and microscopic energy. Macroscopic energy consists of Kinetic Energy ( $KE$ ) and Potential Energy ( $PE$ ), which are associated with the overall motion and position of a system. In contrast, microscopic energy is related to the molecular, atomic, and sub-atomic arrangement of matter. The total of all these microscopic contributions is referred to as the internal energy of the system, commonly denoted by the symbol  $U$ .

$$E = KE + PE + U \quad (4.1)$$

The internal energy of a system originates from the microscopic motions and interactions of the particles that constitute matter. At the molecular level, atoms and molecules possess various forms of energy arising from their motion, mutual

interactions, and internal structure. The total internal energy therefore represents the sum of all microscopic energy contributions within the system. One major contribution is sensible energy, which is associated with the translational, rotational, and vibrational motions of molecules, atoms, and subatomic particles. These microscopic motions constitute the kinetic energy of the particles. Since temperature reflects the average kinetic energy of random molecular motion, an increase in sensible energy generally produces an increase in temperature. A second contribution is latent energy, which arises from intermolecular and interatomic forces. Particles in solids are held together by strong attractive forces, whereas these forces are weaker in liquids and weakest in gases. During a phase transition such as melting or vaporization, energy must be supplied to overcome part of these attractive forces and rearrange the molecular structure. This energy changes the molecular potential energy without necessarily changing the temperature and is therefore referred to as latent energy. The third contribution is chemical energy, which originates from the electronic structure and chemical bonding of atoms within molecules. Chemical bonds store potential energy, which can be released or absorbed during chemical reactions as molecular structures rearrange. For an ideal gas, intermolecular forces are assumed negligible, so the internal energy depends primarily on the kinetic energy of molecular motion and therefore mainly on temperature. In real substances, however, intermolecular attractions and repulsions contribute additional potential energy components, causing internal energy to depend on both temperature and molecular arrangement. Thus, internal energy provides a microscopic interpretation of thermodynamic behavior by linking observable macroscopic properties, such as temperature and heat transfer, to the molecular-level motions and interactions of matter.

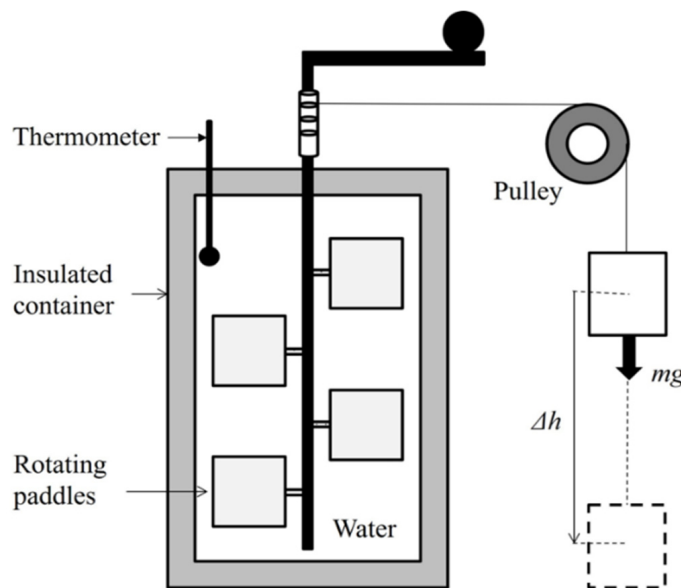
Energy can be transformed from one form to another. A familiar example is found in household appliances, many of which operate by converting electrical energy into other forms, most commonly mechanical energy. The scientific basis of such transformations was firmly established in 1845, when James Prescott Joule quantified the conversion of mechanical energy into heat. The experiment he conducted to demonstrate this principle is now famously known as Joule's paddle-wheel experiment.

### **JOULE'S PADDLE WHEEL EXPERIMENT**

In his famous 1845 experiment, Joule attached a weight ( $m$ ) to a string connected to a paddle wheel, immersed in water inside an insulated container, as illustrated in Fig. (4.1). The weight was first raised to a certain height ( $h$ ) and then allowed to fall. As it descended, the string turned the paddle wheel, which rotated and stirred

the water. This mechanical motion generated heat, which was evidenced by a measurable rise in the water's temperature.

Joule discovered that the mechanical energy released by the falling weight was converted into heat energy through the motion of the paddle wheel. He measured the heat absorbed by the water by recording its temperature before and after stirring. In the early stage of his experiments, he observed that allowing a weight of 896 pounds to fall through 1 foot raised the temperature of one pound of water by 1 degree Fahrenheit. Later refinements of his method gave a more accurate value, showing that 772 foot-pounds of work were required to achieve the same temperature rise. This was the first clear demonstration that a measurable quantity of heat is equivalent to a corresponding amount of mechanical work. Joule's work laid the foundation for the principle of energy conservation, showing that energy is never lost but simply transformed from one form to another. Joule's conclusion of the experiment was that a weight of 772 pounds (350 kg) falling through 1 foot (0.3 m) raises the temperature of 1 pound of water (0.45 kg) by 1 degree Fahrenheit.



**Fig. (4.1).** Joule's paddle wheel experimental setup.

Potential energy loss due to the weight drop is calculated as,

$$\Delta E_p = mg\Delta h.$$



**CHAPTER 5****Work and Heat**

**Abstract:** This chapter examines the central roles of work and heat in the first law of thermodynamics, highlighting how these two modes of energy transfer govern the behavior of physical and chemical systems. The first law establishes that the change in a system's internal energy arises solely from heat exchanged with the surroundings and work performed by or on the system. By exploring the various forms of mechanical work, such as pressure–volume work, and the mechanisms of heat transfer, this chapter clarifies how energy moves across system boundaries. The discussion further emphasizes that heat and work are path-dependent quantities, in contrast to the state function internal energy, and explains their significance in both cyclic and non-cyclic processes.

**Keywords:** Adiabatic reversible expansion, Degrees of freedom, Heat, Heat capacity ratio, Heat capacity, Internal energy, Isothermal reversible expansion, Path variables, Work.

**INTRODUCTION**

While internal energy represents the stored energy of a system, work and heat describe how that energy changes as the system interacts with its surroundings. Understanding these concepts is essential for interpreting physical, chemical, and biological processes. In thermodynamics, work is broadly defined as the energy transferred when a force acts through a distance or when a generalized displacement occurs. Pressure-volume work, the most common form encountered in thermodynamic systems, illustrates how energy can be transferred mechanically during compression or expansion. Heat, on the other hand, is the energy transferred solely due to a temperature difference between the system and its surroundings. Unlike internal energy, both work and heat are path-dependent quantities, meaning their values depend on the specific process a system undergoes rather than on its initial and final states alone.

**WORK**

Work done by gases, commonly illustrated using ideal gas models, is referred to as displacement work. The most familiar form of displacement work is pressure-volume work, which occurs when a gas undergoes expansion or compression. In both cases, the system's volume changes under external pressure, leading to energy transfer in the form of work. The total external pressure exerted on the gas ( $p_{ext}$ ) is

the sum of the outside pressure and the pressure coming from the weight of the piston. Since the process is a compression,  $V_1 > V_2$ . If the force applied by the piston is  $F$ , the work done by the piston by moving  $l$  distance is,

$$w = Fl \quad (5.1)$$

Force  $F$  is the pressure exerted on the area  $A$  ( $A$  is the surface area of the piston).

$$F = p_{ext}A \quad (5.2)$$

By using Eq. (5.1), the work done on the system by the external pressure can be written as:

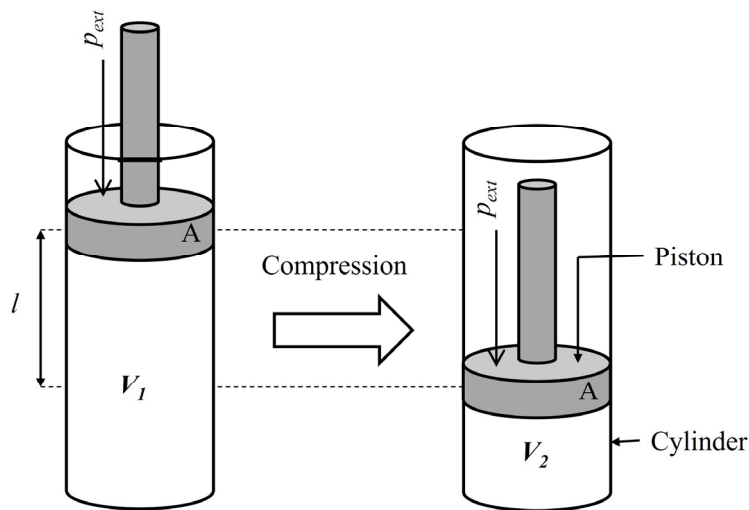
$$w = p_{ext}Al \quad (5.3)$$

$A \times l$  is the change of volume,  $\Delta V$ . Further, the negative sign ( $-$ ) is used in the equation. Therefore,

$$w = -p_{ext}\Delta V \quad (5.4)$$

It is important to understand the reason for using the negative sign ( $-$ ) in the work equation. By convention, work done by the system on the surroundings is taken as negative, while work done on the system by the surroundings is considered positive.

- When the system expands ( $V_2 > V_1$ ), the change in volume is positive ( $\Delta V > 0$ ). Substituting into the equation, the negative sign ensures that  $w < 0$ , indicating that the system is doing work on the surroundings.
- Conversely, when the system is compressed ( $V_1 > V_2$ ), the change in volume is negative ( $\Delta V < 0$ ). The negative sign then makes  $w > 0$ , signifying that work is being done on the system by the surroundings.



**Fig. (5.1).** Compression of an ideal gas from  $V_1$  to  $V_2$  by using a piston under a constant external pressure of  $p_{ext}$ .

The compression illustrated in Fig. (5.1) occurs under constant external pressure. However, if the external pressure varies during the process, the work must be evaluated by considering an infinitesimal path, accounting for incremental changes in pressure and volume. In such cases, the total work is obtained by integrating along the specific path taken. Since work depends on the path of the process, it is represented using the inexact differential symbol  $\delta w$ .

$$\delta w = -p_{ext} dV \quad (5.5)$$

$$\int_{V_1}^{V_2} \delta w = - \int_{V_1}^{V_2} p_{ext} dV \quad (5.6)$$

$$w = - \int_{V_1}^{V_2} p_{ext} dV \quad (5.7)$$

The product of  $p$  and  $V$  should be expressed in energy units, since work derived from pressure-volume interactions represents a form of energy transfer. The most common units for volume and pressure are L and atm, respectively. Therefore, the

**CHAPTER 6****Measuring Heat**

**Abstract:** This chapter introduces the principles and practical methods used to measure heat in chemical and physical processes. Beginning with the core concepts of thermochemistry, it outlines how heat changes accompany reactions, phase transitions, and other transformations, and how these quantities are experimentally determined. A central focus is calorimetry, the quantitative measurement of heat, presented through two primary experimental setups: the constant-pressure calorimeter and the constant-volume calorimeter. The chapter explains how each device operates, the assumptions underlying their use, and the types of thermodynamic data they yield, particularly  $\Delta H$  at constant pressure and  $\Delta U$  at constant volume. Building upon these measurements, the chapter also explores Hess's law and Kirchhoff's law, emphasizing how these powerful tools allow the determination of reaction enthalpies under varying conditions, even when direct calorimetric measurements are impractical.

**Keywords:** Calorimetry, Coffee-cup calorimetry, Constant pressure calorimetry, Constant volume calorimetry, Hess's law, Kirchhoff's law, Standard state.

**INTRODUCTION**

The concept of work in thermodynamic systems is relatively straightforward to quantify, as it depends primarily on the external pressure and the corresponding change in system volume as discussed in the previous chapter. Heat transfer, however, is more challenging to measure. Unlike work, which is tied to mechanical variables that can be directly observed or calculated, heat is an energy exchange driven by temperature differences and cannot be measured directly. Its determination therefore relies on specialized experimental techniques and carefully designed instruments, such as calorimeters.

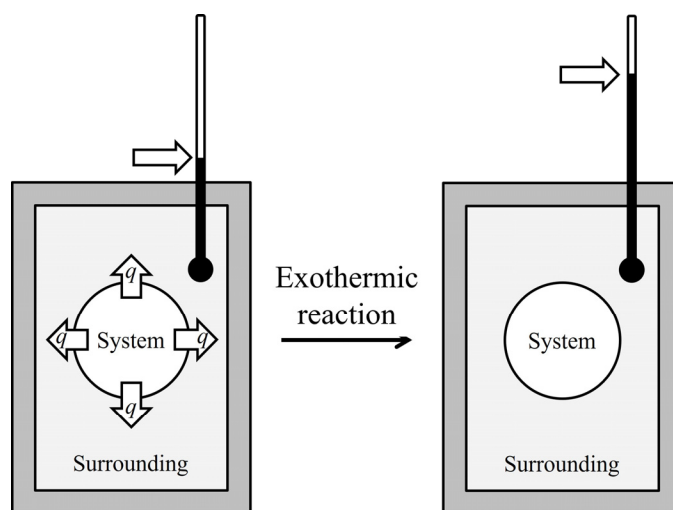
**CALORIMETRY**

The method used to measure heat exchange between a system and its surroundings is known as calorimetry. This technique is central to thermodynamics because it provides a practical way to quantify the energy changes that accompany physical transformations and chemical reactions. In calorimetry, the heat released or absorbed by the system is transferred to a carefully calibrated device called a calorimeter.

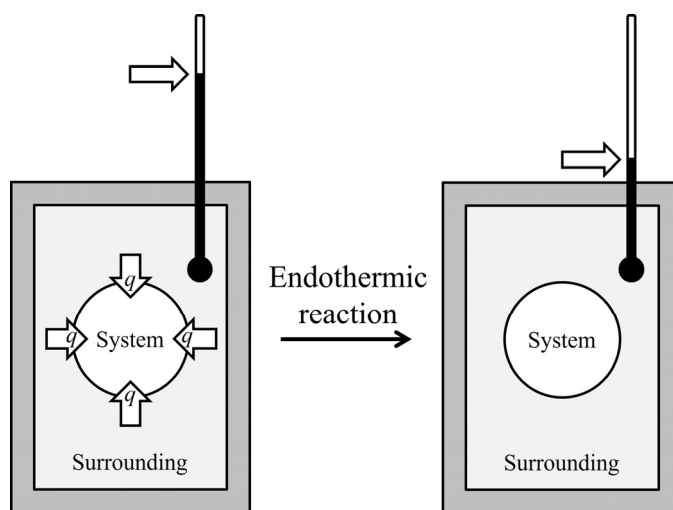
A calorimeter is constructed to minimize energy loss, typically by enclosing the system and its immediate surroundings within a well-insulated container. This insulation ensures that nearly all the heat exchange occurs between the system under study and the calorimeter itself, making the measurement accurate and reliable. The heat transfer is detected as a measurable change in temperature, which acts as a direct indicator of the underlying energy change. Once the temperature change is recorded, the amount of heat transferred can be calculated using the known heat capacity of the calorimeter and the masses of the substances involved. In essence, the calorimeter acts as an intermediary: it absorbs or releases energy in response to the system's thermal change, and this response is converted into quantitative data. The thermal energy change associated with a chemical reaction, phase transition, or physical process is thus manifested as a measurable temperature difference inside the calorimeter. Calorimetry provides a practical, experimentally grounded understanding of energy flow, making it one of the most widely used methods in both chemical research and industrial applications. If a reaction releases heat, it is classified as exothermic ( $q < 0$ ), and the temperature of the calorimeter increases (Fig. 6.1). Conversely, if a reaction absorbs heat, it is classified as endothermic ( $q > 0$ ), and the temperature of the calorimeter decreases (Fig. 6.2). The heat gained or lost by the calorimeter is equal in magnitude but opposite in sign to the heat released or absorbed by the reaction. By combining the calorimeter's heat capacity with the measured temperature change, the amount of heat exchanged during the chemical process can be determined as shown below.

$$q = C\Delta T \quad (6.1)$$

where  $q$  is the heat transferred,  $C$  is the heat capacity of the calorimeter (or of the substances involved), and  $\Delta T$  is the observed change in temperature. For more detailed studies, the masses and specific heat capacities of individual components may also be considered.



**Fig. (6.1).** Change in temperature inside the calorimeter due to an exothermic reaction. The temperature of the thermometer is indicated by the arrow.



**Fig. (6.2).** Change in temperature inside the calorimeter due to an endothermic reaction. The temperature of the thermometer is indicated by the arrow.

A variety of calorimeters have been developed to measure heat exchange under different experimental conditions, allowing precise determination of the thermodynamic properties of substances. Among the advanced techniques, Differential Scanning Calorimetry (DSC) is widely used to study phase transitions and thermal stability, while Isothermal Titration Calorimetry (ITC) provides direct measurements of binding interactions and reaction enthalpies at constant

## Second Law of Thermodynamics

**Abstract:** The second law of thermodynamics establishes the fundamental directionality of natural processes and sets the limits on energy conversion in physical and chemical systems. This chapter introduces the major conceptual formulations of the law, including the Kelvin–Planck and Clausius statements, which collectively describe the impossibility of perfect heat-to-work conversion and the spontaneous flow of heat from hot to cold bodies. The Clausius inequality is presented as a rigorous mathematical criterion that distinguishes reversible from irreversible processes and forms the basis for defining entropy as a thermodynamic state function. Entropy changes for reversible and irreversible transformations are examined, highlighting the inherent increase of total entropy in spontaneous processes. The statistical interpretation of entropy is also discussed, linking macroscopic irreversibility to microscopic probability distributions through the number of accessible microstates. Together, these perspectives provide a comprehensive understanding of spontaneity, equilibrium, and the fundamental limits governing thermodynamic transformations.

**Keywords:** Clausius inequality, Clausius statement, entropy statement, Kelvin–Planck’s statement, Second law, Statistical definition of entropy.

### INTRODUCTION

While the first law of thermodynamics establishes that energy is conserved, it does not indicate the direction in which processes occur. To address this fundamental limitation, the second law of thermodynamics was formulated. This law explains why perpetual motion machines are impossible, why machines can never achieve 100% efficiency, and why chemical reactions and physical changes proceed in the direction that increases the overall disorder of the universe.

To properly comprehend the statements of the second law of thermodynamics, it is essential to first become familiar with a few fundamental terms. One such term is heat reservoir, also known as a thermal energy reservoir. A heat reservoir is an idealized, very large system that can supply or absorb finite amounts of heat without undergoing any noticeable change in temperature. In practice, examples of reservoirs include oceans, large bodies of water, or the atmosphere. In thermodynamics, when such a reservoir supplies heat energy, it is referred to as a source, whereas when it absorbs heat, it is known as a heat sink. Another important concept is the heat engine. A heat engine is a device that operates between a source and a sink, converting part of the heat absorbed from the high-temperature reservoir

into useful work, while rejecting the remaining heat to the low-temperature reservoir. Classic examples include steam engines, internal combustion engines, and gas turbines. In contrast, heat pumps and refrigerators are devices that operate in the reverse direction. Instead of producing work from heat, they consume external work to transfer heat from a colder region to a hotter region. For instance, refrigerators remove heat from the food compartment and release it to the warmer surroundings, while air conditioners pump heat from indoors to outdoors to maintain a cool interior. These concepts, heat reservoirs, sources, sinks, heat engines, and heat pumps, form the foundation for understanding the second law of thermodynamics, as they embody the practical systems through which the law is observed and applied.

There is no single, all-encompassing statement that captures every aspect of the second law of thermodynamics. The law addresses diverse phenomena such as the direction of natural processes, the limitations on converting heat into work, and the concept of entropy. Due to its broad scope, the second law of thermodynamics is expressed through three equivalent yet differently worded statements, which are presented below.

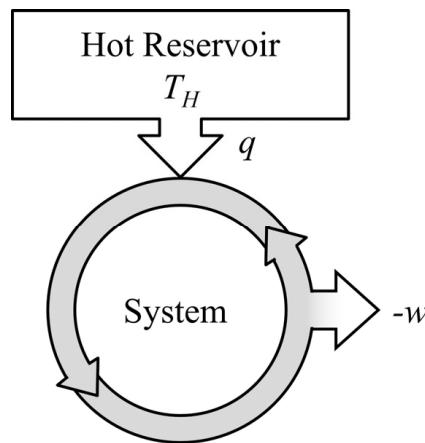
1. Kelvin statement (or Kelvin-Planck's statement)
2. Clausius statement
3. Entropy statement

These statements explain the irreversibility of certain processes and the tendency of natural systems to move towards higher randomness. They provide the basic understanding for spontaneous heat transfers and conversions.

### **Kelvin Statement**

It is impossible for any system to operate in a cycle by extracting heat from a hot reservoir and converting it entirely into work without simultaneously rejecting some heat to a cold reservoir. In other words, no heat engine can achieve 100% thermal efficiency.





**Fig. (7.1).** A heat engine that violates the Kelvin statement of the second law.  $q$  is the heat absorbed by the system, and  $w$  is the amount of work done by the system on its surrounding.

The heat engine illustrated in Fig. (7.1) violates the Kelvin statement of the second law of thermodynamics by converting all the absorbed heat energy ( $q$ ) into work ( $w$ ), thereby implying 100% efficiency. In this case,  $q > 0$ ,  $w < 0$ , and  $q = -w$ . However, the Kelvin statement asserts that no heat engine can operate without rejecting a portion of the absorbed heat to a cold reservoir. Thus, achieving 100% efficiency is impossible. Fig. (7.2) depicts a heat engine that operates in compliance with the Kelvin statement.

In the heat engine shown in Fig. (7.2),  $q_H > 0$ ,  $w < 0$ ,  $q_C < 0$  and  $q_H = -w - q_C$ . This heat engine works at a lower efficiency than 100%, and therefore, it is a ‘possible’ heat engine to exist. Kelvin’s statement explains the thermodynamic irreversibility. In any real-world process, there are always some irreversible effects, such as friction, heat dissipation, or energy losses, that prevent the complete conversion of heat into work.

### Clausius Statement

It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir without converting some work into heat. In other words, heat does not transfer spontaneously from a cold reservoir to a hot reservoir.

The heat engine shown in Fig. (7.3) violates the Clausius statement of the second law by spontaneously transferring heat from a cold reservoir to a hot reservoir. Here,  $q_C > 0$ ,  $q_H < 0$  and  $q_C = -q_H$ . Transferring heat from a cold to a hot reservoir

## Heat Engines

**Abstract:** This chapter provides an overview of heat engines and their fundamental role in converting thermal energy into mechanical work. The concept of efficiency is introduced as a central performance metric, highlighting the inherent limitations imposed by the second law of thermodynamics. Special emphasis is placed on the Carnot cycle, the idealized reversible cycle that establishes the theoretical maximum efficiency attainable by any heat engine operating between two temperature reservoirs. In contrast, the Otto cycle, which underpins the operation of spark-ignition internal combustion engines, is discussed as a practical and widely used model that illustrates how real engines deviate from ideal behavior due to irreversibilities. The chapter also examines the operation of Carnot refrigerators, emphasizing their coefficients of performance and the thermodynamic constraints that limit their achievable performance.

**Keywords:** Carnot cycle, Carnot refrigerator, Coefficient of performance, Efficiency, Otto cycle.

### INTRODUCTION

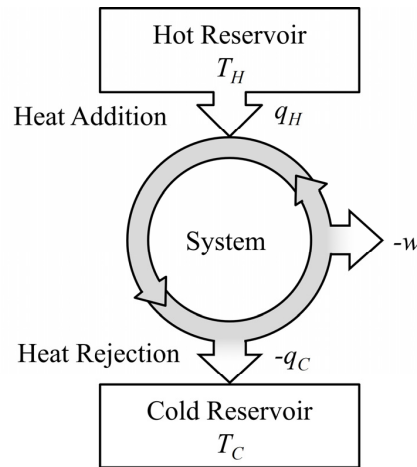
A heat engine is a fundamental concept in thermodynamics that illustrates how thermal energy can be converted into mechanical work. It operates by transferring heat from a high-temperature reservoir to a low-temperature reservoir while extracting part of this energy as useful work. The efficiency of a heat engine depends on how effectively it can convert absorbed heat into work, which is inherently limited by the second law of thermodynamics. Real engines, such as steam engines, internal combustion engines, and gas turbines, are practical applications of this principle and play a central role in powering modern technology and industry.

A heat engine operates in a cycle and does work on its surroundings if heat is added to it. They are expected to work with maximum thermal efficiency ( $\eta$ ), which can be defined by,

$$\eta = \frac{\text{net work output}}{\text{heat input}}$$

The sign convention for work and heat is not considered when calculating the engine efficiencies. An ideal heat engine that converts all the input heat into work

would have an efficiency of one ( $\eta = 1$ ), but this is impossible as it violates the second law of thermodynamics. Any engine that violates any of the thermodynamic laws is called a perpetual motion machine. A perpetual motion machine, though theoretically 100% efficient, has never been built and will never be possible according to the laws of thermodynamics. Non-perpetual engines or real engines take heat from the heat source at high temperature ( $T_H$ ) to do work on their surroundings while rejecting a certain amount of heat to the heat sink at lower temperature ( $T_C$ ). For an engine operating in a cycle with only reversible processes, the total change in entropy over one complete cycle must be zero. In a real heat engine, this entropic cycle can be divided into two parts, such as heat addition and heat rejection (Fig. 8.1).



**Fig. (8.1).** A real heat engine with heat addition to the system and heat rejection from the system.

To maximize the efficiency of real heat engines, the entropy generation during the cyclic process must be minimized. To satisfy this requirement, the entropy at heat rejection should be maximized while minimizing the entropy at heat addition.

$$\Delta S = \frac{q_H}{T_H} - \frac{q_C}{T_C} \quad (8.1)$$

Entropy increase is minimized when heat is supplied at the highest possible temperature, ideally through isothermal heat transfer at  $T_H$ . Likewise, entropy decrease is maximized when heat is rejected at the lowest possible temperature, ideally through isothermal heat transfer at  $T_C$ . The heat addition and heat rejection

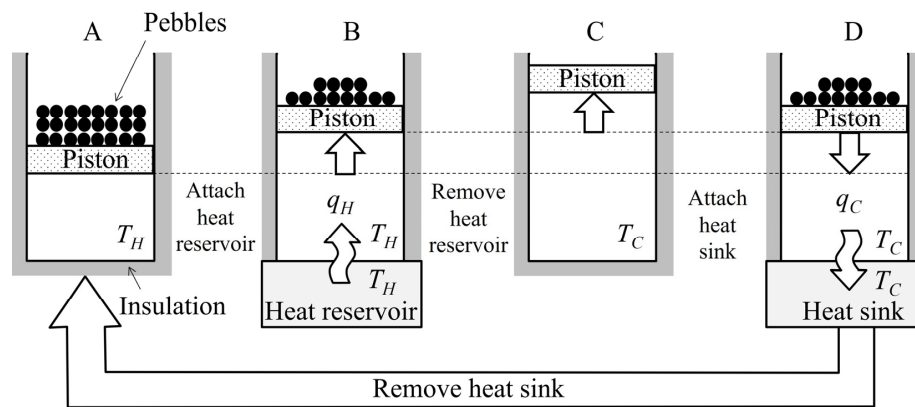
isotherms must be connected to complete the cyclic process of the heat engine. The higher-temperature isotherm needs to go to the lower-temperature isotherm and return to the original isotherm during the cycle. If heat exchange occurs during these connecting steps, the entropy of the entire cycle will increase. Therefore, the connecting steps should be adiabatic to make the two steps isentropic ( $\Delta S = 0$ ) and to keep the entropy of the cycle minimum.

Therefore, the engine cycle should consist of isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression for an engine to generate the maximum amount of work while keeping its entropy minimum. This idealized cycle was first proposed by Sadi Carnot in 1824, and the engine that follows it is known as the Carnot engine, which represents the most efficient heat engine possible.

## HEAT ENGINE CYCLES

### Carnot Cycle

The Carnot cycle represents an idealized, completely reversible cycle in which an ideal gas undergoes expansion and compression within a closed system. It serves as a theoretical standard against which the performance of all real heat engines is measured. No man-made engine has ever achieved, nor can it exceed, the efficiency of the Carnot engine; thus, the Carnot cycle defines the absolute upper limit of efficiency for heat engines operating between two thermal reservoirs. The steps of the Carnot cycle are shown in Fig. (8.2).



**Fig. (8.2).** Schematic representation of the Carnot cycle showing the thermodynamic states of the system: (A) high-temperature state; (B) high-temperature state after partial volume expansion; (C) low-temperature state after volume expansion; and (D) low-temperature state after partial volume compression.

**CHAPTER 9****Third Law of Thermodynamics**

**Abstract:** This chapter presents a comprehensive examination of the third law of thermodynamics and its central role in establishing an absolute scale for entropy. The third law states that the entropy of a perfectly crystalline substance approaches zero as its temperature approaches absolute zero, providing the foundational reference for defining absolute entropy. Building on this principle, the chapter explores the experimental and theoretical methods used to measure entropy, including heat capacity integration and contributions from phase transitions. By integrating theoretical insight with practical measurement techniques, this chapter offers a clear and cohesive understanding of entropy from an absolute, measurable, and standardized perspective.

**Keywords:** Absolute entropy, Absolute zero temperature, Standard entropy, Thermodynamics, Third law.

**INTRODUCTION**

The third law of thermodynamics emerged in the early 20<sup>th</sup> century as scientists sought to understand the behavior of matter at very low temperatures. In 1906, Walther Nernst formulated the Nernst heat theorem, which states that the change in entropy ( $S$ ) for any isothermal process approaches zero as the temperature approaches absolute zero:

$$\lim_{T \rightarrow 0} \Delta S = 0$$

Later, Max Planck refined the concept, providing a general definition for the entropy of a perfect crystal at absolute zero. Planck proposed that, as the temperature approaches absolute zero, the absolute entropy ( $S$ ) of any homogeneous chemical body also approaches zero. In 1907, Albert Einstein proposed a quantum model in which atoms in a crystal lattice are treated as quantum harmonic oscillators with discrete energy levels. This model successfully explained why the heat capacity of solids decreases sharply at low temperatures and predicted that, as the temperature approaches absolute zero, the heat capacity approaches zero:

$$\lim_{T \rightarrow 0} C_V = 0$$

Franz Simon played a key role in confirming the third law of thermodynamics as an experimentally verified principle. Through systematic calorimetric studies of the heat capacities and entropies of solids, liquids, and gases at very low temperatures, he showed that the entropy of real substances approaches a definite value, often zero for perfect crystals, as the temperature nears absolute zero. Together, all these contributions established the third law as a fundamental principle, linking low-temperature thermodynamics with the first and second laws of thermodynamics.

The third law of thermodynamics states that the entropy of a pure, perfectly crystalline substance is zero at absolute zero temperature (0 K).

While the second law of thermodynamics establishes the direction of spontaneous processes and introduces entropy as a fundamental thermodynamic property, it does not define the absolute value of entropy. The third law of thermodynamics extends these concepts by describing the behavior of matter as the temperature approaches absolute zero, thereby providing a reference point for the determination of absolute entropy. Together, the second and third laws establish the theoretical foundation for understanding energy dispersal, equilibrium, and the thermodynamic limits of physical processes. At absolute zero (0 K), all thermal motion ceases, and in a perfect crystal the atoms or ions occupy a completely regular and uniform arrangement. The main importance of the third law of thermodynamics can be summarized as follows.

- It defines the sign of the entropy of any substance at temperatures above absolute zero as positive.
- It provides a fixed reference point that allows us to measure the absolute entropy of any substance at any temperature.

The statistical definition of entropy states  $S = k_B \ln \omega$ , where  $S$  is entropy,  $k_B$  is Boltzmann's constant and  $\omega$  is the number of microstates. At absolute zero temperature, the pure, crystalline substance has one unique ground state and therefore,  $\omega = 1$ , and hence  $S = 0$ .

## ENTROPY AND ABSOLUTE ZERO TEMPERATURE

In the third law of thermodynamics, a perfect crystal at absolute zero has only one possible microscopic arrangement, meaning its entropy is exactly zero. This follows from the complete absence of disorder when every atom or ion occupies a perfectly ordered lattice site. However, in real substances, imperfections can prevent the

crystal from achieving perfect order even at very low temperatures. This leftover disorder gives rise to what is known as ‘residual entropy’. Residual entropy is the entropy that remains in a substance even at absolute zero temperature due to the presence of microscopic disorder in its molecular arrangement. Thus, while the third law sets zero entropy as the limit for an ideal crystal, real crystals often retain a small but finite entropy due to such configurational possibilities. In practice, absolute zero is an ideal temperature that cannot be attained. According to the third law of thermodynamics, reaching absolute zero would require either an infinite number of discrete steps or an infinite amount of time. Cooling methods such as expansion or adiabatic demagnetization reduce a system's temperature by transferring thermal energy from the system to its surroundings. However, as the temperature approaches 0 K, the amount of removable thermal energy becomes increasingly small, making each successive cooling step less effective. Consequently, an infinite number of progressively smaller energy-removal steps would be needed to reach absolute zero. Imagine approaching a goal where every effort only halves the remaining gap. Each move brings you closer but never lets you reach it completely. Cooling a system behaves similarly; each reduction in temperature removes less and less heat energy, making absolute zero unattainable.

### Calculation of Absolute Entropy

The third law of thermodynamics states that the entropy of a perfect crystal at absolute zero is zero. Starting from this reference point, the entropy of a substance at higher temperatures can be found by adding up all the heat absorbed as the substance is warmed, divided by the temperature at which the heat is absorbed. Extra contributions from phase changes, such as melting or boiling, must also be included as they involve sudden increases in entropy. In this way, experimental heat capacity data can be used to calculate the absolute entropy of a substance, which is important for predicting free energy changes, equilibrium, and spontaneity in chemical systems.

Consider a thermodynamic system that absorbs an infinitesimal amount of heat  $dq$  reversibly at temperature  $T$ . The corresponding change in entropy of the system is given by the equation:

$$dS = \frac{dq_{rev}}{T} \quad (9.1)$$

For the processes occurring at constant pressure,  $dq_{rev}$  may be written as:

## CHAPTER 10

# Thermodynamic Potentials and Maxwell Relations

**Abstract:** This chapter explores the central role of thermodynamic potentials in characterizing equilibrium, spontaneity, and energy transformations in thermodynamic systems. Beginning with the fundamental thermodynamic relations, it develops the mathematical outline that links internal energy, enthalpy, Helmholtz energy, and Gibbs energy to their natural variables. Special emphasis is placed on the Helmholtz energy, which is particularly useful for systems at constant temperature and volume, and the Gibbs energy, which governs processes occurring at constant temperature and pressure. From these potentials, the chapter derives the Maxwell relations, a powerful set of equations that connect measurable thermodynamic properties and provide pathways to evaluate quantities that may otherwise be difficult to determine experimentally. These concepts form a unified foundation for analyzing thermodynamic behavior, enabling deeper insight into equilibrium conditions, material properties, and the mathematical structure underlying classical thermodynamics.

**Keywords:** Fundamental thermodynamic relations, Gibbs energy, Helmholtz energy, Maxwell relations, Thermodynamic potentials.

## INTRODUCTION

The implications of the third law extend beyond entropy itself. Since entropy appears in the definitions of Helmholtz energy,  $A$ , and Gibbs energy,  $G$  (often referred to as Helmholtz free energy and Gibbs free energy in some texts), the boundary condition  $S \rightarrow 0$  as  $T \rightarrow 0$  directly governs the behavior of these thermodynamic potentials. At absolute zero, the entropy contribution to energy vanishes, anchoring both Helmholtz and Gibbs energies to unique reference values. To fully appreciate the role of the third law in thermodynamics, it is therefore essential to examine how it constrains and defines the energies that determine spontaneity and equilibrium. For irreversible processes,  $\Delta S_{total} > 0$ . Since  $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$ :

$$\Delta S_{sys} + \Delta S_{surr} > 0 \quad (10.1)$$

To evaluate the spontaneity of a process, one must consider the entropy change of both the system ( $\Delta S_{sys}$ ) and the surroundings ( $\Delta S_{surr}$ ). In practice, however, direct



measuring of  $\Delta S_{surr}$  is often inconvenient. An alternative formulation can be derived that eliminates the need to evaluate  $\Delta S_{surr}$  directly. To illustrate this, consider an exothermic chemical reaction occurring at constant pressure, where the transfer of heat from the system to the surroundings (the same rational is valid for endothermic reactions).

$$q_{surr} = -q_{sys} \quad (10.2)$$

At constant pressure, the heat transfer associated with the system corresponds to its enthalpy change, with the released heat representing the enthalpy decrease during an exothermic reaction,  $q_{sys} = \Delta H_{sys}$ . Therefore, the entropy change in the surroundings ( $\Delta H_{surr}$ ) can be written as,

$$\Delta S_{surr} = \frac{q_{surr}}{T} = -\frac{q_{sys}}{T} = -\frac{\Delta H_{sys}}{T} \quad (10.3)$$

Hence,  $\Delta S_{total}$  can be written as ( $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$ ),

$$\Delta S_{total} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} \quad (10.4)$$

$\Delta S_{total}$  of a given reaction can be calculated from thermodynamics data for the system only by using the above relationship. For a spontaneous process,  $\Delta S_{total} > 0$ . Therefore,

$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0 \quad (10.5)$$

When the above inequality is multiplied by  $-T$ , its direction reverses. Multiplying the above relationship by  $-T$ :

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \quad (10.6)$$

This led the American scientist Josiah Willard Gibbs (1873) to define a new state function, now known as Gibbs energy ( $G$ ).

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} \quad (10.7)$$

For the simplicity of the equation, the ‘sys’ subscript can be omitted from the above equation.

$$\Delta G = \Delta H - T\Delta S \quad (10.8)$$

If the above derivation is carried out under constant volume conditions instead of constant pressure,  $\Delta U$  replaces  $\Delta H$ . To describe such isochoric processes, Hermann von Helmholtz (1882) introduced another thermodynamic state function, based on the internal energy change of the system. This function is now known as Helmholtz energy ( $A$ ).

$$\Delta A = \Delta U - T\Delta S \quad (10.9)$$

The two new thermodynamic energies can be represented as follows.

Gibbs energy  $G = H - TS$

Helmholtz energy  $A = U - TS$

At a constant temperature, both Gibbs and Helmholtz energies should be negative for a process to be spontaneous. From the Clausius inequality, the following expression for the entropy change and heat flow at constant temperature can be written.

$$dS \geq \frac{\delta q}{T} \quad (10.10)$$

$$TdS \geq \delta q \quad (10.11)$$

**CHAPTER 11****Gibbs Energy and Equilibrium Thermodynamics**

**Abstract:** This chapter presents a comprehensive description of Gibbs energy as the central thermodynamic potential governing spontaneity, equilibrium, and phase behavior in chemical and physical systems. The discussion extends to its role in determining equilibrium conditions and driving forces for physical and chemical transformations. The concept of fugacity is introduced as a real-gas correction that enables an accurate description of non-ideal systems, particularly in relation to equilibrium calculations and phase transitions. Phase equilibrium is explained through Gibbs energy minimization, leading to the derivation and application of the Clapeyron and Clausius–Clapeyron equations. The chapter further develops the conditions for chemical equilibrium by linking the Gibbs energy change to equilibrium constants. The van’t Hoff equation is introduced to describe the temperature variation of equilibrium constants, offering insight into the thermodynamic control of reactions under different conditions.

**Keywords:** Fundamental thermodynamic relations, Gibbs energy, Helmholtz energy, Maxwell relations, Thermodynamic potentials.

**INTRODUCTION**

Gibbs energy is a central thermodynamic potential and is particularly suited for systems under constant temperature and pressure, the most common conditions in laboratory and industrial practices. The equality of Gibbs energy across phases or between reactants and products highlights the thermodynamic description of phase equilibria and chemical equilibria, as well as the definition of equilibrium constants. Phase equilibrium describes the conditions under which multiple phases, such as solid, liquid, and vapor, can coexist in a stable balance, governed by the equality of temperature, pressure, and chemical potential across the phases. Chemical equilibrium, in contrast, refers to the dynamic state in which the rates of forward and reverse reactions are equal, resulting in no net change in composition. Thermodynamics links this equilibrium condition to the Gibbs energy change, providing the basis for defining and predicting its dependence on temperature and pressure.

**GIBBS ENERGY**

Gibbs energy ( $G$ ) can be expressed as  $G = H - TS$ , where  $H$  is the enthalpy,  $T$  is the temperature, and  $S$  is the entropy. This shows how  $G$  varies with pressure and

temperature, which are important for discussing phase transitions and chemical reactions. Starting with  $G = H - TS$ , and taking the total differential:

$$dG = dH - d(TS) \quad (11.1)$$

$$dG = dH - TdS - SdT \quad (11.2)$$

Expanding  $dH$  using  $H = U + pV$  and substituting it into the expression for  $dG$  in Eq. (11.2):

$$dG = d(U + pV) - TdS - SdT \quad (11.3)$$

$$dG = dU + pdV + Vdp - TdS - SdT \quad (11.4)$$

Term  $dU$  in Eq. (11.4) can be replaced with the fundamental thermodynamic relation for internal energy with composition term,  $dU = TdS - pdV + \sum_i \mu_i dn_i$ , where  $\mu_i$  is the chemical potential of species  $i$ . The symbol  $n_i$  refers to the number of moles (or amount of substance) of component  $i$  in the system.

$$dG = TdS - pdV + \sum_i \mu_i dn_i + pdV + Vdp - TdS - SdT \quad (11.5)$$

In Eq. (11.5), the positive and negative terms of  $pdV$  and  $TdS$  cancel out, thereby eliminating their contributions from the expression. Therefore,

$$dG = Vdp - SdT + \sum_i \mu_i dn_i \quad (11.6)$$

This relationship clearly shows how Gibbs energy changes with respect to its natural variables: temperature ( $T$ ), pressure ( $p$ ), and composition ( $n_i$ ). Two important consequences follow from this expression:

- At constant composition and constant pressure,  $(\partial G / \partial T)_p = -S$ , meaning that the slope of a plot of Gibbs energy versus temperature is equal to the negative of the entropy.
- Similarly, at constant composition and constant temperature,  $(\partial G / \partial p)_T = V$ , so the slope of Gibbs energy versus pressure corresponds to the volume.

These relationships are fundamental for understanding phase transitions and chemical reactions.

### The Dependence of Gibbs Energy on Temperature

Since temperature is one of the natural variables of Gibbs energy, understanding how Gibbs energy varies with temperature is essential for predicting phase stability, reaction spontaneity, and equilibrium composition. At constant pressure and composition, the slope of  $G$  with respect to temperature is given by:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (11.7)$$

By definition  $G = H - TS$ . Therefore,

$$S = \frac{H - G}{T} \quad (11.8)$$

Substituting  $S$  in Eq. (11.7) with the expression for  $S$  in Eq. (11.8),

$$\left(\frac{\partial G}{\partial T}\right)_p = -\left(\frac{H - G}{T}\right) \quad (11.9)$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -\frac{H}{T} + \frac{G}{T} \quad (11.10)$$


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## Practice Questions and Answers

### PRACTICE QUESTIONS

#### CHAPTER 1

1. Find the pressure of 2.00 mol of an ideal gas at the temperature 273 K and the volume of 22.4 L ( $R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ).
2. Find the volume of  $\text{CO}_2$  gas produced from 200.0 g of  $\text{CaCO}_3$  if the  $\text{CO}_2$  is at a pressure of 740.0 torr and a temperature of 300.0 K (760 torr = 1 atm).
3. Calculate the pressure of nitrogen gas at 300.0 K and a molar volume of 22.40 L by using the Van der Waals equation. Use Table 1.1 for the values of  $a$  and  $b$  coefficients.
4. Find the pressure of 1.000 mol of oxygen at a volume of 0.500 L and a temperature of 298.15 K using the Van der Waals equation of state. Find the percentage difference from the pressure of an ideal gas under the same conditions. Use Table 1.1 for the values of  $a$  and  $b$  coefficients.

#### CHAPTER 2

1. What is a thermodynamic system, and how is it classified?
2. What is the difference between state variables and path variables? Give examples.
3. What information can be obtained from a PV diagram, and why is it important?

#### CHAPTER 3

1. State the Zeroth Law of Thermodynamics and explain its significance in temperature measurement.
2. Give two practical examples of the Zeroth Law in everyday life.

3. A constant-volume ideal gas thermometer is calibrated at the triple point of water ( $T_{tp} = 273.16\text{ K}$ ), where the measured pressure is  $p_{tp} = 112.0\text{ kPa}$ . The bulb is then placed in a system, and the gas pressure is measured to be  $p = 136.25\text{ kPa}$ . Determine the absolute temperature of the system in kelvins (K) and in degrees Celsius  $^{\circ}\text{C}$ .
4. Why is a constant-volume ideal gas thermometer considered a primary standard for temperature, and why must it often be extrapolated to zero pressure?
5. A mercury thermometer reads  $50.0^{\circ}\text{C}$  when placed in a water bath. A constant-volume ideal gas thermometer in the same bath reads  $p = 118.85\text{ kPa}$ . Using reference points  $p_{tp} = 100.0\text{ kPa}$  at  $273.16\text{ K}$  and  $p_{bp} = 136.60\text{ kPa}$  at  $373.15\text{ K}$ , determine the correction to apply to the mercury thermometer.

## CHAPTER 4

1. Explain how Joule's paddle wheel experiment demonstrated the equivalence between mechanical work and heat. Why was this experiment important for the formulation of the first law of thermodynamics?
2. In Joule's experiment, a weight of  $20\text{ kg}$  is attached to a paddle wheel inside an insulated container of water. If the weight is allowed to fall a vertical distance of  $2\text{ m}$ , calculate the work done on the system by the falling weight. (Take  $g = 9.81\text{ m s}^{-2}$ ).
3. During the experiment, Joule observed that  $772\text{ ft lb}$  of work was required to raise the temperature of  $1\text{ lb}$  of water by  $1^{\circ}\text{F}$ . Derive the equivalent value in SI units ( $\text{J kg}^{-1}\text{ K}^{-1}$ ) and compare it with the modern value of the specific heat capacity of water.

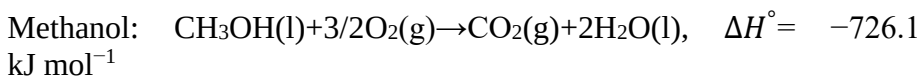
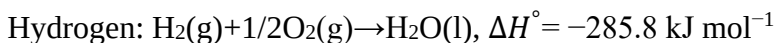
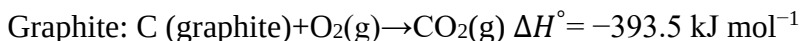
## CHAPTER 5

1. State the first law of thermodynamics and explain the roles of heat and work in this law.
2. One mole of an ideal gas expands isothermally and reversibly from  $10.0\text{ L}$  to  $20.0\text{ L}$  at  $298\text{ K}$ . Calculate the work done by the gas.

3. Why does the temperature of an ideal gas decrease during a reversible adiabatic expansion?
4. A sample of 2.00 mol of a monatomic ideal gas is heated at constant volume from 300 K to 400 K. Calculate the heat absorbed.
5. Why are heat ( $q$ ) and work ( $w$ ) path functions, while internal energy ( $U$ ) is a state function?

## CHAPTER 6

1. A 50.0 g sample of water at 25.0°C absorbs 420 J of heat in a coffee cup calorimeter. What is the final temperature of the water? (Specific heat of water = 4.18 J g<sup>-1</sup> K<sup>-1</sup>)
2. In an isobaric calorimeter, 100 mL of 1.0 M HCl is mixed with 100 mL of 1.0 M NaOH. The temperature rises from 25.0°C to 28.3°C. Calculate the enthalpy of neutralization per mole of water formed. (Density of solution = 1.00 g mL<sup>-1</sup>, specific heat = 4.18 J g<sup>-1</sup> K<sup>-1</sup>)
3. A 1.50 g sample of glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, M = 180 g mol<sup>-1</sup>) is combusted in a bomb calorimeter with heat capacity 5.00 kJ K<sup>-1</sup>. The temperature rises by 1.20 K. Calculate the molar enthalpy of combustion of glucose.
4. The standard enthalpy of combustion of the following compounds is given:



Using these data, calculate the standard enthalpy of formation of liquid methanol (CH<sub>3</sub>OH(l)).

5. The standard enthalpy change of a reaction at 298 K is  $\Delta H^\circ_{(298)} = -100 \text{ kJ}$ . The difference in heat capacities of products and reactants is  $\Delta C_p = +25 \text{ J K}^{-1}$ . Estimate  $\Delta H^\circ$  at 350 K.



**CHAPTER 7**

1. A heat amount  $q = 5000$  J flows spontaneously from a hot reservoir at  $T_H = 400$  K to a cold reservoir at  $T_C = 300$  K. Calculate the total entropy change of the universe (reservoirs) for this process.
2. A small model system has  $N = 100$  indistinguishable particles, and each particle can occupy three equally probable microstates ( $\Omega = 3$ ). Calculate the entropy  $S$  using Boltzmann's formula ( $k_B = 1.380649 \times 10^{-23}$  J K<sup>-1</sup>).
3. A 0.100 kg mass of water (specific heat capacity of water  $\bar{C} = 4184$  J kg<sup>-1</sup> K<sup>-1</sup>) is cooled reversibly by a large reservoir at  $T = 300$  K from  $T_i = 350$  K to  $T_f = 300$  K. Calculate (a) entropy change of the water, (b) entropy change of the reservoir, and (c) total entropy change.
4. A container has  $n = 2.00$  mol of a monatomic ideal gas ( $C_V = 3R/2$ ). The gas is heated at constant volume from  $T_1 = 300$  K to  $T_2 = 600$  K. Calculate the entropy change  $\Delta S$ .
5. One mole of an ideal gas ( $n = 1.00$  mol) at  $T = 298$  K expands isothermally and reversibly from  $V_1 = 10.0$  L to  $V_2 = 40.0$  L. (a) Compute  $\Delta S$  for the gas. (b) Consider a free (irreversible) expansion from the same  $V_1$  to  $V_2$  at the same initial and final temperatures; compare  $\Delta S$  and  $\int \frac{dq}{T}$  to demonstrate the Clausius inequality.

**CHAPTER 8**

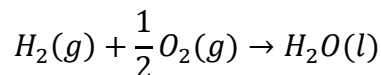
1. A Carnot engine operates between a hot reservoir at  $T_H = 900$  K and a cold reservoir at  $T_C = 300$  K. The engine absorbs  $q_H = 6000$  J/cycle.
 

(a) Find the Carnot efficiency  $\eta$ . (b) Find the work output  $w_{cyc}$  and the heat rejected  $q_C$ . (c) Compute the entropy change of the hot reservoir, the cold reservoir, and the total entropy change for one cycle.
2. An Otto cycle contains  $m = 0.02$  kg of air. Initial state A:  $p_A = 100$  kPa,  $T_A = 300$  K. Compression ratio,  $r = V_A/V_B = 9$ . Take  $\gamma = 1.4$ ,  $R = 287$  J kg<sup>-1</sup> K<sup>-1</sup>, and specific heat capacity at constant volume  $C_v = 718$  J kg<sup>-1</sup> K<sup>-1</sup>. During the constant-volume heat addition, the heat added is  $Q_{in} = 600$  kJ kg<sup>-1</sup> (per kg of air). Calculate: (a)  $T_B$  after isentropic compression; (b)  $T_C$  after heat addition; (c)  $T_D$  after isentropic expansion;

- (d) heat added  $q_{in}$ , heat rejected  $q_{out}$ , net work per cycle  $w_{cyc}$ , and thermal efficiency  $\eta$ .
3. A real heat engine operates between  $T_H = 1000$  K and  $T_C = 300$  K. It absorbs  $q_H = 5000$  J/cycle and delivers  $w_{cyc} = 3000$  J of work per cycle. (a) What is the Carnot (maximum) work available from the same heat input? (b) How much work is “lost” because of irreversibility? (c) Compute the entropy generation  $\Delta S_{gen}$  per cycle and verify that the lost work equals  $T_C \Delta S_{gen}$ . (Take the environment/sink temperature as  $T_C = 300$  K for exergy-loss estimate.)
  4. An Otto cycle engine has a compression ratio of  $r = 8$  with  $\gamma = 1.4$ . The same engine operates as a Carnot engine between maximum and minimum temperatures of  $T_H = 1200$  K, and  $T_C = 300$  K. Compare their efficiencies. Assume  $q_H = 2000$  J is supplied in both cases.
  5. A Carnot refrigerator is designed to maintain a cold storage chamber at  $T_C = 260$  K while rejecting heat to the surrounding environment at  $T_H = 310$  K. The refrigerator extracts  $q_C = 1500$  J/s from the chamber. (a) Calculate the Coefficient of Performance (COP) of the refrigerator. (b) Determine the minimum power input,  $w$ . (c) Find the rate of heat rejected to the surroundings  $q_H$ .

## CHAPTER 9

1. Explain why the entropy of a perfect crystal is zero at 0 K according to the third law of thermodynamics.
2. The molar heat capacity at constant pressure of a substance is approximately constant at  $C_p = 25$  J mol<sup>-1</sup> K<sup>-1</sup> between 0 K and 298 K. Estimate the absolute molar entropy of the substance at 298 K, ignoring phase transitions.
3. Explain why entropy changes during reversible processes are measured using heat transfer, and how the third law of thermodynamics allows calculation of absolute entropy.
4. One mole of ice melts at 273 K with an enthalpy of fusion  $\Delta_{fus}H = 6.01$  kJ mol<sup>-1</sup>. Calculate the entropy change during melting.
5. Consider the following reaction:



$$S^\circ(H_2, g) = 131 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ(O_2, g) = 205 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S^\circ(H_2O, l) = 70 \text{ J mol}^{-1} \text{ K}^{-1}$$

Calculate the standard entropy change of the reaction ( $\Delta_r S^\circ$ ) at 298 K.

## CHAPTER 10

1. What are the fundamental thermodynamic relations, and why are they important?
2. Why are Maxwell relations considered symmetrical relations in thermodynamics?
3. Show that  $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$  using the Helmholtz free energy relation.
4. For an ideal gas, use a Maxwell relation to show that entropy increases with volume at constant temperature.
5. A system of 2 moles of an ideal gas is at  $T = 300 \text{ K}$  and  $V = 10 \text{ L}$ . Using the Maxwell relation, calculate  $\left(\frac{\partial S}{\partial V}\right)_T$ . Gas constant  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

## CHAPTER 11

1. At 298.15 K, the standard enthalpy and Gibbs free energy change for a reaction are  $\Delta_r H^\circ = -40.0 \text{ kJ mol}^{-1}$  and  $\Delta_r G^\circ(298.15 \text{ K}) = -10.0 \text{ kJ mol}^{-1}$ . Calculate  $\Delta_r S^\circ$ .
2. At the normal boiling point of water,  $T_b \approx 373.15 \text{ K}$ , the molar enthalpy of vaporization is  $\Delta_{vap}H = 40.7 \text{ kJ mol}^{-1}$ . Approximate the slope  $\left(\frac{dP}{dT}\right)$  of the liquid–vapor coexistence curve at 1 atm using the Clapeyron equation. The molar liquid volume  $V_\ell$  is  $1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$  (treat the vapor as ideal).

3. A liquid has  $\Delta_{vap}H = 30.0 \text{ kJ mol}^{-1}$ . Its vapor pressure at  $T_1 = 300.0 \text{ K}$  is  $P_1 = 0.050 \text{ bar}$ . Using the Clausius–Clapeyron approximation (assume  $\Delta_{vap}H$  is constant, and vapor behaves ideally), estimate the vapor pressure  $P_2$  at  $T_2 = 320.0 \text{ K}$ .
4. A sample of nitrogen gas at  $300.0 \text{ K}$  and  $80.0 \text{ bar}$  exhibits non-ideal behavior. Under these conditions, its fugacity coefficient is given as  $\phi = 0.85$ .
  - a. Calculate the fugacity  $f$  of the gas (in bar).
  - b. Calculate the molar Gibbs energy difference between the real gas and the corresponding ideal gas at the same  $T$  and  $P$ .
5. For a gaseous reaction at  $T_1 = 300.0 \text{ K}$ , the equilibrium constant,  $K_c(T_1)$ , is  $0.200$ . The standard reaction enthalpy is  $\Delta_r H^\circ = +25.0 \text{ kJ mol}^{-1}$  (endothermic).
  - (a) Using the van't Hoff relation, estimate  $K_c$  at  $T_2 = 350.0 \text{ K}$ .
  - (b) If the reaction has  $\Delta n = +1$  (one more mole of gas on the product side than the reactant side), compute  $K_p(T_2)$  ( $R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$ ).

**ANSWERS****Chapter 1**

1.

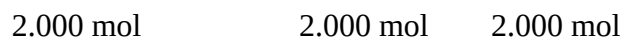
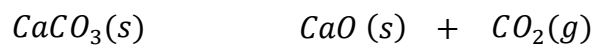
$$pV = nRT$$

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

$$p = \frac{2.00 \text{ mol} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{22.4 \text{ L}}$$

$$p = 2.00 \text{ atm}$$

$$n_{\text{CaCO}_3} = \frac{200.0 \text{ g}}{100.1 \text{ g mol}^{-1}} = 2.000 \text{ mol}$$



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

$$V = \frac{2.000 \text{ mol} \times 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300.0 \text{ K}}{740/760 \text{ atm}}$$

$$V = 50.56 \text{ L}$$

$$2. \left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

$$p = \frac{8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1} \times 300.0 \text{ K}}{(22.40 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} - 3.870 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})} - \frac{0.1370 \text{ m}^6 \text{ Pa mol}^{-2}}{(22.40 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})^2}$$

$$p = \frac{2.494 \times 10^3 \text{ m}^3 \text{ Pa mol}^{-1}}{22.36 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}} - \frac{0.1370 \text{ m}^6 \text{ Pa mol}^{-2}}{501.8 \times 10^{-6} \text{ m}^6 \text{ mol}^{-2}}$$

$$p = 0.1115 \times 10^6 \text{ Pa} - 273.0 \text{ Pa}$$

$$p = 111.2 \times 10^3 \text{ Pa} = 1.098 \text{ atm}$$

Using the Van der Waals equation,

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$V_m = \text{molar volume} = \frac{V}{n} = \frac{0.500 \text{ L}}{1.000 \text{ mol}}$$

$$V_m = 0.500 \text{ L mol}^{-1}$$

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

$$p = \frac{8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{(0.500 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} - 3.186 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})} - \frac{0.1382 \text{ m}^6 \text{ Pa mol}^{-2}}{(0.500 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})^2}$$

$$p = \frac{2.479 \times 10^3 \text{ m}^3 \text{ Pa mol}^{-1}}{4.681 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}} - \frac{0.1370 \text{ m}^6 \text{ Pa mol}^{-2}}{0.250 \times 10^{-6} \text{ m}^6 \text{ mol}^{-2}}$$

$$p = 5.2959 \times 10^6 \text{ Pa} - 0.5480 \times 10^6 \text{ Pa}$$

$$p = 4.7479 \times 10^6 \text{ Pa} = 46.87 \text{ atm}$$

Using the ideal gas equation,

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

$$p = \frac{1.000 \text{ mol} \times 8.314 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{0.500 \times 10^{-3} \text{ m}^3}$$

$$p = 4.9576 \times 10^6 \text{ Pa} = 48.94 \text{ atm}$$

$$\text{Percentage difference from the pressure} = \frac{p_{\text{real}} - p_{\text{ideal}}}{p_{\text{real}}} \times 100\%$$

$$\text{Percentage difference from the pressure} = \frac{46.87 \text{ atm} - 48.94 \text{ atm}}{46.87 \text{ atm}}$$

$$\text{Percentage difference from the pressure} = \frac{-2.07}{46.87} = -4.416\%$$

## Chapter 2

1. A thermodynamic system is a defined quantity of matter or a region in space chosen for study, separated from its surroundings by a boundary. Systems are classified as:

Open system: exchanges both matter and energy with surroundings (*e.g.*, a boiling pot without a lid).

Closed system: exchanges only energy, not matter (*e.g.*, gas in a sealed piston).

Isolated system: exchanges neither matter nor energy (*e.g.*, an insulated thermos bottle).

2. State variables (state functions): Depend only on the present state of the system, not the path taken to reach it. Examples: pressure, temperature, internal energy, entropy.

Path variables (path functions): Depend on the exact path taken during a process. Examples: heat (*q*) and work (*w*). For instance, the change in internal energy between two states is the same

regardless of the path, but the amounts of heat and work involved differ depending on the process.

3. A PV diagram plots pressure ( $p$ ) against volume ( $V$ ) for a thermodynamic system. It provides visual information about the process path, state changes, and work done. The area under the curve represents the work done by or on the system. Different curves (isothermal, isobaric, isochoric, adiabatic) have distinct shapes, allowing identification of process types.

### Chapter 3

1. The Zeroth Law of Thermodynamics states ‘if two systems, A and B, are each in thermal equilibrium with a third system, C, then A and B are in thermal equilibrium with each other’.

Significance: This law establishes the concept of temperature as a measurable property. It ensures that a thermometer (the third system) can reliably measure the temperature of other systems, because thermal equilibrium is transitive. Without this law, consistent comparison of temperatures would not be possible.

2. Medical thermometer: A thermometer placed under the tongue reaches equilibrium with body temperature, allowing an accurate reading.

Refrigerator thermostat: The thermostat equilibrates with the air inside the refrigerator. When the temperature rises above a set point, it activates cooling.

3. a. Determine proportionality constant:

$$\alpha = \frac{p}{T} = \frac{112.0 \text{ kPa}}{273.16 \text{ K}} = 0.4100 \text{ kPa K}^{-1}$$

- b. Calculate temperature:

$$T = \frac{p}{\alpha} = \frac{136.25 \text{ kPa}}{0.4100 \text{ kPa K}^{-1}} = 332.3 \text{ K}$$

4. The constant-volume ideal gas thermometer is a primary standard because it directly defines temperature based on the fundamental behavior of an ideal gas ( $P \propto T$ ).



Extrapolation to zero pressure is necessary because no real gas behaves ideally at high pressures. In the limit  $P \rightarrow 0$ , all real gases behave ideally; the effects of intermolecular interactions are minimized, providing an accurate estimate of the ideal behavior.

- First, calculate the true temperature using the linear interpolation formula.

$$T = T_1 + \frac{(p - p_1)(T_2 - T_1)}{p_2 - p_1}$$

$T =$

$$273.16 \text{ K} + \frac{(118.85 \text{ kPa} - 100.00 \text{ kPa})(373.15 \text{ K} - 273.16 \text{ K})}{136.60 \text{ kPa} - 100.00 \text{ kPa}}$$

$$T = 273.16 \text{ K} + \frac{(18.85 \text{ kPa})(99.99 \text{ K})}{36.6 \text{ kPa}}$$

$$T = 324.66 \text{ K}$$

True temperature =  $324.66 \text{ K} - 273.15 \text{ K}$

=  $51.51^\circ\text{C}$

Correction to apply =  $51.51^\circ\text{C} - 50.00^\circ\text{C} = +1.51^\circ\text{C}$

## Chapter 4

- Joule's paddle wheel experiment showed that mechanical work can be converted into heat. When the weight fell, it rotated the paddle wheel, stirring the water and raising its temperature. By measuring the temperature increase and the work done by the falling weight, Joule established a quantitative relationship between mechanical and thermal energy. This experiment provided the experimental foundation for the first law of thermodynamics, confirming that energy is conserved and can change form.
- Work done by the falling weight ( $w$ )

$$w = mg\Delta h$$

$$w = 20 \text{ kg} \times 9.81 \text{ m s}^{-2} \times 2 \text{ m}$$

$$w = 392.4 \text{ J}$$

The work done on the system is 392.4 J.

3. Convert ft lb to Joules (1 ft lb = 1.3558 J)

$$w = 772 \times 1.3558 \text{ J} = 1046.7 \text{ J}$$

Convert lb to kg (1 lb = 0.4536 kg)

Convert °F to K

$$\Delta T \text{ (K)} = \Delta T \text{ (°F)} \times \frac{5}{9} = 1 \times \frac{5}{9} = 0.5556 \text{ K}$$

$$w = C_p m_L \Delta T$$

$$C_p = \frac{w}{m_L \Delta T} = \frac{1046.7 \text{ J}}{0.4536 \text{ kg} \times 0.5556 \text{ K}} = 4153.2 \text{ J kg}^{-1} \text{K}^{-1}$$

The calculated specific heat is approximately  $4153.2 \text{ J kg}^{-1} \text{K}^{-1}$ , which is very close to the modern accepted value of water,  $4186 \text{ J kg}^{-1} \text{K}^{-1}$ .

## Chapter 5

1. The first law of thermodynamics is the law of conservation of energy, expressed as:  $dU = \delta q + \delta w$ .

where  $dU$  is the change in internal energy,  $\delta q$  is the heat absorbed by the system, and  $\delta w$  is the work done on the system. Heat represents energy transfer due to temperature difference, while work represents energy transfer due to mechanical, electrical, or other macroscopic forces.

2. For reversible isothermal expansion:

$$w_{rev} = -nRT \ln \frac{V_2}{V_1}$$

$$w_{rev} = -(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{mol}^{-1})(298 \text{ K}) \ln \frac{20 \text{ L}}{10 \text{ L}}$$

$$w_{rev} = -1717 \text{ J}$$

3. In a reversible adiabatic expansion, no heat enters the system ( $\delta q = 0$ ). The gas does work on its surroundings, which reduces its internal energy. Since the internal energy of an ideal gas depends only on temperature, the temperature decreases.

4.  $q_v = nC_v\Delta T$

$C_v$  is  $3R/2$  for a monatomic ideal gas.

$$q_v = 2 \text{ mol} \times \frac{3 \times 8.314 \text{ J K}^{-1}\text{mol}^{-1}}{2} \times 100 \text{ K}$$

$$q_v = 2494.2 \text{ J}$$

5. Heat and work depend on the process by which a system moves from one state to another (the path taken), so their values vary with different paths. In contrast, internal energy is a state function; it depends only on the state variables (*e.g.*,  $T, p, V$ ) of the system, not on how the system reached that state.

## Chapter 6

1.  $q = m\bar{C}\Delta T$

$$420 \text{ J} = 50 \text{ g} \times 4.18 \text{ J g}^{-1}\text{K}^{-1} \times \Delta T$$

$$\Delta T = \frac{420 \text{ J}}{50 \text{ g} \times 4.18 \text{ J g}^{-1}\text{K}^{-1}}$$

$$\Delta T = 2.01 \text{ K}$$

$$\text{Final temperature of water} = 25^\circ\text{C} + 2^\circ\text{C} = 27^\circ\text{C}$$

2.  $\text{Density} = \frac{\text{Mass}}{\text{Volume}}$

$$\text{Total volume of the solution} = V_{\text{HCl}} + V_{\text{NaOH}} = 100 \text{ mL} + 100 \text{ mL} = 200 \text{ mL}$$

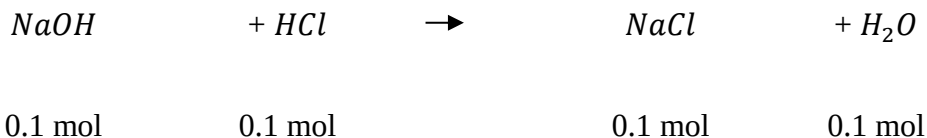
$$\text{Mass of solution} = 1.00 \text{ g mL}^{-1} \times 200 \text{ mL} = 200 \text{ g}$$

$$q = m\bar{C}\Delta T$$

$$q = 200 \text{ g} \times 4.18 \text{ J g}^{-1}\text{K}^{-1} \times (301.3 - 298) \text{ K}$$

$$q = 200 \text{ g} \times 4.18 \text{ J g}^{-1}\text{K}^{-1} \times (301.3 - 298) \text{ K}$$

$$q = 2758.8 \text{ J}$$



Number of moles of  $\text{H}_2\text{O}$  = 0.1 mol

The enthalpy of neutralization per mole of water formed =  $\frac{2758.8 \text{ J}}{0.1 \text{ mol}} = 27588 \text{ J mol}^{-1} = 27.6 \text{ kJ mol}^{-1}$

3. Heat absorbed by the bomb calorimeter =  $q$

$$q = C\Delta T = 5.00 \text{ kJ K}^{-1} \times 1.2 \text{ K} = 6.00 \text{ kJ}$$

Heat absorbed by the calorimeter = -Heat released by the combustion reaction

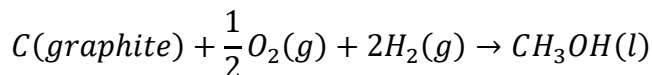
Heat released by the combustion reaction =  $-6.00 \text{ kJ}$

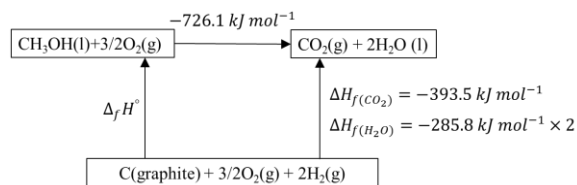
Number of moles of glucose =  $\frac{1.5 \text{ g}}{180.0 \text{ g mol}^{-1}} = 0.00833 \text{ mol}$

Molar enthalpy of combustion of glucose =

$$\frac{-6.00 \text{ kJ}}{0.00833 \text{ mol}} = 720 \text{ kJ mol}^{-1}$$

4. Formation of liquid methanol:





$$\Delta_f H^\circ = (-393.5 - (285.8 \times 2) + 726.1) \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ = (-965.1 + 726.1) \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ = -239 \text{ kJ mol}^{-1}$$

5.  $\Delta H_2 = \Delta H_1 + \Delta C_p \Delta T$

$$\Delta H_{350 \text{ K}} = -100 \text{ kJ} + 25 \text{ J K}^{-1} (350 - 298) \text{ K}$$

$$\Delta H_{350 \text{ K}} = -100 \text{ kJ} + 1.3 \text{ kJ}$$

$$\Delta H_{350 \text{ K}} = -98.7 \text{ kJ}$$

## Chapter 7

1. Entropy change at hot reservoir,  $\Delta S_H = -\frac{q}{T_H}$

Entropy change at cold reservoir,  $\Delta S_C = \frac{q}{T_C}$

Total entropy change,  $\Delta S = \Delta S_H + \Delta S_C$

$$\Delta S = -\frac{q}{T_H} + \frac{q}{T_C}$$

$$\Delta S = q \left( \frac{1}{T_C} - \frac{1}{T_H} \right)$$

$$\Delta S = 5000 \text{ J} \left( \frac{1}{300 \text{ K}} - \frac{1}{400 \text{ K}} \right)$$

$$\Delta S = 4.167 \text{ J K}^{-1}$$

The positive value confirms the process is irreversible and satisfies the second law.

2. Boltzmann's formula for entropy,  $S = Nk_B \ln \Omega$

$$S = 100 \times 1.380649 \times 10^{-23} \text{ J/K } \ln 3$$

$$S = 1.516797 \times 10^{-21} \text{ J/K}$$

3. Heat lost by water,  $q = m\bar{C}\Delta T$

$$q = 0.100 \text{ kg} \times 4184 \text{ J kg}^{-1}\text{K}^{-1} \times (300 \text{ K} - 350 \text{ K})$$

$$q = 0.100 \text{ kg} \times 4184 \text{ J kg}^{-1}\text{K}^{-1} \times (-50 \text{ K})$$

$$q = -20920 \text{ J}$$

Entropy change of water,  $\Delta S_{\text{water}} = m\bar{C} \ln \frac{T_f}{T_i}$

$$\Delta S_{\text{water}} = 0.100 \text{ kg} \times 4184 \text{ J kg}^{-1}\text{K}^{-1} \ln \frac{300}{350}$$

$$\Delta S_{\text{water}} = 0.100 \text{ kg} \times 4184 \text{ J kg}^{-1}\text{K}^{-1} \ln \frac{300}{350}$$

$$\Delta S_{\text{water}} = -64.496 \text{ J K}^{-1}$$

Entropy change of the reservoir,  $\Delta S_{\text{res}} = -\frac{q}{T_{\text{res}}}$

$$\Delta S_{\text{res}} = -\frac{-20920 \text{ J}}{300 \text{ K}}$$

$$\Delta S_{\text{res}} = +69.733 \text{ J K}^{-1}$$

Total entropy change,  $\Delta S = \Delta S_{\text{water}} + \Delta S_{\text{res}}$

$$\Delta S = -64.496 \text{ J K}^{-1} + 69.733 \text{ J K}^{-1}$$

$$\Delta S = +5.237 \text{ J K}^{-1}$$

4. Entropy change for an ideal gas at constant volume,  $\Delta S_V = nC_V \ln \frac{T_f}{T_i}$

$$\Delta S_V = 2.00 \text{ mol} \times \frac{3R}{2} \ln \frac{600 \text{ K}}{300 \text{ K}}$$

$$\Delta S_V = 2.00 \text{ mol} \times \frac{3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{2} \ln 2$$

$$\Delta S_V = 17.288 \text{ J K}^{-1}$$

5. (a) Entropy change for an isothermal reversible expansion,  $\Delta S = nR \ln \frac{V_f}{V_i}$

$$\Delta S = 1.00 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \ln \frac{40.0 \text{ L}}{10.0 \text{ L}}$$

$$\Delta S = 11.526 \text{ J K}^{-1}$$

- (b) For the reversible process,

$$\Delta S = \int_{rev} \frac{dq}{T} = 11.526 \text{ J K}^{-1}$$

For the free (irreversible) expansion into vacuum,  $q = 0$ . Therefore,  $\int \frac{dq}{T} = 0$ . However, the system's entropy change depends only on initial and final equilibrium states and remains the same as in the reversible expansion at  $11.526 \text{ J K}^{-1}$ . For the irreversible expansion,

$$\Delta S = 11.526 \text{ J K}^{-1} \text{ and } \int \frac{dq}{T} = 0$$

So,

$$\Delta S > \int \frac{dq}{T}$$

**Chapter 8**

(a) Efficiency of a Carnot engine,  $\eta$ :

$$\eta = 1 - \frac{T_C}{T_H}$$

$$\eta = 1 - \frac{300 \text{ K}}{900 \text{ K}} = 1 - \frac{1}{3} = 1 - 0.3333 = 0.6667$$

$$\eta = 66.67\%$$

(b) Work output,  $w_{cyc}$ :

$$\eta = \frac{\text{net work output}}{\text{heat input}} = \frac{w_{cyc}}{q_H}$$

$$w_{cyc} = \eta q_H$$

$$w_{cyc} = 0.6667 \times 6000 \text{ J} = 4000 \text{ J}$$

Heat rejected,  $q_C$ :

$$q_C = q_H - w_{cyc}$$

$$q_C = 6000 \text{ J} - 4000 \text{ J} = 2000 \text{ J}$$

(c) Entropy change of the hot reservoir,  $\Delta S_H$ :

According to the reservoir sign convention: + means entropy heat gained. Therefore, the hot reservoir gets a minus (-) sign due to heat loss, and the cold reservoir gets a plus (+) sign due to heat gain.

$$\Delta S_H = -\frac{q_H}{T_H} = -\frac{6000 \text{ J}}{900 \text{ K}} = -6.667 \text{ J K}^{-1}$$

$$\Delta S_C = +\frac{q_C}{T_C} = +\frac{2000 \text{ J}}{300 \text{ K}} = 6.667 \text{ J K}^{-1}$$

The total entropy change,  $\Delta S_{tot}$ :



$$\Delta S_{tot} = \Delta S_H + \Delta S_C$$

$$\Delta S_{tot} = -6.667 \text{ J K}^{-1} + 6.667 \text{ J K}^{-1} = 0 \text{ (expected for a reversible Carnot cycle)}$$

(a)

$$T_B = T_A a$$

$$a \equiv r^{\gamma-1}$$

Therefore,

$$T_B = T_A r^{\gamma-1}$$

$$T_B = 300 \text{ K} \times 9^{1.4-1}$$

$$T_B = 300 \text{ K} \times 9^{0.4}$$

$$T_B = 722.47 \text{ K}$$

(b)

Heat added per kilogram,  $Q_{in} = 600 \text{ kJ kg}^{-1}$ Heat added per mass of air,  $q_{in} = 600 \text{ kJ kg}^{-1} \times 0.02 \text{ kg} = 12 \text{ kJ} = 12000 \text{ J}$ For constant volume heat addition,  $q_{in} = m C_v (T_C - T_B)$ 

$$12000 \text{ J} = 0.02 \text{ kg} \times 718 \text{ J kg}^{-1} \text{ K}^{-1} \times (T_C - 722.47 \text{ K})$$

$$\frac{12000}{0.02 \times 718 \text{ K}^{-1}} = T_C - 722.47 \text{ K}$$

$$T_C = \frac{12000}{0.02 \times 718} \text{ K} + 722.47 \text{ K}$$

$$T_C = 1558.12 \text{ K}$$

$$(c) T_D = \frac{T_C}{r^{\gamma-1}}$$

$$T_D = \frac{1558.12 \text{ K}}{9^{1.4-1}}$$

$$T_D = \frac{1558.12 \text{ K}}{9^{1.4-1}}$$

$$T_D = 646.99 \text{ K}$$

(d)

Heat rejected at constant volume,  $q_{out}$

$$q_{out} = mC_v(T_A - T_D)$$

$$q_{out} = 0.02 \text{ kg} \times 718 \text{ J kg}^{-1} \text{ K}^{-1} \times (300 \text{ K} - 646.99 \text{ K})$$

$$q_{out} = 0.02 \text{ kg} \times 718 \text{ J kg}^{-1} \text{ K}^{-1} \times (-346.99 \text{ K})$$

$$q_{out} = -4982.91 \text{ J}$$

Minus (-) sign indicates the heat rejection.

$$w_{cyc} = q_{in} - q_{out}$$

$$w_{cyc} = 12000 \text{ J} - 4982.91 \text{ J}$$

$$w_{cyc} = 7017.09 \text{ J}$$

Thermal efficiency,

$$\eta = \frac{w_{cyc}}{q_{in}} = \frac{7017.09 \text{ J}}{12000 \text{ J}} = 0.5847$$

$$\eta = 58.47\%$$

1. (a) Carnot efficiency,  $\eta$ :

$$\eta = 1 - \frac{T_C}{T_H}$$

$$\eta = 1 - \frac{300 \text{ K}}{1000 \text{ K}} = 0.7$$

$$\eta = \frac{w_{cyc}}{q_H}$$

$$w_{cyc} = \eta q_H$$

$$w_{cyc} = 0.7 \times 5000 \text{ J}$$

$$w_{cyc} = 3500 \text{ J}$$

(b) Work delivered by the real engine,  $w_{real} = 3000 \text{ J}$

Lost work because of irreversibilities =  $3500 \text{ J} - 3000 \text{ J} = 500 \text{ J}$

(c) Rejected heat from the real engine,  $q_C = q_H - w_{real}$

$$q_C = 5000 \text{ J} - 3000 \text{ J} = 2000 \text{ J}$$

Entropy change of reservoirs per cycle:

$$\Delta S = -\frac{q_H}{T_H} + \frac{q_C}{T_C} = -\frac{5000 \text{ J}}{1000 \text{ K}} + \frac{2000 \text{ J}}{300 \text{ K}} = -5 \text{ J K}^{-1} + 6.667 \text{ J K}^{-1}$$

$$\Delta S = 1.667 \text{ J K}^{-1}$$

Entropy generation,  $\Delta S_{gen} = 1.667 \text{ J K}^{-1}$

$$T_C \Delta S_{gen} = 300 \text{ K} \times 1.667 \text{ J K}^{-1} = 500 \text{ J}$$

This equals the lost work computed in (b). Therefore, the lost work equals  $T_C \Delta S_{gen}$ .

Efficiency of Otto engine,  $\eta_{Otto}$ :

$$\eta_{Otto} = 1 - \frac{1}{r^{\gamma-1}}$$

$$\eta_{Otto} = 1 - \frac{1}{8^{1.4-1}} = 0.5647$$

$$w_{Otto} = \eta_{Otto} \times q_H$$

$$w_{Otto} = 0.5647 \times 2000 \text{ J} = 1129.4 \text{ J}$$

Carnot efficiency,  $\eta_{Carnot}$ :

$$\eta_{Carnot} = 1 - \frac{T_C}{T_H}$$

$$\eta_{Carnot} = 1 - \frac{300 \text{ K}}{1200 \text{ K}} = 0.75$$

$$w_{Carnot} = \eta_{Carnot} \times q_H$$

$$w_{Carnot} = 0.75 \times 2000 \text{ J} = 1500 \text{ J}$$

Carnot cycle produces 1500.0 J of work, which is higher than Otto's 1129.4 J.

(a)

COP of Carnot refrigerator:

$$COP = \frac{T_C}{T_H - T_C}$$

$$COP = \frac{260 \text{ K}}{310 \text{ K} - 260 \text{ K}} = \frac{260}{50} = 5.2$$

(b)

The minimum power input,  $w$ :

$$COP = \frac{q_C}{w}$$

$$w = \frac{q_C}{COP} = \frac{1500 \text{ J/s}}{5.2} = 288.5 \text{ J/s}$$

(c)

The rate of heat rejected to the surroundings  $q_H$ :

$$q_H = q_C + w$$

$$q_H = 1500 \text{ J s}^{-1} + 288.5 \text{ J s}^{-1} = 1788.5 \text{ J s}^{-1}$$

## Chapter 9

1. At absolute zero, a perfect crystal has only one possible microstate ( $\omega = 1$ ). According to Boltzmann's formula  $S = k_B \ln \omega = k_B \ln 1 = 0$ . Thus, the entropy is zero, providing an absolute reference for measuring entropy at higher temperatures.

$$S(T) = \int_{T_0}^T \frac{nC_P dT}{T}$$

$$n = 1$$

$$S(T) = \int_{T_0}^T \frac{C_P dT}{T} = C_P \int_{T_0}^T \frac{dT}{T} = C_P \ln \frac{T}{T_0}$$

$$S(T) = 25 \text{ J mol}^{-1} \text{ K}^{-1} \ln \frac{298 \text{ K}}{1 \text{ K}}$$

1 K is used instead of 0 K to avoid division by zero in the integral while giving a practically accurate estimate of absolute entropy.

$$S(T) \approx 142.43 \text{ J mol}^{-1} \text{ K}^{-1}$$

2. Entropy change is defined as  $\Delta S = \int \frac{dq_{rev}}{T}$ , so experimentally, it is measured by recording the heat exchanged during a reversible process at each temperature. The third law of thermodynamics provides a reference point: at 0 K, a perfect crystal has 0 entropy. Using this reference and measured heat capacities, the absolute entropy at any temperature can be calculated by integrating  $C_P(T)/T$  from 0 K and adding contributions from phase transitions.

$$\Delta_{fus} S = \frac{\Delta_{fus} H}{T}$$

$$\Delta_{fus}S = \frac{6.01 \times 10^3 \text{ J mol}^{-1}}{273 \text{ K}} = 22.01 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r S^0 = \sum S_{products}^0 - \sum S_{reactants}^0$$

$$\Delta_r S^0 = 70 \text{ J mol}^{-1} \text{ K}^{-1} - (131 \text{ J mol}^{-1} \text{ K}^{-1} + \frac{1}{2} \times 205 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$\Delta_r S^0 = 70 \text{ J mol}^{-1} \text{ K}^{-1} - 233.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r S^0 = 163.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

## Chapter 10

1. The fundamental relations are differential forms of thermodynamic potentials derived from the first and second laws of thermodynamics. For example:

$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dA = -pdV - SdT$$

$$dG = Vdp - SdT$$

They are important because they connect measurable properties (such as  $p, V, T$ ) with thermodynamic state functions (such as  $U, H, A, G$ ) and form the basis for deriving Maxwell relations.

2. Maxwell relations arise from the equality of mixed second derivatives of exact differentials. This symmetry ensures that the cross-partial derivatives of thermodynamic potentials are equal, linking different state variables. For example:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This symmetry simplifies analysis by expressing difficult-to-measure properties (like entropy) in terms of measurable ones (like pressure, volume, and temperature).

3. From fundamental thermodynamic relations:  $dA = -pdV - SdT$

$$A = A(V, T)$$

$$\text{Total differential, } dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$

$$\text{Therefore, } \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT = -pdV - SdT$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -p \quad \text{eq. 1 and } \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{eq. 2}$$

In Eq. 1, both sides can be differentiated with respect to  $T$  while keeping  $V$  constant.

$$\left[\frac{\partial}{\partial T}\right]_V \left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_V \quad \text{eq. 3}$$

In Eq. 2, both sides can be differentiated with respect to  $V$  while keeping  $T$  constant.

$$\left[\frac{\partial}{\partial V}\right]_T \left(\frac{\partial A}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T \quad \text{eq. 4}$$

Because of the symmetry of the second derivatives,

$$\left[\frac{\partial}{\partial T}\right]_V \left(\frac{\partial A}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\right]_T \left(\frac{\partial A}{\partial T}\right)_V$$

Therefore, Eq. 3 = Eq. 4

$$-\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

4. From the Helmholtz energy Maxwell relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

For an ideal gas, the equation of state is  $pV = nRT$ . Differentiating with respect to  $T$  by keeping  $V$  constant,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V} > 0$$

The derivative  $\left(\frac{\partial S}{\partial V}\right)_T$  is positive, because  $n, R, V > 0$ . This means that at constant temperature, entropy increases with volume.

5. From the Maxwell relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

For an ideal gas, the equation of state is  $pV = nRT$ . Differentiating with respect to  $T$  by keeping  $V$  constant,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

Substituting values:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \frac{2 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{10 \text{ L}}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = 1.6628 \text{ J K}^{-1} \text{ L}^{-1}$$



**Chapter 11****1.**

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T}$$

$$\Delta_r S^\circ = \frac{-40\,000 \text{ J mol}^{-1} - (-10\,000 \text{ J mol}^{-1})}{298.15 \text{ K}} = \frac{-30\,000 \text{ J mol}^{-1}}{298.15 \text{ K}}$$

$$\Delta_r S^\circ = -100.62 \text{ J K}^{-1} \text{ mol}^{-1}$$

**2.**

$$V_g = \frac{RT}{P} = \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 373.15 \text{ K}}{101325} \approx 0.03062 \text{ m}^3 \text{ mol}^{-1}$$

$$\Delta V \approx 0.03062 \text{ m}^3 \text{ mol}^{-1} - 1.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \approx 0.0306017 \text{ m}^3 \text{ mol}^{-1}$$

$$\frac{dP}{dT} = \frac{40\,700 \text{ J mol}^{-1}}{373.15 \text{ K} \times 0.0306017 \text{ m}^3 \text{ mol}^{-1}} \approx 3\,564 \text{ Pa K}^{-1}$$

**3.**

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{P_2}{0.050 \text{ bar}} = -\frac{30\,000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\left(\frac{1}{320.0 \text{ K}} - \frac{1}{300.0 \text{ K}}\right)$$

Evaluate the right-hand side  $\approx 0.75170$ .

So,

$$\frac{P_2}{0.050 \text{ bar}} = e^{0.75170} \approx 2.1206 \Rightarrow P_2 \approx 0.1060 \text{ bar}.$$

4.

(a)

Fugacity is  $f = \phi P$ .

Given  $\phi = 0.85$  and  $P = 80.0$  bar. Therefore,

$$f = 0.85 \times 80.0 = 68.0 \text{ bar.}$$

(b)

$$\Delta G_m = RT \ln \frac{f}{p^0}$$

$$\Delta G_m = RT \ln \phi$$

$$\Delta G_m = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \ln 0.85$$

$$\Delta G_m = -405.35 \text{ J K}^{-1} \text{ mol}^{-1}$$

5.

(a)

van 't Hoff equation:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right).$$

$$\ln \frac{K_2}{0.200} = -\frac{25\,000 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{350.0 \text{ K}} - \frac{1}{300.0 \text{ K}} \right)$$

$$\ln \frac{K_2}{0.200} \approx 1.4184$$

$$K_2 = 0.200 \times e^{1.4184} \approx 0.8373.$$

(b)

With  $\Delta n = +1$ :

$$K_p(T_2) = K_c(T_2) \times (RT_2)^{\Delta n}$$

$$K_p(T_2) = 0.8373 \text{ mol L}^{-1} \times (0.08314 \text{ L bar mol}^{-1}\text{K}^{-1} \times 350.0 \text{ K})^1$$

$$K_p(T_2) \approx 0.8373 \times 29.10 \approx 24.36 \text{ bar.}$$

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