THERMODYNAMICS BASICS

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PREFACE

This Book with the title ***'Thermodynamics Basics'*** covers the fundamentals of thermodynamics basics. The five chapters'of this book was written in an easily digestible and reproducible format with required information. An effort has been made to present the book in this form and if it proves helpful to the students, we shall consider my effort has been amply rewarded.

We owe a debt of gratitude to our colleagues, who were chiefly instrumental in favouring us to undertaking this work.

Valuable comments and Suggestions for the book will be acknowledged with thanks.

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CHAPTER 1

INTRODUCTION TO THERMODYNAMICS

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, entropy, and the physical properties of matter and radiation. The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities, but may be explained in terms of microscopic constituents by statistical mechanics. Thermodynamics applies to a wide variety of topics in science and engineering, especially physical chemistry, biochemistry, chemical engineering and mechanical engineering, but also in other complex fields such as meteorology.

Historically, thermodynamics developed out of a desire to increase the efficiency of early steam engines, particularly through the work of French physicist Sadi Carnot (1824) who believed that engine efficiency was the key that could help France win the Napoleonic Wars. Scots-Irish physicist Lord Kelvin was the first to formulate a concise definition of thermodynamics in 1854 which stated, ”Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency.” German physicist and mathematician Rudolf Clausius restated Carnot’s principle known as the Carnot cycle and gave so the theory of heat a truer and sounder basis. His most important paper, ”On the Moving

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Force of Heat", published in 1850, first stated the second law of thermodynamics. In 1865 he introduced the concept of entropy. In 1870 he introduced the virial theorem, which applied to heat.

The initial application of thermodynamics to mechanical heat engines was quickly extended to the study of chemical compounds and chemical reactions. Chemical thermodynamics studies the nature of the role of entropy in the process of chemical reactions and has provided the bulk of expansion and knowledge of the field. Other formulations of thermodynamics emerged. Statistical thermodynamics, or statistical mechanics, concerns itself with statistical predictions of the collective motion of particles from their microscopic behavior. In 1909, Constantin Carathéodory presented a purely mathematical approach in an axiomatic formulation, a description often referred to as geometrical thermodynamics.

thermodynamic system employs the four laws of thermodynamics that form an axiomatic basis. The first law specifies that energy can be transferred between physical systems as heat, as work, and with transfer of matter. The second law defines the existence of a quantity called entropy, that describes the direction, thermodynamically, that a system can evolve and quantifies the state of order of a system and that can be used to quantify the useful work that can be extracted from the system.

In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of the thermodynamic system and its surroundings. A system is composed of particles, whose average motions define its properties, and those properties are in turn related to one another through equations of state. Properties can be combined to express internal energy and thermodynamic potentials, which are useful for determining conditions for equilibrium and spontaneous processes.

With these tools, thermodynamics can be used to describe how systems respond to changes in their environment. This can be applied to a wide variety of topics in science and engineering, such as engines, phase transitions, chemical reactions, transport phenomena, and even black holes. The results of thermodynamics are essential for other fields of physics and for chemistry, chemical engineering, corrosion engineering, aerospace engineering, mechanical engineering, cell biology, biomedical engineering, materials science, and economics, to name a few. This is focused mainly on classical thermodynamics which primarily studies systems in thermodynamic equilibrium. Non-equilibrium thermodynamics is often treated as an extension of the classical treatment, but statistical mechanics has brought many advances to that field.

1.1 Definition and Scope of Thermodynamics

Thermodynamics in physics is a branch that deals with heat, work and temperature, and their relation to energy, radiation and physical properties of matter. To be specific, it explains how thermal energy is converted to or from other forms of energy and how matter is affected by this process. Thermal energy is the energy that comes from heat. This heat is generated by the movement of tiny particles within an object, and the faster these particles move, the more heat is generated.

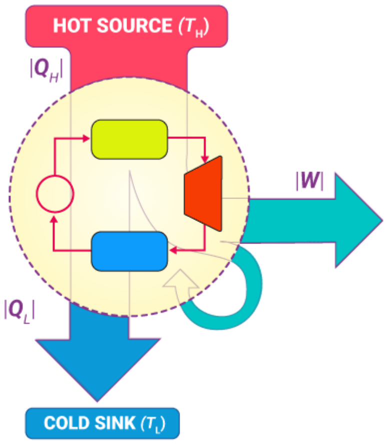


Figure 1.1 Thermodynamics

Thermodynamics is not concerned about how and at what rate these energy transformations are carried out. It is based on the initial and final states undergoing the change. It should also be noted that Thermodynamics is a macroscopic science. This means that it deals with the bulk system and does not deal with the molecular constitution of matter. The term “thermodynamics” is made of two terms, “thermo” and “dynamics” where the term “thermo” refers to heat, and the term “dynamics” refers to a mechanical motion that requires “work.” So the field of physics that studies the relationship between heat and other types of energy is called thermodynamics. Creating a clear boundary makes thermodynamics much simpler. The “system” refers to everything that is contained within the boundary, and the “surroundings” refers to all that is outside of it. Once the boundary diagram has been created, the flow across system boundaries can be used to describe the movement and transfer of energy. The word “universe” refers to both the surroundings and the system.

Thermodynamics, science of the relationship between heat, work, temperature, and energy. In broad terms, thermodynamics deals with the transfer of energy from one place to another and from one form to another. The key concept is that heat is a form of energy corresponding to a definite amount of mechanical work. Heat was not formally recognized as a form of energy until about 1798, when Count Rumford (Sir Benjamin Thompson), a British military engineer, noticed that limitless amounts of heat could be generated in the boring of cannon barrels and that the amount of heat generated is proportional to the work done in turning a blunt boring tool. Rumford’s observation of the proportionality between heat generated and work done lies at the foundation of thermodynamics. Another pioneer was the French military engineer Sadi Carnot, who introduced the concept of the heat-engine cycle and the principle of reversibility in 1824. Carnot's work concerned the limitations on the maximum amount of work that can be obtained from a steam engine operating with a high-temperature heat transfer as its driving force. Later that century, these ideas were developed by Rudolf Clausius, a German mathematician and physicist, into the first and second laws of thermodynamics, respectively.

1.1.1 Different Branches of Thermodynamics

Classical Thermodynamics: The behaviour of matter is examined using a macroscopic perspective in classical thermodynamics. In order to determine the characteristics and predict the characteristics of the matter conducting the process, individuals take into account units like temperature and pressure.

Statistical Thermodynamics: The development of atomic and molecular theories in the late 19th and early 20th centuries gave rise to statistical mechanics, also known as statistical thermodynamics, which added an interpretation of the microscopic interactions between individual particles or quantum-mechanical states to classical thermodynamics. This field explains classical thermodynamics as a natural consequence of statistics, classical mechanics, and quantum theory at the microscopic level. It does this by connecting the microscopic, bulk properties of materials that can be observed on the human scale to the macroscopic, individual atom, and molecule properties.

Chemical Thermodynamics: Chemical thermodynamics is the study of how energy interacts with chemical processes or state changes in accordance with the laws of thermodynamics. Determining the spontaneity of a certain transition is the main goal of chemical thermodynamics.

Equilibrium Thermodynamics: Equilibrium thermodynamics is the study of matter and energy transfers in systems or substances that can be moved from one state of thermodynamic equilibrium to another by agents in their environment. The phrase "thermodynamic equilibrium" refers to a condition of equilibrium in which all macroscopic flows are zero. In the case of the most basic systems or bodies, this means that their intensive properties are uniform and that their pressures are perpendicular to their boundaries. Unbalanced potentials or driving forces between the system's macroscopically diverse components do not exist in an equilibrium state.

Non-equilibrium Thermodynamics: Systems that are not in thermodynamic equilibrium are the focus of the field of thermodynamics known as non-equilibrium thermodynamics. The majority of systems in nature are not in thermodynamic equilibrium because they are not in stationary states and are subject to fluxes of matter and energy to and from other systems on a continual and irregular basis. More general notions than those covered by equilibrium thermodynamics are needed for the thermodynamic study of non-equilibrium systems.

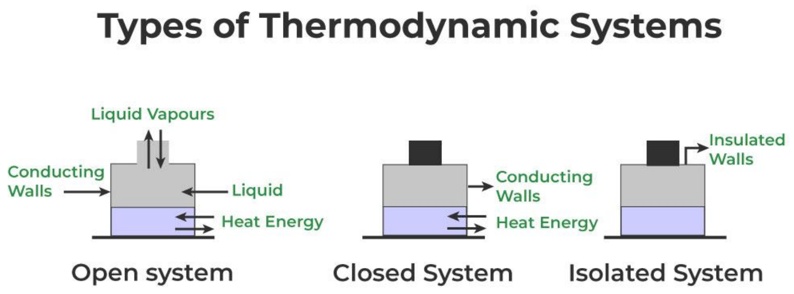
1.1.2 Basic Concepts of Thermodynamics

Anything outside the thermodynamic system to which energy or matter is exchanged is called its surroundings. Taking into consideration the interaction between a system and its surroundings, a system said to be an open system if it can exchange both energy and matter with its surroundings may be divided into three classes

Open system: A system is said to be an open system if it can exchange energy and matter with its surroundings.

Closed system: A system is said to be a closed system if it can exchange only energy (not matter) with its surroundings.

Isolated system: A system is said to be isolated if it can neither exchange energy nor matter with its surroundings.



Surroundings: The term "surroundings" refers to everything outside the system that affects how it behaves. There is a boundary separating the system from its surroundings. It could be stationary, mobile, or fictitious. It won't take up any space in terms of mass or volume. For example, consider a closed beaker with liquid inside as shown below. The liquid inside the beaker is the system, while the outline of the beaker represents the boundary of the system. And matter outside the system and boundary is called its surroundings.

Heat: Heat is energy that is transmitted between objects or systems as a result of a temperature difference. Heat is conserved energy, which means it cannot be created or destroyed. However, it can be moved from one location to another. Additionally, heat can be transformed into and out of various types of energy.

Work: The work done by a system or on a system during a process depends not only on the system's starting and final states but also on the path chosen for the process. When a force acting on a system moves the body in its own direction, work has been done. Force and displacement combine to create the work (W) that is done to or by a system.

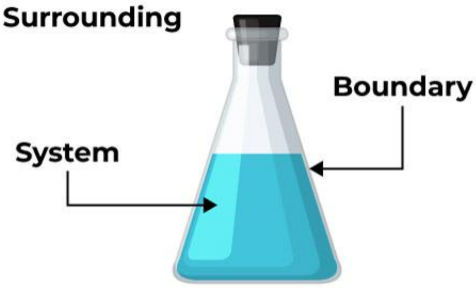


Figure 1.2 System and Surroundings

Internal Energy: The kinetic and potential energies of the molecules are added up to form internal energy. The system's internal energy is represented by the letter U. Kinetic energy is the energy that molecules or atoms possess due to their motion. Two molecules have some potential energy because they are attracted to one another. The total kinetic and potential energy of the atoms or molecules that make up a system is what is known as the system's internal energy.

1.1.3 Thermodynamic Properties or Variables

the variables which are required to specify the state of the thermodynamic system are called thermodynamic variables. Entropy is a measurement of energy present in a system or process but is not available to do work. It is also defined as the measure of disorder in the system. Enthalpy is the measurement of the total energy of a thermodynamic system.

Types of Thermodynamic Variables

Intensive variables: The variables which are independent of the size of the system are called intensive variables. e.g. Temperature, pressure, and specific beat capacity.

Extensive variables: The variables which depend on the size or mass of the system are called extensive variables. e.g. Volume, energy, entropy, heat capacity, and enthalpy.

1.1.4 Thermodynamic Equilibrium

Thermodynamic equilibrium is a state of a system in which there is no net change occurs within the system over time i.e., the state of a thermodynamic system in which macroscopic properties such as temperature, pressure, and chemical composition, remain constant. There are different types of thermodynamic equilibrium:

Thermal Equilibrium: In the state of thermal equilibrium, the temperature of the system remains constant i.e., there is no net heat transfer occurring within the system.

Mechanical Equilibrium: When in a system either there is no net force acting or there is no pressure difference, then this state of the system is called mechanical equilibrium. This state is also sometimes referred to as a state of mechanical balance.

Chemical Equilibrium: A thermodynamic system is said to be in chemical equilibrium when the rates of forward and reverse reactions become equal. When the system reaches chemical equilibrium, the concentrations of reactants and products remain constant over time.

Phase Equilibrium: A system is said to be in Phase equilibrium when different phases of a substance such as solid, liquid, and gas, coexist in a system at the same time. In other words, the system is in phase equilibrium when the rates of phase changes, such as evaporation and condensation, are equal.

1.1.5 Thermal Equilibrium

When two bodies having different temperatures are placed in contact, then the energy flows from a body at a higher temperature to a body at a lower temperature. The flow of energy continues from one body to another to attain the same temperature.

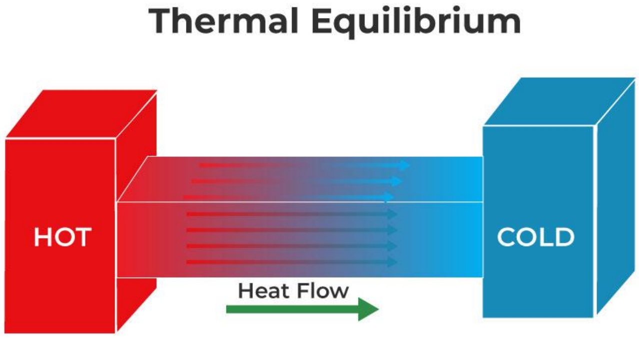


Figure 1.3 Thermal Equilibrium

When both the bodies in contact have the same temperature and there is no energy for the body till both bodies are between them, then these bodies are in thermal equilibrium. Thus, two bodies or systems in contact are said to be in thermal equilibrium if both are at the same temperature. A thermodynamic system is said to be in thermodynamic equilibrium if its variables like pressure, volume, temperature, number of particles, etc. do not change with time. Any isolated system is in thermodynamic equilibrium.

1.1.6 Thermodynamic Processes

Quasi-Static Process (Quasi-Static means nearly static): A process in which the system departs only infinitesimally from the equilibrium state is known as a quasi-static process In this process, the change in pressure or change in volume or change in temperature of the system is very very small.

Isothermal Process: A process in which the pressure and volume of the system change at constant temperature are called the isothermal process. In this case, P and V change but T is constant. i.e. dT (change in temperature) = 0.

Adiabatic Process: A process in which pressure, volume, and temperature of the system change, but there is no exchange of heat between the and its surroundings is called the adiabatic process. In this case, P. V and T change but Q = 0. The system should be compressed or allowed to expand suddenly so that there is no time for the exchange of heat between the system and its surroundings. Since these two conditions are not fully realized in practice, so no process is perfectly adiabatic.

Isochoric Process: A thermodynamic process that takes place at constant volume is called the isochoric process. It is also known as the isovolumic process. In this case, dV = 0.

Isobaric Process: A thermodynamic process that takes place at constant pressure is called the isobaric process. In this case, dP = 0.

Cyclic Process: A cyclic process consists of a series of changes that return the system to its initial state.

1.1.7 Thermodynamic Potentials

The stored energy in a system is measured by its thermodynamic potentials. Potentials measure how a system's energy transforms from its initial state to its final one. Depending on the constraints of the system, such as temperature and pressure, different potentials are used.

Different forms of thermodynamic potentials are mentioned below:

Internal Energy (U): It is equal to the sum of the ability to do work and the ability to release heat.

Gibbs Energy (G): It is the ability to do non-mechanical work.

Enthalpy (H): It is the ability to do non-mechanical work and the ability to emit heat.

Helmholtz Energy (F): It is the ability to do both mechanical and non-mechanical work.

Enthalpy

In a thermodynamic system, energy is measured by enthalpy. Enthalpy is a measure of a system's total heat content and is equal to the system's internal energy plus the sum of its volume and pressure. Enthalpy is a property or state function that resembles energy; it has the same dimensions as energy and is therefore measured in joules or ergs. The value of enthalpy is entirely dependent on the temperature, pressure, and composition of the system, not on its history.

Entropy in Thermodynamics

Entropy is the measurement of the amount of thermal energy per unit of temperature in a system that cannot be used for useful work. Entropy is a measure of a system's molecular disorder or randomness since work is produced by ordered molecular motion. Entropy theory offers a deep understanding of the direction of spontaneous change for many common events.

1.1.8 Scope of Thermodynamics

Thermodynamics is a fundamental branch of physical science that deals with the study of energy, heat, work, and the relationships between them in various physical and chemical processes. The scope of thermodynamics is quite extensive and plays a crucial role in understanding and analyzing a wide range of natural and man-made systems.

Laws of Thermodynamics: Thermodynamics is built upon four fundamental laws, but the first and second laws are the most well-known and widely applicable. The First Law of Thermodynamics, also known as the law of energy conservation, states that energy cannot be created or destroyed, only converted from one form to another. The Second Law of Thermodynamics introduces concepts like entropy and the direction of heat flow in processes, providing fundamental insights into the behavior of systems.

Properties of Matter: Thermodynamics deals with the behavior of matter, including gases, liquids, and solids, and how their properties change under various conditions. It provides a framework for understanding phase transitions, heat capacity, and other thermodynamic properties.

Heat Engines and Refrigeration: Thermodynamics is essential in the design and analysis of heat engines, such as steam engines, internal combustion engines, and gas turbines. It also applies to refrigeration and air conditioning systems, allowing engineers to optimize their efficiency.

Chemical Thermodynamics: In the field of chemistry, thermodynamics plays a crucial role in understanding chemical reactions and their energetics. Concepts like enthalpy, Gibbs free energy, and chemical potential are used to predict the feasibility and spontaneity of chemical reactions.

Phase Equilibria: Thermodynamics helps explain and predict the behavior of systems at phase boundaries, such as phase transitions, vapor-liquid equilibria, and solubility of substances in solvents.

Thermodynamic Cycles: Many engineering processes involve cyclic operations, such as the Rankine cycle in power plants and the Carnot cycle in ideal heat engines. Thermodynamics is used to analyze and optimize these cycles for efficiency.

Statistical Thermodynamics: This branch of thermodynamics connects the macroscopic behaviors described by the laws of thermodynamics with the microscopic behaviors of individual particles. It provides a statistical foundation for thermodynamic concepts and is crucial for understanding the behavior of gases, liquids, and solids at the molecular level.

Applications in Various Fields: Thermodynamics finds applications in various scientific and engineering disciplines, including physics, chemistry, engineering, biology, environmental science, and material science. It is used to model and analyze a wide range of processes, from chemical reactions to the behavior of celestial bodies.

Environmental Considerations: Thermodynamics is increasingly applied to assess the environmental impact of various processes, including energy production and consumption, and to design more sustainable systems and technologies.

1.2 Systems and Surroundings

1.2.1 Thermodynamics systems

A thermodynamic system is a body of matter and/or radiation separate from its surroundings that can be studied using the laws of thermodynamics. A thermodynamic system may be an isolated system, a closed system, or an open system. An isolated system does not exchange matter or energy with its surroundings. A closed system may exchange heat, experience forces, and exert forces, but does not exchange matter. An open system can interact with its surroundings by exchanging both matter and energy. The physical condition of a thermodynamic system at a given time is described by its state, which can be specified by the values of a set of thermodynamic state variables. A thermodynamic system is in thermodynamic equilibrium when there are no macroscopically apparent flows of matter or energy within it or between it and other systems.

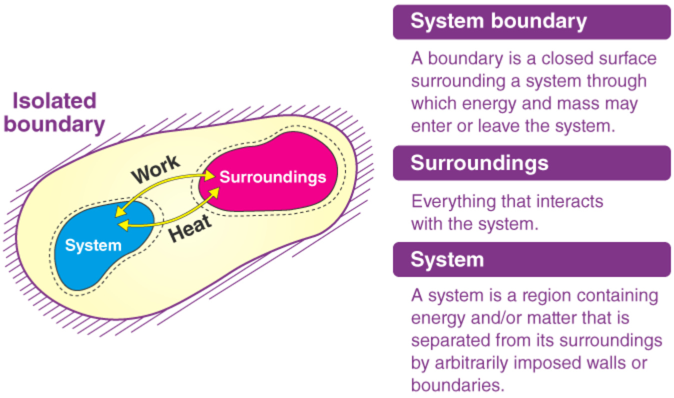
Thermodynamics is the scientific study of heat and temperature, as well as the interconversion of energy into other types of energy. Because thermodynamics deals with a bulk system rather than the molecular structure of matter, it is referred to as macroscopic science. A thermodynamic system is a group of matter and radiation that is enclosed in space by walls with defined permeabilities that isolate it from its surroundings. Other thermodynamic processes or physical components that are not thermodynamic systems may be present in the surroundings. When the boundary of a thermodynamic system is described as being permeable to everything, the energy can be exchanged between the system and the surrounding. A thermodynamic system's state can be completely described in a variety of ways using various sets of thermal state variables. Washing machines, refrigerators, and air conditioners are examples of thermodynamic systems.

We use cars and bikes in our daily routine to travel. To keep them going, we fill in petrol or diesel as per the design of the vehicle. The petrol or diesel in the vehicle undergoes combustion inside the engine and is an ideal example of a thermodynamic system. The system which involves the processing of heat and converting it to useful work involves thermodynamic processes. Nuclear power, electronic heat sink and rocket launch involve thermodynamics. Thermodynamics is the branch of science that deals with heat and temperature and the inter-conversion of heat and other forms of energy. Since thermodynamics deals with the bulk system and does not deal with the molecular constitution of matter, it is known as macroscopic science.

Some examples of thermodynamic systems are washing machines, refrigerators and air-conditioners. Air-conditioner is a closed system that circulates refrigerant inside the system, altering the pressure of the refrigerant at different points to promote the transfer of heat. A refrigerator is an open system that absorbs heat from a closed space and passes it to a warmer area. In this article, let us study in detail the thermodynamic system and its types.

A system that is delimited from the surroundings by real or hypothetical boundaries is known as a thermodynamic system. A thermodynamic system refers to that part of the universe in which observations are made, and the remaining universe constitutes the surroundings. The surroundings contain everything other than the system. The system and the surroundings together make up the universe.

The universe = The system + The surroundings



System boundary

A boundary is a closed surface surrounding a system through which energy and mass may enter or leave the system.

Surroundings

Everything that interacts with the system.

System

A system is a region containing energy and/or matter that is separated from its surroundings by arbitrarily imposed walls or boundaries.

A thermodynamic system is embedded in its environment or surroundings, through which it can exchange heat with, and do work on. It exchanges the heat to its surroundings through a boundary. The boundary is the wall that separates the system and the environment. Thermodynamic systems can exchange energy or matter with the external environment and can also undergo internal transformations. The below figure shows the thermodynamic system, surroundings and boundary concept. A car, the engine burns gasoline inside the cylinder and is considered as a thermodynamic system; the radiator, piston, exhaust system and air outside form the environment of the system. The inner surfaces of the cylinder and piston are considered as the boundary.

1.2.2 Thermodynamics Surroundings

thermodynamics, ”surroundings” refers to everything outside of the system under consideration. The system and its surroundings together make up the entire thermodynamic universe. Understanding the concept of surroundings is essential to analyze and describe thermodynamic processes.

System and Surroundings: To apply thermodynamics to a physical or chemical system, you must define a ”system” that you are interested in studying. The system is the part of the universe that you focus on, and it can be as simple as a gas inside a container, a chemical reaction taking place, or a more complex entity. The surroundings, on the other hand, encompass everything external to the system.

Boundary: The system and its surroundings are separated by an imaginary or real boundary. This boundary can be physical, like the walls of a container, or it can be conceptual, defining a region in space or within a particular volume. The boundary helps define what is inside the system and what is part of the surroundings.

Interactions: Energy and matter can be exchanged between the system and its surroundings. These exchanges may take the form of heat transfer and work done, and they play a crucial role in thermodynamic processes. For example, in a chemical reaction, heat may be absorbed or released as the reactants transform into products, and work may be done on or by the system.

Open, Closed, and Isolated Systems: The classification of a system depends on the nature of the interaction with its surroundings. An open system can exchange both energy and matter with its surroundings. A closed system can exchange energy (typically in the form of heat and work) but not matter with its surroundings. An isolated system does not exchange energy or matter with its surroundings.

State Functions: Thermodynamic properties known as state functions, such as internal energy (U), enthalpy (H), and entropy (S), depend only on the current state of the system, regardless of how the system reached that state or the interactions with the surroundings. These state functions are essential for analyzing thermodynamic processes, as they provide a description of the system’s condition.

First Law of Thermodynamics: The First Law of Thermodynamics states that the change in internal energy of a system is equal to the heat added to the system minus the work done by the system. This law describes how energy can be transferred between the system and its surroundings and the conservation of energy in thermodynamic processes.

Second Law of Thermodynamics: The Second Law of Thermodynamics deals with the direction of energy flow and introduces the concept of entropy. It provides insights into the efficiency of processes and the tendency of natural processes to increase the overall entropy of the universe.

1.3 Thermodynamic Properties

In thermodynamics, a physical property is any property that is measurable, and whose value describes a state of a physical system. Thermodynamic properties are defined as characteristic features of a system, capable of specifying the system's state. Some constants, such as the ideal gas constant, R, do not describe the state of a system, and so are not properties. On the other hand, some constants, such as Kf (the freezing point depression constant, or cryoscopic constant), depend on the identity of a substance, and so may be considered to describe the state of a system, and therefore may be considered physical properties.

1. Temperature (T): Temperature is a fundamental thermodynamic property that measures the degree of hotness or coldness of a system. It is typically measured in degrees Celsius (°C) or Kelvin (K). Temperature affects the thermal energy of a system and is crucial for various thermodynamic processes and equations, including the ideal gas law and the concept of thermal equilibrium.

2. Pressure (P): Pressure is another fundamental property in thermodynamics that quantifies the force exerted on a unit area. It is usually measured in units like pascals (Pa) or atmospheres (atm). Pressure plays a crucial role in describing the behavior of gases and liquids, as well as in defining states of matter, such as the distinction between solids, liquids, and gases.

3. Volume (V): Volume is a property that represents the amount of space occupied by a system. It is commonly measured in units like cubic meters (m^3) or liters (L). Volume is significant when studying changes in the physical state of matter, such as phase transitions, and it is closely related to the concept of density.

4. Internal Energy (U): Internal energy is the total energy contained within a system. It includes both kinetic energy (associated with the movement of particles) and potential energy (associated with the forces between particles). The change in internal energy during a thermodynamic process is related to the heat and work done on or by the system, as described by the first law of thermodynamics.

5. Enthalpy (H): Enthalpy is defined as $H = U + PV$, where U is the internal energy, P is pressure, and V is volume. It is a useful property for systems at constant pressure. Enthalpy changes are particularly important in the study of chemical reactions, where they represent the heat exchange between a system and its surroundings at constant pressure.

6. Entropy (S): Entropy is a measure of the degree of disorder or randomness in a system. It is closely associated with the second law of thermodynamics, which states that the entropy of an isolated system tends to increase over time. Entropy helps explain the direction of natural processes and is a fundamental concept in the study of heat engines, refrigeration systems, and thermodynamic efficiency.

7. Gibbs Free Energy (G): Gibbs free energy, denoted as G, is a thermodynamic potential that combines the effects of both enthalpy and entropy. It is used to predict whether a chemical reaction will occur spontaneously at constant temperature and pressure. When the Gibbs free energy is negative, a reaction is thermodynamically favorable.

8. Helmholtz Free Energy (A): Helmholtz free energy, denoted as A, is another thermodynamic potential that combines internal energy and entropy. It is particularly useful for systems at constant volume and is often employed in the study of phase transitions and the stability of thermodynamic states.

9. Specific Heat (C): Specific heat is a material-specific property that quantifies the amount of heat required to raise the temperature of a unit mass of a substance by one degree. It is typically expressed as either the specific heat capacity at constant volume (Cv) or at constant pressure (Cp). Specific heat plays a crucial role in determining the energy requirements of heating or cooling processes.

10. Heat Capacity (C): Heat capacity, denoted as C, is the amount of heat required to change the temperature of an entire system. It is the product of specific heat and the mass of the system. Heat capacity is essential in practical applications, such as designing heating and cooling systems.

11. Thermal Expansion (α): Thermal expansion is a property that describes how a substance's volume changes with temperature. It is characterized by the coefficient of linear expansion (α) for solids and the coefficient of volume expansion (β) for liquids. Understanding thermal expansion is critical in various engineering applications, including the design of bridges and buildings.

12. Compressibility (κ): Compressibility is a property that quantifies a substance's ability to be reduced in volume under the influence of an external pressure. It is essential in the study of gases and fluids, and it can be described by the isothermal compressibility (κT) or the adiabatic compressibility (κS).

13. Specific Enthalpy (h): Specific enthalpy, denoted as h, is the enthalpy per unit mass of a substance. It is particularly useful in fluid dynamics, where it helps determine the energy content of a fluid stream. Specific enthalpy is crucial in applications like power generation and heat exchangers.

14. Saturation Properties: Saturation properties are specific thermodynamic properties associated with phase transitions, such as the vaporization or condensation of a substance. These properties include saturation temperature, saturation pressure, and specific volume at saturation. Understanding these properties is vital in designing refrigeration and steam power cycles.

15. Triple Point and Critical Point: The triple point of a substance is the unique set of conditions (temperature and pressure) at which it coexists in all three phases (solid, liquid, and gas). The critical point represents the highest temperature and pressure at which a substance can exist in a distinct liquid and gas phase. These points are crucial for defining the thermodynamic behavior of substances.

1.4 State of a System

In thermodynamics, the system's state consists of a state of a variable that identifies the variable set of values at a particular interval of time. The thermodynamic state has variable pressure, temperature volume, and entropy values. The determination of the values of these factors defines all the thermodynamic properties going on in the system. The prime motto for defining these values is to reach the state of thermodynamics equilibrium state. The total specification of the system to state the laws of thermodynamics in terms of thermodynamic values is the state of the system. The remaining part of the system is the surrounding which is responsible for the exchange of the energies, which eventually change the properties of the element. The complete balance in the thermodynamic state leads the system to the thermodynamic equilibrium.

The definite value of the parameters responsible for the thermodynamic state is variable values. These values keep changing with the change in any of the properties of the system. These properties are the state functions and completely depend on the state variables of thermodynamics. To understand easily the factors which create an atmosphere are the properties and the variable changes are the principle of states. All these factors are interdependent and continue changing to each other. To reach thermal equilibrium, the system undergoes an internal change at a point where each set of variables is in an equal manner. The system can change completely to a new state by exposing it to external surroundings. The process follows the change in the values of temperature, pressure, volume, and entropy of the elements. Some processes are reversible and can attain the previous state. But some process of the system is irreversible, and in a thermodynamic state, they are unable to reverse themselves to their previous forms. Some of the special processes attain both reversible and irreversible forms. Many of the thermodynamics properties have the involvement of reversible procedures in the thermodynamic state.

A thermodynamic state refers to the specific condition or configuration of a system at a given point in time. It is defined by a set of measurable properties or variables that describe the system's thermodynamic characteristics. These properties include temperature (T), pressure (P), volume (V), internal energy (U), and others, each of which provides valuable information about the system's state.

1. State Variables and Properties

Thermodynamic state variables, also known as state properties, are properties of a system that depend only on its current state and not on the path it took to reach that state. These variables provide a comprehensive description of the system's thermodynamic condition. Some of the key state properties include:

Temperature (T): Temperature is a measure of the system's thermal energy and its degree of hotness or coldness. It is typically measured in degrees Celsius (°C) or Kelvin (K) and plays a fundamental role in determining the system's behavior, especially in processes involving heat transfer.

Pressure (P): Pressure is the force exerted on a unit area within the system. It is essential for describing the mechanical behavior of gases and fluids, and it is usually measured in pascals (Pa) or atmospheres (atm).

Volume (V): Volume represents the amount of space occupied by the system. It is vital for understanding the physical dimensions of the system and is measured in units like cubic meters (m^3) or liters (L).

Internal Energy (U): Internal energy is the total energy contained within the system, which includes both kinetic and potential energy. The change in internal energy during a process is related to heat transfer and work done on or by the system, as described by the first law of thermodynamics.

Enthalpy (H): Enthalpy is defined as $H = U + PV$, where U is the internal energy, P is pressure, and V is volume. It is particularly useful in processes occurring at constant pressure and is critical for studying heat exchange in chemical reactions.

Entropy (S): Entropy is a measure of the degree of disorder or randomness within the system. It is related to the second law of thermodynamics, which states that the entropy of an isolated system tends to increase over time. Understanding entropy is essential for predicting the direction of natural processes.

Specific Heat (C): Specific heat is a material-specific property that quantifies the amount of heat required to raise the temperature of a unit mass of a substance by one degree. It is crucial for determining the energy requirements of heating or cooling processes.

Gibbs Free Energy (G) and Helmholtz Free Energy (A): These thermodynamic potentials are useful in predicting whether a chemical reaction will occur spontaneously under constant temperature and pressure (G) or constant volume (A).

2. State Space and State Points

The collection of all possible states a system can occupy is known as state space. State space is defined by the combinations of state variables within certain limits and boundaries, based on the physical constraints and properties of the system. Each specific combination of state variables represents a unique state point within the state space. State points can be depicted graphically on phase diagrams, which illustrate the regions where different phases of matter (solid, liquid, gas) exist.

3. State Postulate

One of the fundamental principles of thermodynamics is the state postulate, which asserts that the complete description of a thermodynamic system at equilibrium is achieved by specifying a set of state properties. In other words, if the values of a system's state properties are known, the system's thermodynamic state is fully defined. This postulate forms the basis for the study of thermodynamic equilibrium and the formulation of thermodynamic laws.

4. Equilibrium and Non-Equilibrium States

A thermodynamic system can exist in two primary states: equilibrium and non-equilibrium. In an equilibrium state, the system's properties remain constant with time and do not vary from one point within the system to another. For example, if a gas is in thermal equilibrium, its temperature is the same throughout the entire volume. In contrast, a non-equilibrium state is characterized by gradients or variations in properties within the system. For instance, if heat is applied to one end of a metal rod, the rod's temperature will vary from one point to another until it reaches thermal equilibrium.

5. Paths and Processes

When a system undergoes a series of state changes, it follows a specific path in its state space. A thermodynamic process describes the evolution of the system from one state to another. The path a system takes during a process can be represented on a P-V diagram, where changes in pressure and volume are depicted. Different types of thermodynamic processes include isothermal (constant temperature), isobaric (constant pressure), isochoric (constant volume), and adiabatic (no heat exchange) processes.

6. State Functions and Path Functions

Thermodynamic properties are classified into two categories: state functions and path functions. State functions, such as temperature, pressure, and internal energy, depend only on the initial and final states of a system and not on the path taken during a process. In contrast, path functions, like work and heat, depend on the specific path or route followed during a process.

7. Phase Transitions and State Changes

The concept of the thermodynamic state is particularly significant when studying phase transitions. These transitions, such as the solid-liquid-gas transformations, involve changes in state properties, and understanding the state of the system is vital for predicting and explaining these changes. For example, the phase diagram of water shows the different regions where water can exist as ice, liquid water, or water vapor, each characterized by a specific set of state properties (temperature and pressure). By knowing the state of water, one can predict whether it will freeze, boil, or remain in a liquid state under given conditions.

Importance of State in Thermodynamics

- Predicting Behavior: By knowing the state of a system, we can predict how it will behave under different conditions. This is essential for designing and optimizing engineering systems, such as engines, refrigeration cycles, and chemical processes.
- Quantifying Changes: The concept of a thermodynamic state allows us to quantify changes in a system's properties, such as the amount of work done, heat transferred, or energy added or removed. This is essential for energy balance calculations.
- Understanding Equilibrium: Equilibrium states are critical for studying phase transitions, chemical reactions, and other natural processes. Equilibrium thermodynamics provides a framework for determining the conditions under which these processes occur.
- Comparing Systems: The state of a system enables us to compare different systems and assess their thermodynamic characteristics. This is valuable in scientific research, industrial applications, and environmental studies.

1.5 Thermodynamic Processes and Cycles

1.5.1 Thermodynamic Processes

Thermodynamic processes are the paths that bring a thermodynamic system from its initial state to its final state. The state of a system can be indicated by parameters like volume, temperature, pressure, and internal energy. Thermodynamics has become an integral element of our daily lives. Whether you're in a car, sitting comfortably in an air-conditioned room, or sipping a cold beverage from the refrigerator, thermodynamics is used practically everywhere, either directly or indirectly. When "Sadi Carnot" the father of thermodynamics, introduced thermodynamic theorems and cycles, few could have predicted that his ideas would one day play such a pivotal role in the invention of the vehicle, which has become an essential part of our lives. The thermodynamic cycles were further developed by Sterling Diesel, Otto, and Ericson, resulting in more inventions and improvements in automobiles. Before heading towards the Thermodynamic processes first we'll see some concepts related to thermodynamics.

A thermodynamic process involves a change from one type of equilibrium microstate to another type of system. The process can be interpreted by the initial and final states of the system. Temperature pressure, energy, and volume of the system have to be considered as parameters for the initial state. After the completion of the time for which we are observing the system, we can measure the same parameters to figure out the final state of the system. Usually, these changes are governed by energy transfer which leads to work done on the system or by the system. An example of a thermodynamics process is increasing the pressure of gas in a container where the temperature is constant.

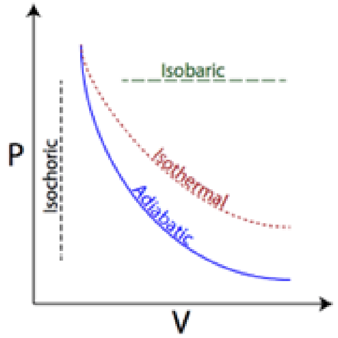


Figure 1.4 Thermodynamic Processes

➥ Types of Thermodynamic Processes

Many different parameters can be used to express the state of any thermodynamic system such as temperature, pressure and volume, and internal energy. The value of any of these parameters can be found if two out of three parameters are fixed. We can do so by using the equation, PV = RT. The state of the system does not remain constant and can be changed through different thermodynamics processes such as:

1. Isothermal Process

The Isothermal Process is the process in which the temperature remains constant in the system. Some heat transfer does take place but it is typically at an extremely slow rate which enables it to attain thermal equilibrium.

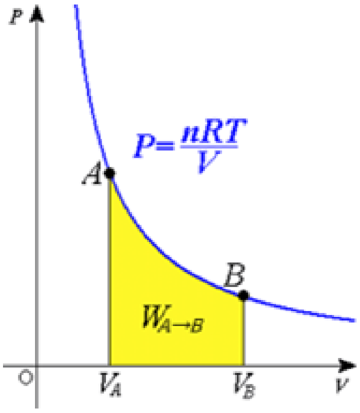


Figure 1.5 Isothermal Process

Since, W = $\int$ PdV

From Gas Law,

PV = nRT

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

Putting the value of P, we get:

$$W = nRT \int_{VA}^{VB} \frac{dV}{V}$$

$W = nRTln\frac{VB}{VA}$

If VB ¿ VA, the work done will be positive.

If VB ¡ VA, the work done is negative.

Internal energy is constant in such systems because the temperature is constant, ΔU = 0. Therefore, according to the first law of thermodynamics,

Q = ΔU + W

Therefore, Q = W.

2. Isobaric Process

A thermodynamics process in which the pressure of the system does not change with time is called an isobaric process.

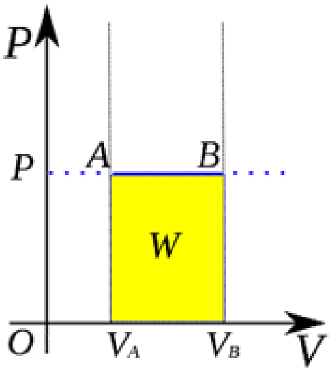


Figure 1.6 Isobaric Process

Work done, $W = P(V_B - V_A)$

If ΔV = positive, the work done will be positive.

If ΔV = negative, the work done will be negative.

3. Isochoric Process

In isochoric thermodynamic process, the volume of the system does not change. An example of such a process is gas inside a closed container. The work done by such a system is zero. However, if the system is heated, there will be changes in the internal energy of the system.

According to the first law of thermodynamics,

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

Where Δ = heat transferred

and ΔU = change in internal energy.

Therefore, $\Delta Q = \Delta U$.

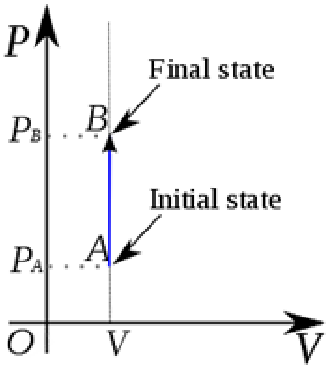


Figure 1.7 Isochoric Process

4. Adiabatic Process

In an adiabatic process, no heat is exchanged between the surroundings and the system.

PV^{γ} = K or constant

Since, W = $\int$PdV

Using the value of P

$$W = K \int_{Vi}^{Vf} \frac{dV}{V\gamma}$$

$$W = K \frac{Vf^{1-\gamma} - Vi^{1-\gamma}}{1-\gamma}$$

According to the first law of thermodynamics, Q = ΔU + W

Since, Q= 0, ΔU = -W

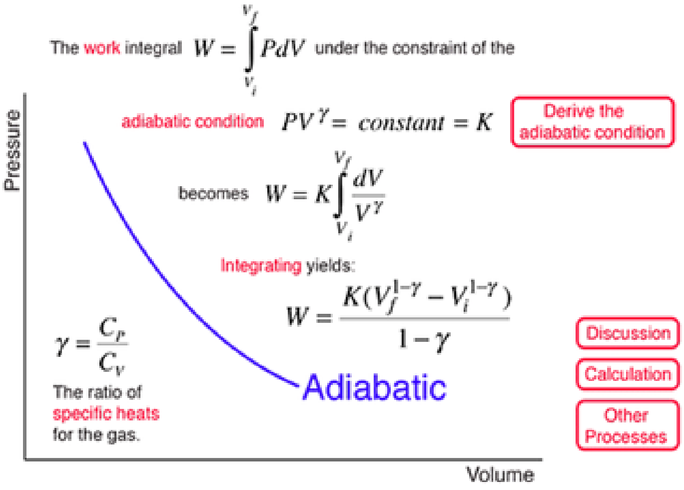


Figure 1.8 Adiabatic Process

5. Reversible Process

The thermodynamics process that can be reversed, that is, brought back into the initial state by very small changes in the properties of the system is a reversible process. During a reversible process, there is no increase in the entropy of the system and the whole system is in perfect equilibrium with the surroundings.

The work done by the system in a reversible process,

$W = \int PdV,$

where P = pressure of the system and V = volume.

On heating, ice cubes can be converted into the water while when we freeze water we get ice cubes. Hence, this is a reversible process.

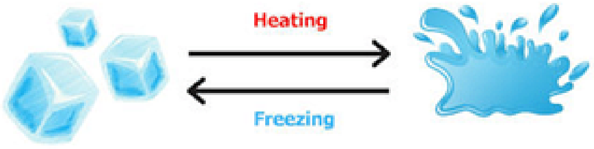


Figure 1.9 Reversible Process

6. Irreversible Process

During a thermodynamics process, if there is an increase in the entropy of the system then the system cannot return to its original state. The surroundings will also go through some thermodynamic changes and will not be able to return to their original or initial state and this type of process is called irreversible process.

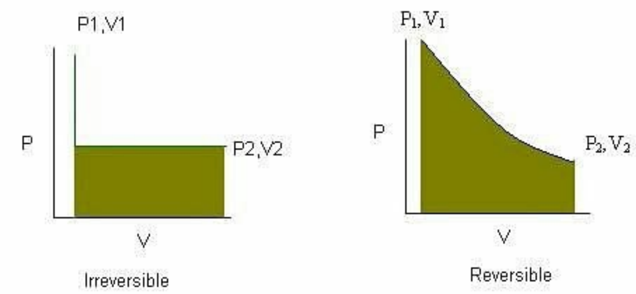


Figure 1.10 Irreversible Process

7. Cyclic Process

A cyclic process is a thermodynamics process in which a system goes through a cyclic change during which all its properties change periodically but return to their initial state ultimately and the total change in the internal energy of the system remains zero.

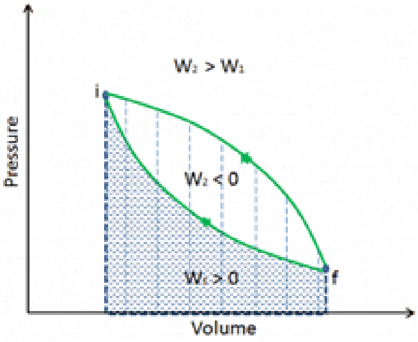


Figure 1.11 Cyclic Process

➥ Applications of Thermodynamic Processes

- ✧ Heat Engines: Thermodynamic processes are fundamental to the operation of heat engines, such as steam engines, internal combustion engines, and gas turbines. These engines convert thermal energy into mechanical work.
- ✧ Refrigeration and Air Conditioning: Thermodynamics plays a crucial role in the design and operation of refrigeration and air conditioning systems, where heat transfer and phase changes are central to the processes.

- ✧ Chemical Reactions: Thermodynamics helps chemists predict whether a chemical reaction will proceed spontaneously or require external energy input. The concept of Gibbs free energy is used to determine the spontaneity of reactions.
- ✧ Power Generation: Power plants, both fossil fuel and nuclear, use thermodynamic principles to generate electricity efficiently. Steam cycles, gas turbines, and combined heat and power (CHP) systems are examples of thermodynamically driven power generation processes.
- ✧ Renewable Energy: Thermodynamics is essential in renewable energy technologies such as solar panels, wind turbines, and geothermal power systems, as it helps optimize energy conversion and storage processes.
- ✧ Material Processing: In metallurgy and materials science, thermodynamics is used to understand phase transitions, alloy formation, and heat treatment processes.
- ✧ Transportation: Understanding thermodynamic processes is crucial in the design of more fuel-efficient and environmentally friendly vehicles, including electric and hybrid vehicles.

1.5.2 Thermodynamic Cycles

Thermodynamic cycles are used to explain how heat engines, which convert heat into work, operate. A thermodynamic cycle is used to accomplish this. The application determines the kind of cycle that is employed in the engine. The thermodynamic cycle consists of a series of interrelated thermodynamic processes involving heat and works going in and out of the body, simultaneously changing pressure, temperature, and other changes in body state, and eventually returning to the initial state.

A thermodynamic cycle is a series of thermodynamic actions that, when carried out repeatedly, leave the system in the same state as when it was first created. Thermodynamic cycles are used to explain how heat engines, which convert heat into work, operate. The thermodynamic cycle is a closed cycle that has many changes due to temperature, pressure, and volume, but whose end and initial states are equal. This cycle is important because it allows the piston in the engine to move continuously and the fluid working in the refrigerator to expand/compress. Without this cycle, the vehicle will not be able to continue running or the refrigerator will not be able to cool when restarted.

➥ Types of Thermodynamic Cycles

There are various types of cycles in thermodynamics, and some of those important cycles are listed as follows:

1. Carnot Cycle

The French physicist Sadi Carnot proposed the imagined Carnot cycle in 1824. It is a thermodynamic cycle. Transforming heat into work or work into heat, is the most effective cycle that is currently known to exist. The Carnot cycle consists of four processes that can be reversed:

Isothermal expansion: When a working substance (usually a gas) comes into thermal contact with a heated reservoir, it expands and takes heat from the reservoir with it. Adiabatic expansion: The functioning substance is thermally detached and extends, taking care of business with its environmental elements.

Isothermal compression: The functioning substance is in warm contact with a chilly supply and packs, emitting intensity to the repository.

Adiabatic compression: The functioning substance is thermally secluded and packed, taking care of business based on its environmental factors. The Carnot cycle can be addressed on a temperature-entropy graph as a closed circle. The proficiency of the Carnot cycle is determined by the situation.

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

Where,

T_C is the temperature of the cool supply,and T_H is the temperature of the hot repository.

The Carnot cycle is an optimal cycle, and no genuine motor can accomplish its effectiveness. In any case, the Carnot cycle is a valuable hypothetical model that can be utilized to look at the proficiency of various motors. The Carnot cycle is likewise significant in the field of refrigeration. A fridge works by retaining heat from a cold space and delivering it to a hot space. The Carnot cycle can be utilized to determine the greatest effectiveness of a cooler.

Here is a diagram of the Carnot cycle:

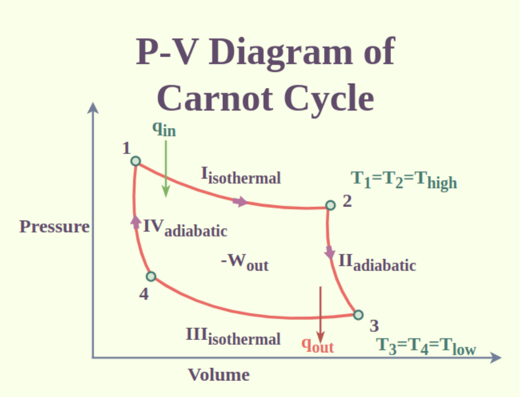


Figure 1.12 Carnot Cycle

The four processes are labeled as 1-2, 2-3, 3-4, and 4-1. The arrows indicate the direction of heat flow and work done. An essential idea in thermodynamics is the Carnot cycle. As a helpful theoretical model for comprehending these appliances, it sets a maximum efficiency limit for heat engines and refrigerators.

2. Rankine Cycle

A steam turbine's method of converting heat into mechanical work is described by the Rankine cycle, a thermodynamic cycle. The cycle is named after Scottish engineer William John Macquorn Rankine, who created it in the middle of the 19th century.

The Rankine cycle has four steps, which are as follows:

Step 1: Isentropic compression: Within a pump, the working fluid (water) is compressed from low pressure to high pressure. Since no heat is added to or lost from the fluid during this isentropic process.

Step 2: Heat addition: The heated compressed water is next converted to steam by vaporization in a boiler. A combustion process, such as burning coal or natural gas, is usually used to generate heat.

Step 3: Isentropic expansion: A turbine expands the steam, turning its thermal energy into mechanical work. Additionally, since no heat is added to or taken from the fluid, this process is isentropic.

Step 4: Condensation: After that, a condenser converts the steam back into water. In this process, heat is released and often transmitted to a cooling medium like water or air.

The fundamental thermodynamic cycle used in all steam power plants is the Rankine cycle. Other applications, such as solar thermal power plants and geothermal power plants, also make use of it.

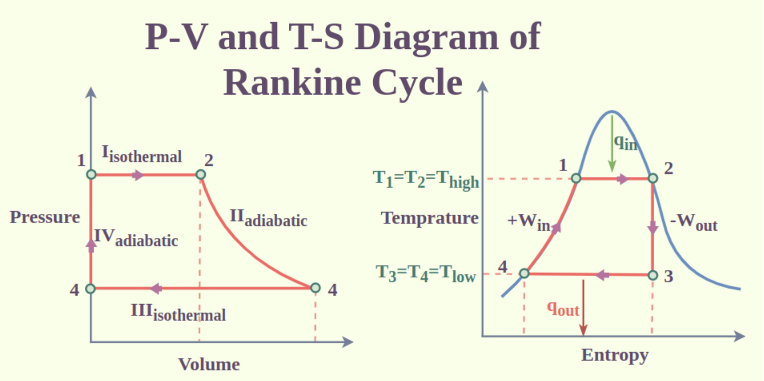


Figure 1.13 Rankine Cycle

The Rankine cycle is a thermodynamically reversible cycle, which means that all of the heat input may be converted back into labour. Friction, heat transmission, and other variables cause losses in practice nevertheless. As a result, the Rankine cycle's efficiency is normally between 30 and 40%. The Rankine cycle is available in a variety of forms, including the supercritical, reheat, and regenerative cycles. Through a reduction in the quantity of heat rejected by the environment, these modifications aim to increase the cycle's efficiency.

3. Otto Cycle

Nikolaus August Otto, who patented the first four-stroke internal combustion engine in 1876, is the inspiration for the Otto cycle. Many modern internal combustion engines still use the Otto cycle, however other cycles, such as the Atkinson cycle, are still used in some applications. The Otto cycle is a simplified thermodynamic cycle that depicts how a common spark ignition piston engine works. It is the Highest frequent thermodynamic cycle seen in car engines. The Otto cycle is made up of four processes:

Isentropic compression: In the cylinder, the piston compresses the air-fuel mixture. Because this is an isentropic process, no heat is transmitted to or from the system.

Constant Volume Heat Addition: The air-fuel mixture is ignited by a spark, causing it to combust and expand. Because the expansion occurs at a steady rate, no work is done during this process.

Isentropic Expansion: The expanding gases force the piston down, causing it to accomplish work on the environment. This is an additional isentropic process.

Constant Volume Heat Rejection: The cylinder's exhaust gases are evacuated, and the piston returns to the top of the cylinder. Because this is a constant-volume process, no work is done during this time.

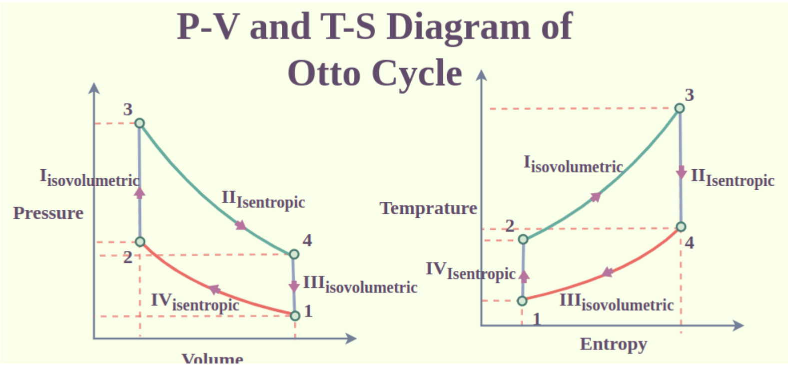


Figure 1.14 Otto Cycle

The Otto cycle is an imagined cycle, although actual engines do not follow it exactly. The Otto cycle, on the other hand, is a valuable model for understanding how spark ignition engines work. The compression ratio, which is the ratio of the volume of the cylinder at the end of the intake stroke to the volume of the cylinder at the conclusion of the compression stroke, determines the Otto cycle's efficiency. The cycle is more effective with a higher compression ratio.

4. Diesel Cycle

The operation of a diesel engine is described by the Diesel cycle, a thermodynamic cycle. It has a four-stroke cycle, which means that one cycle of operation requires the piston in the engine to make four strokes. There are four strokes:

Intake Stroke: A vacuum is created as the piston descends in the cylinder, drawing in air.

Compression Stroke: The air is compressed as the piston rises in the cylinder. Since a diesel engine normally has a higher compression ratio than a petrol engine, the air in the cylinder is compressed to a significantly higher pressure.

Combustion Stroke: Injection of fuel into the cylinder occurs at the conclusion of the compression stroke. Fuel is ignited by the heat from the compressed air, which causes it to burn quickly. The piston is pushed downward by the expanding gases, producing power.

Exhaust Stroke: Pushing the engine's exhaust gases outside, the piston rises within the cylinder.

Here is a P-V and T-S diagram of the Diesel cycle:

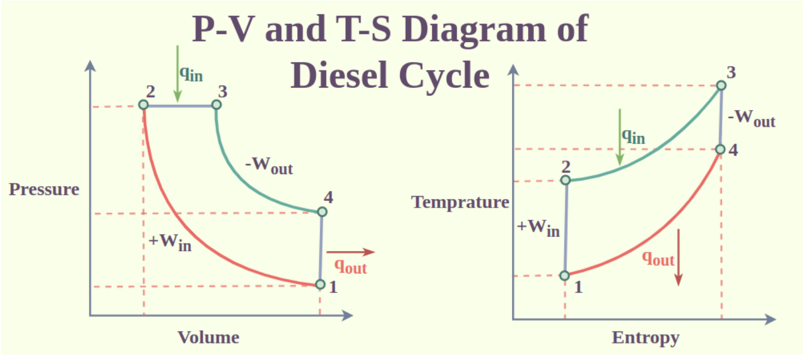


Figure 1.15 Diesel Cycle

Compared to the Otto cycle, which is utilized in petrol engines, the Diesel cycle is more effective. This is so that the gasoline may ignite more readily and completely. A diesel engine's increased compression ratio raises the temperature at the end of the compression stroke. Diesel engines are therefore more efficient than petrol engines.

Additionally, the Diesel cycle is stronger than the Otto cycle. This is due to the fact that a spark plug is not used to ignite the fuel in a diesel engine, thus there is no chance of a misfire if the spark plug breaks. As a result, diesel engines are frequently utilized in settings where dependability is crucial, such as heavy-duty vehicles and buses.

The Diesel cycle's four strokes are identified by the numbers 1-2-3-4. The direction of the piston movement is shown by the arrows. The lines' colors represent several thermodynamic processes:

- Isentropic Compression in Blue
- Red: Continuously Adding Heat
- Isentropic Growth in Yellow
- Green: Continuously Rejecting Heat

5. Brayton Cycle

One type of heat engine that uses air or another gas as its working fluid operates according to a thermodynamic cycle called the Brayton cycle. Modern gas turbine engines and air-breathing jet engines also follow the Brayton cycle; however, the original Brayton engine had a piston compressor and piston expander.

The Carnot efficiency, which is determined by the following equation, is what determines the Brayton cycle's efficiency:

$$\eta = 1 - \frac{T_C}{T_{[H]}}$$

Where,

η is the Brayton cycle's effectiveness.

T_C is the cold reservoir temperature

T_H is the hot reservoir temperature

Here are some more specifics on the four steps of the Brayton cycle:

Step 1: Without any heat transmission, the working fluid is compressed during an isentropic compression process. This is an unrealistic method that cannot be carried out in real life. However, by making the compression process as isentropic as feasible, the Brayton cycle's effectiveness can be increased.

Step 2: In a process called constant pressure heat addition, the working fluid is heated at a fixed pressure. Typically, this is accomplished by burning fuel with the help of air. The working fluid receives heat from combustion, which raises its temperature and pressure.

Step 3: Isentropic expansion is a process in which no heat is transferred and the working fluid expands. This is an unrealistic method that cannot be carried out in real life. Making the expansion process as isentropic as possible, however, can boost the Brayton cycle's effectiveness.

Step 4: In a process called constant pressure heat rejection, the working fluid is cooled at a fixed pressure. Most frequently, a heat exchanger is used to do this. The environment's temperature and pressure decrease as a result of the working fluid's heat being transferred to it.

Heat may be converted into work very effectively using the Brayton cycle. However, the heated reservoir's temperature has a limit on the cycle's efficiency. In reality, the materials used to build the engine have a limit on how hot the hot reservoir can go.

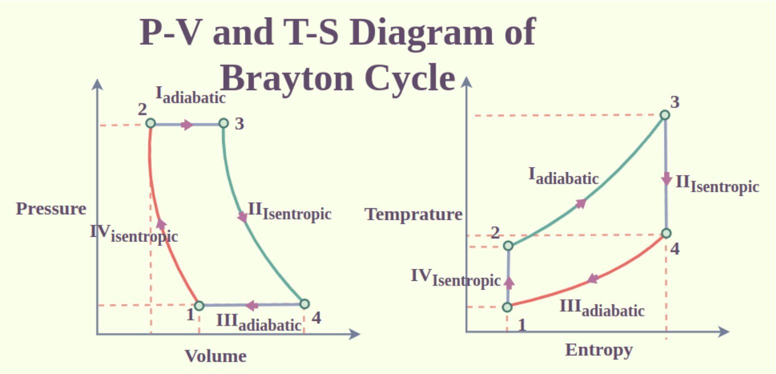


Figure 1.16 Brayton Cycle

There are numerous applications for the Brayton cycle, including:

- Gas Turbine Engines
- Jet Engines
- Turbochargers
- Air Compressors
- Spacecraft Power Systems

6. Stirling Cycle

The operation of a Stirling engine, a particular kind of heat engine, is described by the Stirling cycle, a thermodynamic cycle. It bears the name of Scottish cleric Robert Stirling, who developed the engine in 1816. Because of its great efficiency and versatility in heat sources, the Stirling engine is popular for use in applications like electricity production, heating, and cooling.

The Stirling cycle consists of four main processes:

Compression: The cycle starts with an isothermal compression process, in which the working fluid (usually a gas, such helium or hydrogen) inside the engine is heated by an external heat source (such as a burner or solar radiation). The gas expands as a result of the heat, raising the pressure.

Heat Addition: The working fluid enters a regenerator, a heat exchanger that stores and releases thermal energy, after compression. The working fluid is in contact with a high-temperature heat source during a constant volume heat addition procedure after that. As a result, the temperature and pressure rise and the expansion continues.

Expansion: From the hot side of the engine to the cold side, where it enters the expansion area, the working fluid is expanded and heated. Since the gas cools and its pressure drops during this expansion, it is an isothermal process, meaning that the temperature stays constant.

Heat Rejection: The working fluid then enters a constant volume heat rejection procedure on the cold side of the engine. A low-temperature heat sink, like air or water, contracts and loses pressure when heat is released into it.

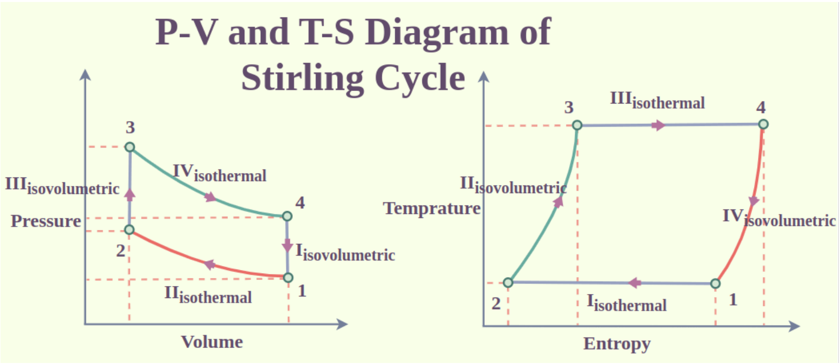


Figure 1.17 Stirling Cycle

After heat rejection, the working fluid goes back to the compression space to start the cycle over. The Stirling cycle is a closed-loop process, which means the working fluid stays inside the engine and goes through the same cycle repeatedly.

➥ Processes in Thermodynamic Cycles

Heat Addition and Rejection: The working fluid enters a regenerator, a heat exchanger that stores and releases thermal energy, after compression. The working fluid is in contact with a high-temperature heat source during a constant volume heat addition procedure after that. As a result, the temperature and pressure rise and the expansion continues. The working fluid then enters a constant volume heat rejection procedure on the cold side of the engine. A low-temperature heat sink, like air or water, contracts and loses pressure when heat is released into it.

Compression and Expansion: The cycle starts with an isothermal compression process, in which the working fluid (usually a gas, such as helium or hydrogen) inside the engine is heated by an external heat source (such as a burner or solar radiation). The gas expands as a result of the heat, raising the pressure. From the hot side of the engine to the cold side, where it enters the expansion area, the working fluid is expanded and heated. Since the gas cools and its pressure drops during this expansion, it is an isothermal process, meaning that the temperature stays constant.

Isentropic and Adiabatic Processes: Isentropic expansion is a process in which no heat is transferred and the working fluid expands. This is an unrealistic method that cannot be carried out in real life. Making the expansion process as isentropic as possible, however, can boost the Brayton cycle's effectiveness. Adiabatic processes are those processes in thermodynamic cycles, which involve the transfer of energy without the transfer of heat or mass to the surrounding. In both expansion and compression condition remains the same. Change of temperature of a gas by applying and removing the pressure is an example of an Adiabatic process.

Constant Volume and Constant Pressure Processes: The air-fuel mixture is ignited by a spark, causing it to combust and expand. Because the expansion occurs at a steady rate, no work is done during this process. The cylinder's exhaust gases are evacuated, and the piston returns to the top of the cylinder. Because this is a constant-volume process, no work is done during this time. In a process called constant pressure heat addition, the working fluid is heated at a fixed pressure. Typically, this is accomplished by burning fuel with the help of air. The working fluid receives heat from combustion, which raises its temperature and pressure. In a process called constant pressure heat rejection, the working fluid is cooled at a fixed pressure. Most frequently, a heat exchanger is used to do this. The environment's temperature and pressure decrease as a result of the working fluid's heat being transferred to it.

1.6 Zeroth Law of Thermodynamics

The zeroth law of thermodynamics is one of the four principal laws of thermodynamics. It provides an independent definition of temperature without reference to entropy, which is defined in the second law. The law was established by Ralph H. Fowler in the 1930s, long after the first, second, and third laws had been widely recognized. The zeroth law states that if two thermodynamic systems are both in thermal equilibrium with a third system, then the two systems are in thermal equilibrium with each other. Two systems are said to be in thermal equilibrium if they are linked by a wall permeable only to heat, and they do not change over time. Another formulation by Maxwell is ”All heat is of the same kind”. Another statement of the law is ”All diathermal walls are equivalent”. The zeroth law is important for the mathematical formulation of thermodynamics. It makes the relation of thermal equilibrium between systems an equivalence relation, which can represent equality of some quantity associated with each system. A quantity that is the same for two systems, if they can be placed in thermal equilibrium with each other, is a scale of temperature. The zeroth law is needed for the definition of such scales, and justifies the use of practical thermometers.

The Zeroth Law of Thermodynamics was not initially recognized as a distinct law in the development of thermodynamics. Instead, it emerged as an implicit principle that had always been applied, even before its formal articulation. Its recognition as a fundamental law came as a result of the need to systematize the foundations of thermodynamics. Historically, the principle that systems in thermal equilibrium share the same temperature was utilized long before the formal statement of the Zeroth Law. The work of early thermodynamicists, such as Joseph Black, James Joule, and others, laid the groundwork for understanding temperature and heat exchange. The formalization of the Zeroth Law occurred in the early 20th century when thermodynamicists sought to clarify the fundamental concepts of the field. It was introduced to ensure a consistent and logical framework for understanding temperature and thermal equilibrium.

Zeroth Law of Thermodynamics states that when two bodies are in thermal equilibrium with another third body than the two bodies are also in thermal equilibrium with each other. Ralph H. Fowler developed this law in the 1930s, many years after the first, second, and third laws of thermodynamics had achieved widespread acceptance. Here Thermal Equilibrium implies that when two systems are in contact with a barrier permeable only to heat, so there will be no change or transfer of heat. Consider two systems A and B, separated by a wall that does not allow any exchange of energy between them. Such a wall is known as an insulating wall or adiabatic wall. The third system C is separated from systems A and B by a conducting or diathermic wall as shown in the figure.

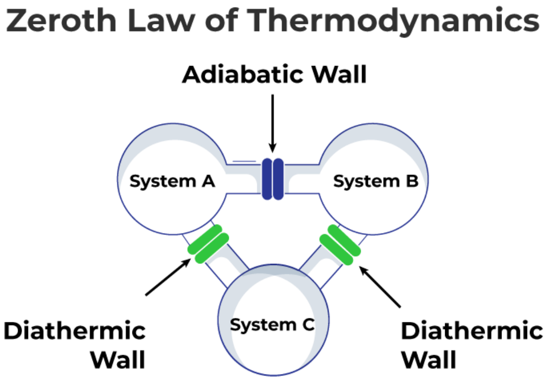
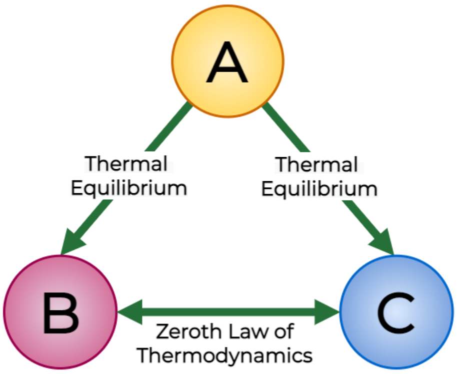


Figure 1.18 Zeroth Law of Thermodynamics

Since energy can be exchanged between systems A and C, both A and C are in thermal equilibrium. Similarly, energy can be exchanged between the systems B and C, so both B and C are also in thermal equilibrium. In other words, both systems A and B are in thermal equilibrium with the third system C separately. When the adiabatic wall between systems A and B is removed, no transfer of energy takes place between them. This shows that systems A and B are also in thermal equilibrium with each other. Zeroth Law of Thermodynamics states that heat energy flows between two bodies when they are kept in contact with each other.

For example, if we take three bodies P, Q, and R at different temperatures which are in contact with each other then the heat transfers among the three bodies till they reach thermal equilibrium, in this case, they reach the constant temperature. Thermal equilibrium can also be achieved even when the temperature of the bodies is different. For example, if we take two bodies A and B, and contain them in adiabatic chambers (which do not allow heat to pass through them) then the, if they allow being in contact still there, is no heat transfer as adiabatic chambers do not allow heat to pass through it so they are considered to in thermal equilibrium. The zeroth law of thermodynamics follows the translation relation between various bodies i.e. if we take three bodies A, B, and C then if A and B are in thermal equilibrium and B and C are in thermal equilibrium then A and c are also considered to be in thermal equilibrium.

Zeroth's law of thermodynamics, if system A is in thermal equilibrium with system C, then



Temperature of System A = Temperature of System C

Similarly, if system B is in thermal equilibrium with system C, then

Temperature of System B =Temperature of System C

Now, from the above relation, we have

Temperature of System A = Temperature of System B

Thermal Equilibrium: The zeroth law of thermodynamics recognizes that temperature is a valuable measurement since it predicts whether or not heat will flow between things. Regardless matter how the items interact, this is true. Heat can move between two things even if they are not physically interacting, as per the radiation method of heat transmission. The zeroth law of thermodynamics says that no heat flow will occur if the systems are in thermal equilibrium. Thermodynamics is distinguished from other studies by temperature. This trait is capable of distinguishing between hot and cold. When two or more bodies of different temperatures come into touch, they eventually reach a similar temperature and are said to be in thermal equilibrium.

1.6.1 Zeroth Law and Higher-Level Thermodynamic Principles

While the Zeroth Law is considered one of the fundamental principles of thermodynamics, it is closely related to and supports the other laws and concepts in the field:

First Law of Thermodynamics: The Zeroth Law helps in defining temperature and thermal equilibrium, which are essential for the First Law. The First Law, also known as the law of energy conservation, states that energy cannot be created or destroyed, but it can change from one form to another. Temperature is a key factor in understanding energy transfer.

Second Law of Thermodynamics: The Second Law, which deals with the direction of natural processes, relies on the concept of entropy, which in turn depends on temperature. The Zeroth Law's role in defining temperature and thermal equilibrium is fundamental to understanding the Second Law.

Third Law of Thermodynamics: The Third Law provides insights into the behavior of matter at absolute zero temperature. The Zeroth Law, by establishing the concept of temperature, contributes to the foundation for the Third Law's discussions on absolute zero and entropy.

1.6.2 Zeroth Law in Everyday Life

The principles of the Zeroth Law have a profound impact on everyday life, often without people realizing it:

Cooking: In cooking, achieving the correct temperature for various processes, such as boiling, baking, and frying, is essential. The Zeroth Law helps ensure that food is cooked properly and safely.

Climate Control: Heating and cooling systems in homes and businesses rely on temperature control. The Zeroth Law plays a role in maintaining indoor comfort and energy efficiency.

Medicine: In the medical field, temperature measurement is critical for diagnosing and monitoring patients' health. Thermometers, which are based on the principles of the Zeroth Law, are essential tools for healthcare professionals.

Meteorology: Meteorologists use temperature data to make weather predictions and understand atmospheric processes. Temperature measurements are fundamental in analyzing climate patterns and extreme weather events.

1.6.3 Application of Zeroth Law of Thermodynamics

- Temperature Scales: The concept of temperature established by the Zeroth Law underlies the creation and calibration of temperature scales. The Celsius, Kelvin, and Fahrenheit scales are examples of temperature scales developed based on the principles of thermal equilibrium.

- Thermometry: The design and use of thermometers, which are instruments for measuring temperature, rely on the principles of the Zeroth Law. Various types of thermometers, such as liquid-in-glass thermometers, bimetallic thermometers, and digital thermometers, are based on the expansion or contraction of materials in response to temperature changes.

- Control Systems: In engineering and control systems, the Zeroth Law is essential for maintaining temperature control. It ensures that sensors and controllers accurately maintain the desired temperature by establishing thermal equilibrium.

- Climate Science: In climate science, understanding thermal equilibrium and temperature is crucial for analyzing the Earth's energy balance, predicting climate change, and studying temperature patterns in the atmosphere, oceans, and land.

- Thermal Comfort: In everyday life, the principles of the Zeroth Law are applied to achieve thermal comfort in buildings, vehicles, and indoor environments. It helps in designing heating, ventilation, and air conditioning (HVAC) systems to maintain desired temperatures.

1.7 Temperature and Temperature Scales

1.7.1 Thermodynamic temperature

Temperature is a measure of the average kinetic energy of the particles in a system. In simpler terms, it quantifies how fast the particles are moving within a substance. The faster the particles move, the higher the temperature, and vice versa. Temperature is typically measured in degrees Celsius (°C) or Kelvin (K).

Thermodynamic temperature, by contrast, is an absolute measure of the average total internal energy of an object or objects namely its kinetic energy (energy of motion) plus contributions from other factors. It applies to the average energy of a collection of atoms or subatomic particles for example, the atoms in a block of iron, or the air molecules in a room. It is expressed in number of kelvins above absolute zero, the theoretical point at which nothing can get colder. Usually, most of an object's kinetic energy is embodied in what is called "translational motion," which occurs when it moves around in space. In gases, atoms or molecules fly around in all directions, colliding with barriers and with each other. (Their individual speeds are different, but for any given set of objects at a given temperature, one range of speeds is more probable than others.) The average speed of the atoms and molecules depends on their energy content.

In solids, where atoms are constrained by bonds and cannot move independently, kinetic energy takes the form of collective motions called phonons. Thermal energy can also flow through solids in the motion of unbound, mobile electrons. In addition, objects or parts of complex objects can have kinetic energy in the form of vibration and rotation, and these, too, add to the total energy content. Thermodynamic temperature is proportional to the average of all the energies in all the ways in which it is possible for an object to move. These are known as "degrees of freedom." So, for a single helium atom, there are only three degrees of freedom: motion in the up-down, left-right, back-forth directions. A two-atom molecule of nitrogen, however, there are two additional degrees of freedom: one of rotation and one of vibration. In general, the more components there are in a complex object such as a large molecule, the greater the number of possible motions and degrees of freedom.It is extremely difficult to measure this internal energy directly. Instead, scientists measure its effect when it moves as heat (thermal energy in transit) to or from a system of objects. When heat no longer flows between these objects in other words, when they are in thermal equilibrium that is their thermodynamic temperature.

Thus, internal energy and temperature are different, though directly related. The SI unit of energy is the joule. A "derived" SI unit, the joule itself is defined in terms of three SI base units the kilogram, the meter and the second. But thermodynamic temperature is expressed in kelvins. There needs to be a way to connect the two. The bridge between those two realms is the Boltzmann constant (kB, or often just k), which relates the kinetic energy content (E) of matter to its temperature (T): E = kBT. For the simplest collection of particles such as atoms, the average kinetic energy is $\frac{1}{2}$ mv2 distributed over the three degrees of freedom, where m is the mass and v is the velocity, so the total translational energy is $\frac{3}{2}$ 3/2 kBT.

Measurement of Temperature: Temperature is typically measured using devices called thermometers. Thermometers operate on various principles, but they all rely on the fact that certain properties of materials change with temperature. The expansion of a liquid (e.g., mercury or alcohol), the resistance of a wire (as in a resistance thermometer), or the voltage of a thermocouple are all examples of properties that change with temperature and can be used to measure it.

➥ Importance of Temperature in Thermodynamics

Energy Transfer: Temperature is closely linked to the transfer of thermal energy, commonly referred to as heat. The direction of heat transfer depends on the temperature difference between two systems. Heat naturally flows from a hotter object to a cooler one.

Ideal Gas Law: In the ideal gas law, temperature is a critical parameter. The law describes the relationship between the pressure, volume, and number of moles of an ideal gas. It states that at a constant pressure, the volume of a gas is directly proportional to its temperature. This relationship is represented as V/T = constant.

Carnot Cycle: The efficiency of a Carnot heat engine, which serves as an idealized model for heat engines, is dependent on the temperatures of the hot and cold reservoirs. Understanding the temperature difference is crucial for maximizing the efficiency of heat engines.

Phase Transitions: Temperature plays a significant role in phase transitions, such as the melting of ice or the boiling of water. The temperature at which these transitions occur is critical in many industrial and environmental processes.

Chemical Reactions: Temperature influences the rate and direction of chemical reactions. Reactions generally occur more quickly at higher temperatures, and temperature can be used to control the feasibility of certain chemical processes.

➥ **Applications of Temperature in Thermodynamics**

✧ Heating and Cooling Systems: The design and operation of heating, ventilation, and air conditioning (HVAC) systems rely on temperature control to maintain comfortable indoor environments.

✧ Power Generation: In power plants, temperature control is crucial for maintaining the efficiency of turbines and other equipment.

✧ Chemical Processes: Temperature control is essential for controlling chemical reactions, and it influences reaction rates and product yields.

✧ Refrigeration and Cooling: Refrigeration systems use temperature control to maintain low temperatures for preserving food and other products.

✧ Environmental Monitoring: Temperature is a key parameter in environmental studies and weather forecasting, influencing climate patterns, weather conditions, and ecosystems.

1.7.2 Scale of temperature

Scale of temperature is a methodology of calibrating the physical quantity temperature in metrology. Empirical scales measure temperature in relation to convenient and stable parameters or reference points, such as the freezing and boiling point of water. Absolute temperature is based on thermodynamic principles: using the lowest possible temperature as the zero point, and selecting a convenient incremental unit. Celsius, Kelvin, and Fahrenheit are common temperature scales. Other scales used throughout history include Rankine, Rømer, Newton, Delisle, Reaumur, Gas mark, Leiden and Wedgwood.

Scales of temperature are parameters used to measure the temperature, and a thermometer is used. Celsius, Fahrenheit, and Kelvin are the three most popular temperature scales. Thermometers measure temperature using these three units, using predefined reference points to aid in comparison. Water has a freezing point of 0 °C and a boiling temperature of 100 °C on the Celsius scale with unit degrees Celsius. In contrast, it has a freezing point of 32 °F and a boiling point of 212 °F on the

Fahrenheit scale with a unit degree Fahrenheit. The third is the Kelvin scale, a widely used temperature scale in science. It is an absolute temperature scale with 0 K at absolute zero temperature with unit Kelvin.

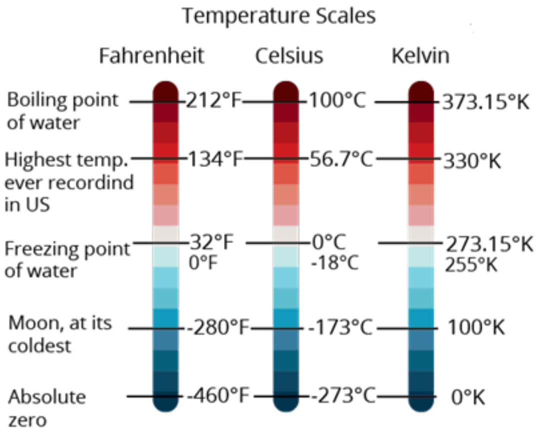


Figure 1.19 Scale of temperature

➥ Understanding Temperature Scales

It is vital to know the various types of temperature scales, how to use them, and in which cases to measure the correct temperature. Here we have discussed the three different types of temperature scales in Thermodynamics and details related to converting them from degrees to Fahrenheit and vice versa:

Fahrenheit: The first precise temperature scales were Fahrenheit. Daniel Gabriel Fahrenheit, a Polish-born Dutch physicist, introduced a mercury-based thermometer in the year 1714. According to The Royal Society of England, this was the world's first known practical and accurate thermometer. The unit in a Fahrenheit scale is expressed as a number followed by °F, or simply F. The freezing point of water is 32, and the boiling point is 212 on this scale. Fahrenheit is used to measure temperature in only a few nations today; these are the United States, Belize, Palau, the Bahamas, the Marshall Islands, the Cayman Islands, and the Federated States of Micronesia.

Celsius: Celsius is a more scientific scale. A Swedish astronomer, Anders Celsius, is credited with being the first to conduct and publish the scientific definition of an international temperature scale through experiments. In a proposal to the Royal Swedish Academy of Sciences in 1742, Celsius proposed a scale based on two fixed points: 0 (water's freezing point) and 100 (water's boiling point). Celsius named his scale "Centigrade" at first, but an international conference on weights and measures renamed it "Celsius" in honor of Anders Celsius in 1948. It is a part of the metric system, and a unit in the Celsius scale is expressed as a number followed by °C, or simply C.

Kelvin: For scientists, Kelvin is an absolute temperature that uses zero (0) as the minimum fixed point. There is no temperature below zero on a Kelvin scale, also referred to as the SI unit for temperature. In 1848, a British mathematician and scientist, William Thomson, aka Lord Kelvin, proposed an absolute temperature scale independent of the qualities of a substance like ice or the human body. On the Kelvin scale, water freezes at 273.15 degrees Kelvin (0 degrees Celsius) and boils at 373.15 degrees Kelvin (100 degrees Celsius). Scientists primarily use the Kelvin scale, and a unit in this scale is expressed as a number followed by the letter K.

➥ Temperature Conversions

Temperature conversion from one scale to another is occasionally essential. Here are formulas to convert temperatures from Kelvin degrees to Fahrenheit and other scales, and vice versa:

Celsius - Fahrenheit = T (°F) = 9/5 T (°C) + 32

Fahrenheit - Celsius = T (°C) = 5/9 (T (°F) - 32)

Celsius - Kelvin = T (K) = T (°C) + 273.15

Kelvin - Celsius = T (°C) = T (K) - 273.15

Fahrenheit - Kelvin = T (K)= 5/9 (T (°F) - 32) + 273.15

Kelvin - Fahrenheit = T (°F) = 9/5 (T (K) - 273.15) + 32

➥ Types of Temperature Scales

1. Fahrenheit Scale

Figure 1.20 Fahrenheit Scale

Close-up of a dial displaying Fahrenheit and Celsius numbers The Fahrenheit scale of temperature is the common form of temperature measurement used in the United States and some parts of the Caribbean. It was created by the German scientist Daniel Gabriel Fahrenheit in the early 18th century, and adapted its measurements standards from a previous scale created by Ole Roemer. Water freezes at 32 degrees Fahrenheit, and boils at 212 degrees F. The Fahrenheit temperature scale includes negative temperatures, below 0 degrees F. The coldest possible temperature, absolute zero, is -459.67 degrees F.

2. Celsius Scale

Figure 1.21 Celsius Scale

Outside the United States, most of the world uses the Celsius scale to measure temperatures. Two versions of the Celsius scale were created in the early 18th century one by Swedish scientist Anders Celsius, and another by the French Jean Pierre Cristin. The Celsius scale is sometimes referred to as the centigrade scale, because it is based on a 100 degree division between the freezing and boiling points of water: water freezes at 0 degrees Celsius and boils at 100 degrees C. Because of how the boiling and freezing points are arranged, each degree of Fahrenheit is 1.8 times the size of a degree Celsius. Like Fahrenheit, Celsius includes negative temperatures. Absolute zero falls at -273.15 degrees C.

3. Kelvin Scale

Figure 1.22 Kelvin Scale

The Kelvin scale was adapted from the Celsius scale in the 19th century by the British scientist William Thompson, later Lord Kelvin. Kelvin was designed in order to set the zero point of the temperature scale at absolute zero. Because of this, absolute zero is located at 0 K Kelvin does not use degrees in its notation. You can convert from Celsius to Kelvin by adding 273.15 to a Celsius temperature. Water freezes at 273.15 K, and boils at 373.15 K. Because of its direct relation to absolute zero, Kelvin temperature is widely used in scientific equations and calculations. For instance, the ideal gas law, used to show the relationship between mass, pressure, temperature and volume, uses Kelvin as its standard unit.

4. Rankine Scale

While not widely used apart from some U.S. engineering fields the Rankine scale provides an absolute zero-based equivalent to the Fahrenheit scale. Essentially, it is for the Fahrenheit scale what Kelvin is for Celsius. The scale was created by Scottish scientist William John Rankine in the 19th century, shortly after the creation of the Kelvin scale. Temperatures can be converted from Fahrenheit to Rankine by adding 459.67. Absolute zero is thus located at 0 degrees Rankine. Water freezes at 491.67 degrees R, and boils at 671.67 degrees R.

Figure 1.23 Rankine Scale

➥ Use of Thermometer in Measuring Temperature

The accuracy of measurement is determined by the levels provided by the thermometer and the technique employed by the user. Thermometers are divided into two categories: clinical thermometers and laboratory thermometers. A clinical thermometer is used to determine the temperature of the human body, which is displayed in degrees Celsius (°C) and Fahrenheit (°F). In contrast, a laboratory thermometer can be used to monitor the temperature in laboratories since it ranges between 10 °C to 110 °C.

CHAPTER 2

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is a formulation of the law of conservation of energy in the context of thermodynamic processes in which two principle forms of energy transfer, heat and thermodynamic work, are distinguished that modify a thermodynamic system of a constant amount of matter. The law also defines the internal energy of a system, an extensive property for taking account of the balance of these energies in the system. Energy cannot be created or destroyed, but it can be transformed from one form to another. In an isolated system the sum of all forms of energy is constant. An equivalent statement is that perpetual motion machines of the first kind are impossible; work done by a system on its surroundings requires that the system's internal energy be consumed, so that the amount of internal energy lost by that work must be resupplied as heat by an external energy source or as work by an external machine acting on the system to sustain the work of system continuously. The ideal isolated system, of which the entire universe is an example, is often only used as a model. Many systems in practical applications require the consideration of internal chemical or nuclear reactions, as well as transfers of matter into or out of the system. For such considerations, thermodynamics also defines the concept of open systems, closed systems, and other types.

Thermodynamics Basics.
By Dr. Ch. Ravikiran, Dr. V. Sivarama Krishna, Dr. Shaik Hussain

A thermodynamic system in an equilibrium state possesses a state variable known as internal energy(E). Between the two systems, the change in the internal energy is equal to the difference of the heat transfer into the system and the work done by the system. The first law of thermodynamics states that the energy of the universe remains the same. Though it may be exchanged between the system and the surroundings, it can't be created or destroyed. The law basically relates to the changes in energy states due to work and heat transfer. It redefines the conservation of energy concept. To help you understand the meaning of the first law, we can take the common example of a heat engine. In a heat engine, the thermal energy is converted into mechanical energy, and the process also is vice versa. Heat engines are mostly categorised as open systems. The basic working principle of a heat engine is that it makes use of the different relationships between heat, pressure and volume of a working fluid which is usually a gas. Sometimes phase changes might also occur involving a gas to liquid and back to gas.

Energy cannot be generated or destroyed, according to the first law of thermodynamics, but it can be converted from one form to another. Heat, internal energy, and work are all addressed by the first law of thermodynamics. Energy cannot be generated or destroyed, according to the first law of thermodynamics, but it can be converted from one form to another. According to this law, some of the heat provided to the system is utilized to change the internal energy, while the remaining is used to perform work. First law of thermodynamics is also known as the law of conservation of energy.

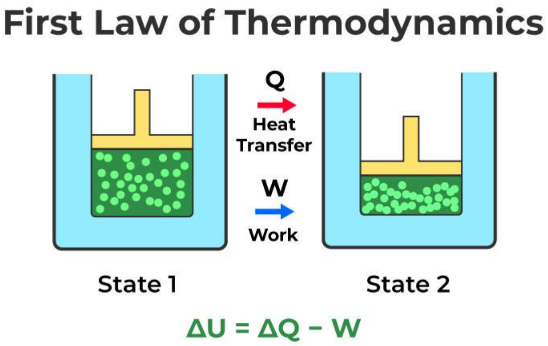


Figure 2.1 First Law of Thermodynamics

First Law of Thermodynamics Equation

The equation for the first law of thermodynamics is given as

$\Delta U = q + W$

Where,

ΔU = Change in internal energy of the system q = Algebraic sum of heat transfer between system and surroundings

W = Work interaction of the system with its surroundings

2.1 The Internal Energy

Internal energy is the total energy contained within a system due to the microscopic motion and interactions of its particles. It is a macroscopic property that characterizes the state of a system, and it encompasses various forms of energy, including kinetic and potential energy of atoms and molecules. Internal energy is a state function, meaning it depends only on the current state of the system and is independent of the path taken to reach that state. Internal energy refers to all the energy within a given system, including the kinetic energy of molecules and the energy stored in all of the chemical bonds between molecules.

To better understand internal energy, let's break it down into its components:

Kinetic Energy: The internal energy includes the kinetic energy associated with the random motion of particles within the system. This motion includes translational, rotational, and vibrational kinetic energy.

Potential Energy: Internal energy also consists of potential energy, which arises from intermolecular forces, such as electrostatic interactions and chemical bonds, between the particles in the system. Changes in these forces lead to changes in potential energy.

Other Forms of Energy: Internal energy may also contain other forms of energy, like thermal energy, nuclear energy, and electromagnetic energy, depending on the specific system and its constituents.

1. Sign Convention

It's important to understand the sign convention used in the first law of thermodynamics. When heat is added to a system, it is considered positive, and when heat is lost by the system, it is considered negative. Similarly, when work is done by the system (e.g., expansion), it is positive, and when work is done on the system (e.g., compression), it is negative. The choice of sign convention is essential for accurately representing the energy interactions in thermodynamic processes.

2. Relation to Temperature and Heat

Internal energy is closely related to temperature and heat. In fact, temperature is a measure of the average kinetic energy of the particles in a system. When a system gains heat (Q), the kinetic energy of its particles increases, leading to an increase in temperature and a corresponding increase in internal energy. Conversely, when heat is lost from the system, the temperature and internal energy decrease.

3. Role of Internal Energy in Different Phases

The internal energy of a substance can vary depending on its phase (solid, liquid, gas). For a given substance, the internal energy depends on temperature and pressure. At a molecular level, the internal energy of a substance in a particular phase is influenced by the strength of intermolecular forces.

Solid Phase: In a solid, the particles are closely packed and have limited kinetic energy, but there is potential energy associated with the vibrations of the particles in their lattice positions. The internal energy in a solid is primarily potential energy.

Liquid Phase: In a liquid, the particles have more kinetic energy than in a solid, leading to increased random motion. The internal energy of a liquid is a combination of kinetic and potential energy.

Gas Phase: In a gas, the particles have significantly more kinetic energy, as they are in constant, rapid motion. The internal energy of a gas is predominantly kinetic energy.

4. Specific Heat and Internal Energy

Specific heat is a property that quantifies the amount of heat required to raise the temperature of a given mass of a substance by a certain amount. It is represented by the symbol ”C” and varies with the substance and its phase. Specific heat is directly related to the internal energy change of a system when heat is added or removed. The equation connecting specific heat (C), mass (m), temperature change (ΔT), and the heat transferred (Q) is:

$Q = m * C * \Delta T$

This equation demonstrates how the internal energy of a system changes when heat is added or removed, and it highlights the relationship between specific heat and internal energy.

5. Enthalpy and Internal Energy

Enthalpy (H) is another thermodynamic property closely related to internal energy. It is defined as the internal energy plus the product of pressure and volume: $H = U + PV$

Where:

H is enthalpy.

U is internal energy.

P is pressure.

V is volume.

Enthalpy is particularly useful in the study of systems at constant pressure, which is common in many chemical and physical processes. When the pressure is held constant, the change in enthalpy (ΔH) is equal to the heat transferred (Q) to or from the system. This relationship is often expressed as:

$\Delta H = Q$ (at constant pressure)

For many practical applications, enthalpy is a more convenient property to work with than internal energy, especially when dealing with chemical reactions.

6. Internal Energy and Thermodynamic Processes

Internal energy plays a crucial role in various thermodynamic processes, which can be categorized into several types:

Isobaric Processes: These are processes that occur at constant pressure. For such processes, the change in enthalpy (ΔH) is equal to the heat added or removed.

Isochoric Processes: These are processes that occur at constant volume. In an isochoric process, the change in internal energy (ΔU) is equal to the heat added or removed because the volume remains constant.

Adiabatic Processes: Adiabatic processes involve no heat transfer ($Q = 0$). Therefore, any change in internal energy is solely due to the work done (W).

Isothermal Processes: These processes occur at constant temperature. In an isothermal process, there is no change in internal energy ($\Delta U = 0$), as the temperature remains constant.

Understanding internal energy is crucial in analyzing and predicting the behavior of systems during various thermodynamic processes. It allows scientists and engineers to design efficient systems, optimize processes, and control the transfer of heat and work.

7. Internal Energy and the Second Law of Thermodynamics

The second law of thermodynamics provides insight into the direction of natural processes and the limitations of energy conversion. It introduces the concept of entropy (S), a measure of the disorder or randomness in a system. According to the second law, natural processes tend to increase the entropy of the universe, which can be summarized as follows:

1. Heat naturally flows from a hot object to a cold object.

2. Work is done more easily to disperse energy than to concentrate it.

The second law also leads to the concept of heat engines and refrigerators. Heat engines, such as steam engines and internal combustion engines, operate based on the principles of the second law, converting heat into useful work while increasing the entropy of the surroundings. Refrigerators, on the other hand, transfer heat from a cooler space to a warmer space, which also increases the entropy of the universe.

8. The Microscopic View of Internal Energy

At a microscopic level, internal energy is a reflection of the interactions between particles in a system. These interactions include:

Kinetic Interactions: The translational, rotational, and vibrational motion of particles results in kinetic energy. Collisions between particles can transfer kinetic energy and alter the system's temperature.

Potential Interactions: The potential energy is determined by the strength of intermolecular forces, such as van der Waals forces, hydrogen bonds, and chemical bonds. Changes in the arrangement of particles can lead to changes in potential energy.

Chemical Reactions: Chemical reactions involve the breaking and formation of chemical bonds, resulting in changes in the internal energy of the system. Energy is either released (exothermic reactions) or absorbed (endothermic reactions) during these processes.

Understanding these microscopic interactions is essential for predicting and explaining the behavior of systems in thermodynamics. Statistical mechanics, a branch of physics that connects macroscopic thermodynamic properties to the microscopic behavior of particles, provides a deeper insight into the connection between internal energy and the behavior of matter.

9. Measurement of Internal Energy

The measurement of internal energy is a challenging task due to the vast number of particles involved in a system and their complex interactions. However, there are several methods for indirectly determining changes in internal energy:

Calorimetry: Calorimetry is a technique that measures heat exchange between a system and its surroundings. It is commonly used to determine changes in internal energy. A calorimeter is a device designed to isolate the system from its surroundings and measure the temperature changes resulting from heat transfer.

Work Done: In some cases, work done during a process can be measured directly. The work-energy theorem states that the work done on a system is equal to the change in its internal energy, assuming no heat transfer. For example, the work done in an expanding gas cylinder can be determined by measuring the force and displacement.

Enthalpy Changes: In many chemical reactions, changes in enthalpy (ΔH) can be measured experimentally using calorimetry or other techniques. The change in enthalpy is directly related to the change in internal energy and the heat transfer during the reaction.

Thermodynamic Tables and Diagrams: Thermodynamic tables and diagrams, such as the steam tables for water, provide extensive data on the internal energy of substances at various conditions (e.g., temperature and pressure). Engineers and scientists use these references to estimate internal energy changes in practical applications.

Equations of State: The internal energy of a gas can be estimated using equations of state, such as the ideal gas law, which relates pressure, volume, temperature, and the number of moles of a gas. These equations provide a simplified description of the behavior of gases under various conditions.

10. Applications of Internal Energy

- ✧ Thermodynamics and Heat Engines: Internal energy is central to the study of thermodynamics and the design of heat engines, which power machines and vehicles, making it possible to convert heat into useful work. Understanding the behavior of internal energy is crucial for increasing the efficiency of these engines.
- ✧ Chemical Reactions: In chemistry, the change in internal energy during chemical reactions (ΔU) is a key parameter. It helps determine whether a reaction is exothermic (releases heat) or endothermic (absorbs heat), which has implications for reaction kinetics and energy storage.
- ✧ Refrigeration and Air Conditioning: The principles of internal energy play a critical role in the design and operation of refrigeration and air conditioning systems, where heat is transferred from one environment to another. The efficiency and performance of these systems are closely related to the internal energy changes during the process.
- ✧ Material Science: Internal energy affects the properties of materials, including their thermal expansion, electrical conductivity, and phase transitions. Engineers and scientists consider internal energy when designing materials for specific applications.
- ✧ Environmental Science: The behavior of internal energy is relevant in environmental science, particularly in climate science. Understanding the heat capacity of the Earth's atmosphere and oceans is essential for predicting and addressing global climate change.

2.2 Heat and Work

In thermodynamics, heat and work are two ways to add or remove energy from a system. Heat is the transfer of thermal energy between two systems. Heat is driven by temperature differences. Work is the transfer of mechanical energy between two systems. Work involves a force exerted through a distance. Heat and work are both path functions. Their magnitude depends on the path followed during a process as well as the end state.

2.2.1 Heat

heat is the thermal energy transferred between systems due to a temperature difference. In colloquial use, heat sometimes refers to thermal energy itself. Thermal energy is the kinetic energy of vibrating and colliding atoms in a substance. An example of formal vs. informal usage may be obtained from the right-hand photo, in which the metal bar is ”conducting heat” from its hot end to its cold end, but if the metal bar is considered a thermodynamic system, then the energy flowing within the metal bar is called internal energy, not heat. The hot metal bar is also transferring heat to its surroundings, a correct statement for both the strict and loose meanings of heat. Another example of informal usage is the term heat content, used despite the fact that physics defines heat as energy transfer. More accurately, it is thermal energy that is contained in the system or body, as it is stored in the microscopic degrees of freedom of the modes of vibration.

Heat is energy in transfer to or from a thermodynamic system, by a mechanism that involves the microscopic atomic modes of motion or the corresponding macroscopic properties. This descriptive characterization excludes the transfers of energy by thermodynamic work or mass transfer. Defined quantitatively, the heat involved in a process is the difference in internal energy between the final and initial states of a system, and subtracting the work done in the process. This is the formulation of the first law of thermodynamics. The measurement of energy transferred as heat is called calorimetry, performed by measuring its effect on the states of interacting bodies. For example, heat can be measured by the amount of ice melted, or by change in temperature of a body in the surroundings of the system. In the International System of Units (SI) the unit of measurement for heat, as a form of energy, is the joule (J).

Heat is a form of energy transfer that occurs due to a temperature difference between two objects or systems. It is the process of energy flowing from a region of higher temperature to a region of lower temperature. The transfer of heat can happen through conduction, convection, and radiation.

Conduction: Conduction is the transfer of heat through direct contact between two objects at different temperatures. It occurs when energy is transferred from the hotter object to the colder one through molecular collisions. The rate of heat conduction depends on the thermal conductivity of the materials involved.

Convection: Convection is the transfer of heat through the movement of a fluid (gas or liquid). As a fluid is heated, it becomes less dense and rises, while cooler, denser fluid descends. This creates a circulation of fluid that helps distribute heat. Convection is essential in phenomena like natural convection (e.g., hot air rising) and forced convection (e.g., using fans or pumps to enhance heat transfer).

Radiation: Radiation is the transfer of heat in the form of electromagnetic waves (infrared radiation) and does not require a medium. All objects emit and absorb thermal radiation, and the rate of radiation transfer is determined by factors like the temperature and emissivity of the objects involved. In thermodynamics, heat is typically represented as ”Q” and is considered positive when heat is added to a system and negative when heat is lost from the system.

2.2.2 Work

In thermodynamics, work is the amount of energy that is transferred from one system to another without a transfer of entropy. It is a generalization of the concept of mechanical work in mechanics. Work is measured in joules (symbol: J). It is governed by external factors such as: External force, Pressure, Volume,Change in temperature. Work can change the internal energy. For example, if you compress a spring, you have done work to your surroundings. The energy stored in the spring could be used to raise a weight as the spring uncoils. The quantity of work done by a closed system on its surroundings is defined by factors strictly confined to the interface of the surroundings with the system and to the surroundings of the system. For example, an extended gravitational field in which the system sits.

Thermodynamic work is one of the principal processes by which a thermodynamic system can interact with its surroundings and exchange energy. This exchange results in externally measurable macroscopic forces on the system's surroundings, which can cause mechanical work, to lift a weight, for example, or cause changes in electromagnetic,or gravitational variables. The surroundings also can perform work on a thermodynamic system, which is measured by an opposite sign convention. For thermodynamic work, appropriately chosen externally measured quantities are exactly matched by values of or contributions to changes in macroscopic internal state variables of the system, which always occur in conjugate pairs, for example pressure and volume or magnetic flux density and magnetization.

In the International System of Units (SI), work is measured in joules (symbol J). The rate at which work is performed is power, measured in joules per second, and denoted with the unit watt (W).

Work, in the context of thermodynamics, is the transfer of energy through a mechanical process. When work is done on a system or by a system, it involves the application of force over a distance, resulting in energy transfer. Work can be done in several ways:

Mechanical Work: This is the most common form of work. It occurs when a force is applied to an object, and the object moves a certain distance. The work done is the product of the force and the distance over which it is applied, often represented as "W."

$W = F \times d$

Where:

W is the work done.

F is the force applied.

d is the distance over which the force is applied.

Electrical Work: In electrical systems, work is done when an electric current flows through a resistance, resulting in the conversion of electrical energy into other forms, such as heat.

Other Types of Work: Work can also be done in the form of shaft work, piston-cylinder work, and various other mechanical processes depending on the specific system under consideration. Work is a path-dependent quantity, meaning it depends on the specific process that takes place. In thermodynamics, work is often represented as ”W” and is considered positive when work is done on the system and negative when work is done by the system.

2.3 Conservation of Energy

Conservation of energy, principle of physics according to which the energy of interacting bodies or particles in a closed system remains constant. The first kind of energy to be recognized was kinetic energy, or energy of motion. In certain particle collisions, called elastic, the sum of the kinetic energy of the particles before collision is equal to the sum of the kinetic energy of the particles after collision. The notion of energy was progressively widened to include other forms. The kinetic energy lost by a body slowing down as it travels upward against the force of gravity was regarded as being converted into potential energy, or stored energy, which in turn is converted back into kinetic energy as the body speeds up during its return to Earth. For example, when a pendulum swings upward, kinetic energy is converted to potential energy. When the pendulum stops briefly at the top of its swing, the kinetic energy is zero, and all the energy of the system is in potential energy. When the pendulum swings back down, the potential energy is converted back into kinetic energy. At all times, the sum of potential and kinetic energy is constant. Friction, however, slows down the most carefully constructed mechanisms, thereby dissipating their energy gradually. During the 1840s it was conclusively shown that the notion of energy could be extended to include the heat that friction generates. The truly conserved quantity is the sum of kinetic, potential, and thermal energy. For example, when a block slides down a slope, potential energy is converted into kinetic energy. When friction slows the block to a stop, the kinetic energy is converted into thermal energy. Energy is not created or destroyed but merely changes forms, going from potential to kinetic to thermal energy. This version of the conservation-of-energy principle, expressed in its most general form, is the first law of thermodynamics. The conception of energy continued to expand to include energy of an electric current, energy stored in an electric or a magnetic field, and energy in fuels and other chemicals. For example, a car moves when the chemical energy in its gasoline is converted into kinetic energy of motion. With the advent of relativity physics (1905), mass was first recognized as equivalent to energy. The total energy of a system of high-speed particles includes not only their rest mass but also the very significant increase in their mass as a consequence of their high speed. After the discovery of relativity, the energy-conservation principle has alternatively been named the conservation of mass-energy or the conservation of total energy.

The conservation of energy is a fundamental and unassailable principle in the field of thermodynamics, which is the study of energy and its transformations. This principle, often referred to as the First Law of Thermodynamics, plays a central role in understanding the behavior of physical systems and underpins many aspects of engineering, physics, chemistry, and other scientific disciplines.

2.3.1 Historical Development

The concept of energy conservation, while formalized within the framework of thermodynamics, has deep historical roots. The idea that energy cannot be created or destroyed but can only change forms has been explored by scientists and philosophers for centuries.

In the 17th century, Sir Isaac Newton's work on mechanics laid the groundwork for the conservation of mechanical energy, which involves the kinetic and potential energy of objects in motion. This principle was later extended by scientists like Gottfried Wilhelm Leibniz and Daniel Bernoulli.

The 19th century witnessed significant developments in the understanding of energy conservation. James Joule's experiments on the relationship between mechanical work and heat, often referred to as the mechanical equivalent of heat, provided compelling evidence for the conservation of energy. Joule's work demonstrated that the mechanical work done on a system is converted into an equivalent amount of heat, and vice versa. This led to the unification of the concepts of heat and work as forms of energy transfer.

The culmination of these efforts came in the mid-19th century with the formulation of the First Law of Thermodynamics, often attributed to Rudolf Clausius and William Thomson (Lord Kelvin). This law formalized the concept of energy conservation and provided a framework for understanding the behavior of physical systems, particularly in the context of heat and work.

The First Law of Thermodynamics, also known as the law of energy conservation, states that the change in the internal energy of a closed system is equal to the heat added to the system minus the work done by the system. Mathematically, it can be expressed as:

$\Delta U = Q - W$

Where:

ΔU is the change in the internal energy of the system.

Q is the heat added to the system.

W is the work done by the system.

This law can also be expressed in differential form, which is often more practical for analyzing continuous processes:

$dU = \delta Q - \delta W$

Where:

dU is the differential change in internal energy.

δQ represents the differential amount of heat added to the system.

δW represents the differential amount of work done by the system.

2.3.2 The First Law encapsulates several essential concepts

1. Energy Conservation: The central idea of the First Law is that energy is a conserved quantity. It cannot be created or destroyed; it can only change forms. In a closed system, the total energy remains constant. Any increase in the internal energy of the system is a result of adding heat or doing work on the system.

2. Heat and Work as Energy Transfer Mechanisms: The First Law recognizes that heat and work are two primary mechanisms through which energy is transferred to or from a system. Heat represents the energy transfer due to temperature differences, while work is the energy transfer through mechanical processes. This distinction is crucial for understanding how energy flows within a system.

3. Path Independence: The First Law does not specify the exact path that a system takes in transitioning between states. It acknowledges that there can be multiple ways to reach the same final state, and the total energy change is independent of the specific process. This path independence allows for flexibility in how systems can change and evolve.

4. Sign Conventions: To maintain consistency, there are established sign conventions for heat and work in thermodynamics. When heat is added to a system or work is done on a system, they are considered positive. Conversely, when heat is lost from a system or work is done by a system, they are considered negative. These conventions help ensure that the First Law is applied consistently.

2.3.3 Law of Conservation of Energy

The law of conservation of energy states that energy can neither be created nor be destroyed. Although, it may be transformed from one form to another. If you take all forms of energy into account, the total energy of an isolated system always remains constant. All the forms of energy follow the law of conservation of energy. In brief, the law of conservation of energy states that

So in an isolated system such as the universe, if there is a loss of energy in some part of it, there must be a gain of an equal amount of energy in some other part of the universe. Although this principle cannot be proved, there is no known example of a violation of the principle of conservation of energy.

The amount of energy in any system is determined by the following equation:

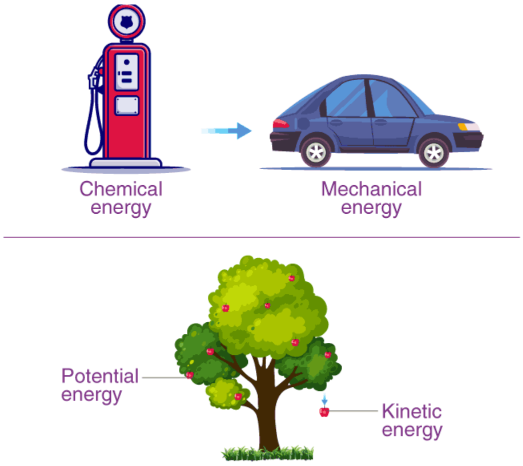


Figure 2.2 Energy Transformation

UT = Ui + W + Q

UT is the total energy of a system

Ui is the initial energy of a system

Q is the heat added or removed from the system

W is the work done by or on the system

The change in the internal energy of the system is determined using the equation

$\Delta U = W + Q$

2.3.4 Law of Conservation of Energy Derivation

Considering the potential energy at the surface of the earth to be zero. Let us see an example of a fruit falling from a tree.

Consider a point A, which is at height ‘H’ from the ground on the tree, the velocity of the fruit is zero hence potential energy is maximum there.

$$E = mgH \tag{2.1}$$

When the fruit falls, its potential energy decreases, and kinetic energy increases.

At point B, which is near the bottom of the tree, the fruit is falling freely under gravity and is at a height X from the ground, and it has speed as it reaches point B. So, at this point, it will have both kinetic and potential energy.

E = K.E + P.E

$$P.E = mgX \tag{2.2}$$

According to the third equation of motion,

$$v_2 = 2g(H - X)$$

$$\frac{1}{2}mv^2 = \frac{1}{2}m.2g(H - X)$$

$$K.E = \frac{1}{2}m.2g(H - X)$$

$$K.E = mg(H - X)$$

$$K.E = mg(H - X) \tag{2.3}$$

Using (1), (2) and (3)

E = mg(H – X) + mgX

E = mg(H – X + X)

E = mgH

Similarly, if we see the energy at point C, which is at the bottom of the tree, it will come out to be mgH. We can see as the fruit is falling to the bottom, here, potential energy is getting converted into kinetic energy. So there must be a point where kinetic energy becomes equal to potential energy. Suppose we need to find that height ‘x’ from the ground. We know at that point,

K.E = P.E

$$P.E = K.E = \frac{E}{2} \tag{2.4}$$

As the body is at height X from the ground,

$$P.E = mgX \tag{2.5}$$

Using (4) and (5) we get,

$$mgX = \frac{mgH}{2}$$

$$X = \frac{H}{2}$$

H/2 is referred to as the new height.

2.3.5 Mathematical Formulation

The mathematical formulation of the First Law of Thermodynamics provides a quantitative expression of energy conservation in various processes. The change in internal energy (ΔU) is related to the heat added (Q) and the work done (W) by the system. Let's examine how this works in different scenarios:

1. Heating a System: When heat is added to a system (Q ¿ 0), it increases the internal energy of the system (ΔU ¿ 0). This is commonly seen in processes like heating water, where the internal energy of the water increases as heat is supplied.

2. Cooling a System: When heat is lost from a system (Q ¡ 0), it decreases the internal energy of the system (ΔU ¡ 0). For example, when a container of hot coffee cools down, it loses internal energy to its surroundings in the form of heat.

3. Doing Work on a System: When work is done on a system (W ¿ 0), it increases the internal energy of the system (ΔU ¿ 0). For instance, compressing a gas in a piston-cylinder system does work on the gas and raises its internal energy.

4. Work Done by a System: When work is done by a system (W ¡ 0), it decreases the internal energy of the system (ΔU ¡ 0). In a classic example, a gas expanding and pushing a piston does work on the surroundings while losing internal energy.

2.3.6 Applications

- Heat Engines: Heat engines, such as internal combustion engines in cars and steam turbines in power plants, operate based on the principles of the First Law. They convert thermal energy into mechanical work, exemplifying the transformation of energy through heat and work.
- Refrigeration and Air Conditioning: Refrigeration and air conditioning systems rely on the transfer of heat to maintain desired temperature conditions. Heat pumps, for example, move heat from a cooler environment to a warmer one, providing heating or cooling as needed.
- Chemical Reactions: Chemical reactions often involve the exchange of heat with the surroundings. The First Law helps scientists and engineers understand how

reactions affect the internal energy of a system and how heat and work can be utilized or controlled for practical purposes.

- Thermal Comfort: Understanding heat transfer is crucial in designing buildings for thermal comfort. Insulation, heating, and cooling systems all play a role in maintaining a comfortable indoor environment while adhering to energy conservation principles.

- Renewable Energy: The principles of energy conservation are fundamental in renewable energy technologies like solar panels, wind turbines, and geothermal systems, where energy conversion and heat transfer play a critical role.

- Environmental Processes: Environmental scientists use the First Law to understand the energy balance of ecosystems and natural processes, such as heat transfer in Earth's atmosphere and oceans.

- Material Processing: Industrial processes often involve the heating and cooling of materials, as well as the performance of mechanical work. Energy conservation principles are vital for optimizing these processes and minimizing energy waste.

2.3.7 Implications for the Physical World

- Unifying Different Forms of Energy: The First Law unifies various forms of energy, from thermal and mechanical energy to chemical and electrical energy. It underscores the idea that energy is a universal currency that can be transformed and transferred between different forms.

- Principle of Energy Efficiency: Energy conservation principles highlight the importance of efficiency in energy conversion processes. Efficient systems maximize the conversion of energy from one form to another, minimizing waste and increasing the usefulness of energy.

- Fundamental to Science and Engineering: The First Law is a cornerstone of physics and engineering. It provides the foundation for analyzing and predicting the behavior of physical systems, enabling the design and optimization of countless technologies and processes.

- Environmental Considerations: Energy conservation is a critical concept in addressing environmental challenges. Efforts to reduce energy consumption and greenhouse gas emissions are closely tied to the principles of energy conservation.

- Limitations and Boundary Conditions: The First Law does not provide information about the specific mechanisms or efficiency of energy conversion processes. To address these aspects, additional principles and laws, such as the Second Law of Thermodynamics, are needed.

2.4 First Law of Thermodynamics Statement

The First Law of Thermodynamics, often referred to as the law of energy conservation, states that energy cannot be created or destroyed in an isolated system. Instead, it can only change forms or be transferred from one part of the system to another. This law emphasizes the principle of energy conservation, which is a fundamental concept in physics. In simpler terms, the total energy of a closed system remains constant.

The statement of the First Law of Thermodynamics can be expressed as:

$\Delta U = Q - W$

Where:

ΔU represents the change in the internal energy of the system.

Q represents the heat added to the system.

W represents the work done by the system or on the system.

This equation tells us that any change in the internal energy of a system (ΔU) is equal to the heat added to the system (Q) minus the work done by the system (W).

2.4.1 Explanation of the Terms in the First Law Statement

1. Internal Energy (ΔU)

Internal energy is a measure of the total energy contained within a system. It includes both kinetic and potential energy at the molecular level. The change in internal energy (ΔU) represents how the total energy of the system changes over time. If ΔU is positive, it means the internal energy of the system has increased, and if it's negative, it means the internal energy has decreased.

2. Heat (Q)

Heat is a form of energy transfer between a system and its surroundings that occurs due to a temperature difference. When heat is added to a system (Q ¿ 0), it increases the internal energy of the system. Conversely, when heat is lost from the system (Q ¡ 0), it decreases the internal energy.

3. Work (W)

Work is another way in which energy can be added to or extracted from a system. Work can be done on a system or by a system. When work is done on a system (W ¿ 0), it increases the system's internal energy, while work done by the system (W ¡ 0) results in a decrease in internal energy.

2.4.2 Implications of the First Law of Thermodynamics

The First Law of Thermodynamics has several important implications and applications in the field of thermodynamics, physics, and engineering:

1. Conservation of Energy

The First Law reinforces the principle of energy conservation. It tells us that the total energy of an isolated system remains constant. This law is a fundamental concept that underpins our understanding of how energy behaves in various physical and chemical processes.

2. Energy Transfer

The law explains how energy can be transferred between a system and its surroundings. It highlights the roles of heat and work as mechanisms for energy transfer. Heat represents the transfer of thermal energy, while work represents the transfer of mechanical energy.

3. Heat Engines

The First Law of Thermodynamics is crucial in understanding the operation of heat engines, such as steam engines and internal combustion engines. These engines convert heat into mechanical work. The First Law governs the efficiency and performance of these engines.

4. Calorimetry

Calorimetry is the science of measuring heat. The First Law is fundamental in calorimetry, which involves measuring the heat exchange in various processes and reactions. Calorimeters are devices designed to measure the heat transfer accurately.

5. Thermodynamic Processes

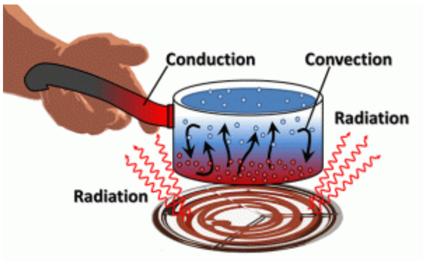
The First Law helps in understanding and analyzing different thermodynamic processes, including isothermal, adiabatic, and isobaric processes. These processes involve changes in temperature, pressure, volume, and internal energy, and the First Law provides a framework for analyzing them.

2.5 Heat Transfer Mechanisms

Heat transfer is a discipline of thermal engineering that concerns the generation, use, conversion, and exchange of thermal energy (heat) between physical systems. Heat transfer is classified into various mechanisms, such as thermal conduction, thermal convection, thermal radiation, and transfer of energy by phase changes. Engineers also consider the transfer of mass of differing chemical species (mass transfer in the form of advection), either cold or hot, to achieve heat transfer. While these mechanisms have distinct characteristics, they often occur simultaneously in the same system.

Heat conduction, also called diffusion, is the direct microscopic exchanges of kinetic energy of particles (such as molecules) or quasiparticles (such as lattice waves) through the boundary between two systems. When an object is at a different temperature from another body or its surroundings, heat flows so that the body and the surroundings reach the same temperature, at which point they are in thermal equilibrium. Such spontaneous heat transfer always occurs from a region of high temperature to another region of lower temperature, as described in the second law of thermodynamics.

Heat convection occurs when the bulk flow of a fluid (gas or liquid) carries its heat through the fluid. All convective processes also move heat partly by diffusion, as well. The flow of fluid may be forced by external processes, or sometimes (in gravitational fields) by buoyancy forces caused when thermal energy expands the fluid (for example in a fire plume), thus influencing its own transfer. The latter process is often called ”natural convection”. The former process is often called ”forced convection.” In this case, the fluid is forced to flow by use of a pump, fan, or other mechanical means. Thermal radiation occurs through a vacuum or any transparent medium (solid or fluid or gas). It is the transfer of energy by means of photons or electromagnetic waves governed by the same laws.



Heat transfer is the energy exchanged between materials (solid/liquid/gas) as a result of a temperature difference. The thermodynamic free energy is the amount of work that a thermodynamic system can perform. Enthalpy is a thermodynamic potential, designated by the letter ”H”, that is the sum of the internal energy of the system (U) plus the product of pressure (P) and volume (V). Joule is a unit to quantify energy, work, or the amount of heat. Heat transfer is a process function (or path function), as opposed to functions of state; therefore, the amount of heat transferred in a thermodynamic process that changes the state of a system depends on how that process occurs, not only the net difference between the initial and final states of the process.

Thermodynamic and mechanical heat transfer is calculated with the heat transfer coefficient, the proportionality between the heat flux and the thermodynamic driving force for the flow of heat. Heat flux is a quantitative, vectorial representation of heat-flow through a surface. In engineering contexts, the term heat is taken as synonymous to thermal energy. This usage has its origin in the historical interpretation of heat as a fluid (caloric) that can be transferred by various causes, and that is also common in the language of laymen and everyday life.

The transport equations for thermal energy (Fourier’s law), mechanical momentum (Newton’s law for fluids), and mass transfer (Fick’s laws of diffusion) are similar, and analogies among these three transport processes have been developed to facilitate prediction of conversion from any one to the others. Thermal engineering concerns the generation, use, conversion, storage, and exchange of heat transfer. As such, heat transfer is involved in almost every sector of the economy. Heat transfer is classified into various mechanisms, such as thermal conduction, thermal convection, thermal radiation, and transfer of energy by phase changes.

Heat transfer is an essential discipline in thermal engineering that deals with the transfer, conversion, usability, and creation of heat or thermal energy. Transfer of heat occurs through various mechanisms like conduction, convection, radiation, and change of phases. All these mechanisms have distinct characteristics, but these mechanisms can simultaneously occur in an identical system. Heat transfer rate is reliant on the temperature difference. The rate of heat transfer is proportional to the difference in the temperatures between two mediums; such that, if the difference rises, then the transfer rate increases, and if temperature difference decreases, then simultaneously heat transfer rate decreases. There is a class of applications of the rate of the temperature difference and heat transfer rate in automobile engineering, structural engineering, thermal engineering, metallurgical engineering, energy-saving, and so on.

2.5.1 Types of Heat Transfer Mechanisms

Enclosure cooling involves a combination of heat transfer mechanisms.

1. Conduction

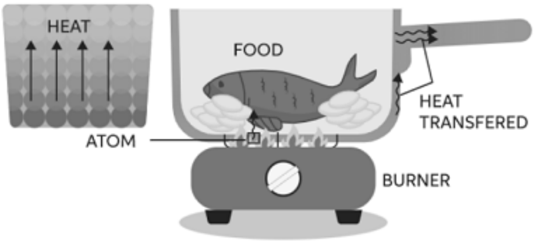


Figure 2.3 Conduction

Heat conduction is a mechanism in which heat is shifted from the higher temperature zone to the lower temperature zone. Conduction occurs because of the interaction of the adjacent atoms, electrons, or ions existing in the body. In the conduction mechanism, the collision between molecules is the only reason for the heat transfer. The conduction process typically occurs in solids as heat is supplied to one end and molecules travel faster to the farther end. The area which has lower kinetic energy will try to obtain the energy from the higher kinetic energy area. This indicates that particles that would be moving with low velocity will collide with the higher velocity particles and thus gain velocity from them.

Types of conduction materials

Conduction materials consist of metals, plasmas, superconductors, electrolytes, semiconductors, and non-metallic conductors such as graphite and conductive polymers. But the conduction properties in each of the above mentioned elements are different. The conductivity in metals is generally high as they have free electrons through which electricity can pass easily. Semiconductors also conduct electricity, but they will not always conduct electricity. They will show conduction only when they meet particular conditions.

Metals and semiconductors as conduction material

Metals: Metals usually have high conduction properties. All metals have different conducting powers based on their conductivity applied in electrical appliances as they provide a smooth flow of electricity. The metals have electrons in their outer shell, which get readily dissociated from the parent atoms making the conductance of electricity possible through the metals.

Semiconductors: The bandgap between the conductance band and valence is more in semiconductors than metals. Still, it is less than non-metals, so there are no free electrons for conductance in semiconductors. But semiconductors conduct electricity through them at specific temperature or pressure. When the temperature is increased, few of the electrons get free, thus conducting electricity quickly. Electronic appliances used are made with semiconductors.

2. Convection

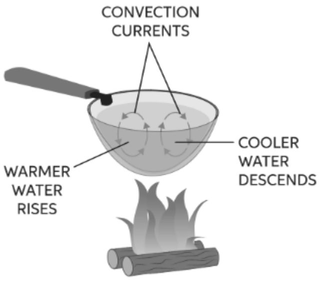


Figure 2.4 Convection

Convection is the mechanism of heat transfer from higher temperature to lower temperature zone by the flow of material particles. The convection mode of heat transfer is used by only fluids, that is, liquids and gases. Mathematically, the convection heat transfer can be represented as follows:

$H=hA\Delta T$

Here, H is the heat transfer through the convection process, h is the convective heat transfer coefficient, A is the surface area, and ΔT is the difference in temperature. The convection heat transfer coefficient depends upon density, viscosity, thermal conductivity, and specific heat capacity of the fluid.

Convection heat transfer process

In the convection heat transfer method, a part of the fluid in contact with heat gets expanded when the fluid is being warmed up. Due to thermal expansion of the fluid, the fluid becomes less dense with respect to the other regions of the fluid. This heated part of the fluid rises, and moves towards the colder part of the fluid; this cycle of heating and replacing sets up convectional current, which occurs in the transfer of energy.

In the convection process, both buoyancy and gravitational forces working on the fluid are necessary. For instance, the lower part of a liquid near the heat source is expanded when the liquid is warmed up. Due to this thermal expansion of liquid, the density of this part reduces, and the liquid becomes lighter with respect to the upper part. Due to buoyancy and gravitational force, the liquid of the lower region rises, and the liquid of the upper region (heavier) moves down. Hence, convection heat transfer occurs.

Types of convection process

There are the following two convection processes:

Natural or free convection: In this kind of convection, particles of a liquid flow due to differences in density or thermal expansion. Like trade winds, land and sea breeze occurs due to natural convection.

Forced convection: In this kind of convection, particles of a liquid are forced to flow from one region to another by some external force. Example-exhaust fan, air heat system, human heart, etc.

3. Radiation

Radiation can be described as a release of vibrations, ions, or rays. Radiation does not need an energy storage tool. The subject is either reflected or consumed. The force consumed increases the object's kinetic strength and so raises the surface temperature.

Electromagnetic radiation is generated when particles in matter begin to flow and generate heat. The heat that dissipates is recognized as thermal radiation. Some instances of thermal radiation are infrared radiation, which is emitted by fauna, and cosmic microwave background radiation.

When thermal energy is transformed into electrical energy, the emission of electromagnetic wave occurs. It is known as thermal radiation. Radiation is viable for all kinds of matter, which is at a temperature above absolute zero. In radiation, the heat gets transferred in the form of infrared waves. As electromagnetic radiation can flow through vacuum, the radiation moves through space unless obstructed.

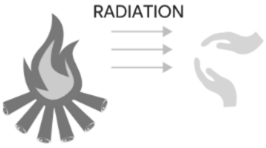


Figure 2.5 Radiation

Thermal radiation is different from the conduction and convection heat flow processes in the context of the medium of travel. Thermal radiation can flow without a medium; that is, it can travel through vacuum. Some characteristics of electromagnetic radiation rely on the wavelength and frequency of the same. Thermal radiation possesses the properties of electromagnetic radiation. Radiation waves can move through a non-absorbing medium to reach higher temperatures.

The concept of black body radiation

A black body is an opaque body with a surface that is perfectly non-reflective. Black body radiation is the radiation that is emitted by a black body and surrounds a body in a situation of absolute thermodynamic equilibrium. It is an ideal situation to understand and construct theories on the nature of radiation.

Emitted thermal energy is supposed to approximate black body radiation, and various everyday objects emit this kind of energy. An enclosure with perfect insulation, put in thermal equilibrium, includes internal black body radiation, which can get emitted if a very tiny hole is punctured on the surface in a way that the equilibrium is not disturbed. The black body radiation will then be seen to get emitted through the tiny hole. In normal room temperatures, a black body seems to be black, as most of the energy delivered lies in the infrared spectrum, which is invisible to the human eye.

4. Advection

By transferring matter, energy including thermal energy is moved by the physical transfer of a hot or cold object from one place to another. This can be as simple as placing hot water in a bottle and heating a bed, or the movement of an iceberg in changing ocean currents. A practical example is thermal hydraulics. This can be described by the formula:

$$\phi_q = vpc_p\Delta T$$

where

ϕ_q is heat flux (W/m2),

ρ is density (kg/m3),

c_p is heat capacity at constant pressure (J/kg·K),

Δ T is the difference in temperature (K),

v is velocity (m/s).

2.6 Work Transfer Mechanisms

Work transfer mechanisms in thermodynamics are central to our understanding of how energy is exchanged within and between systems, particularly in the context of heat engines, refrigeration systems, and other thermodynamic processes. These mechanisms encompass various forms of work, including mechanical, electrical, and chemical work, each of which plays a unique role in the study and application of thermodynamics.

Work is a critical concept in thermodynamics as it represents the transfer of energy between a system and its surroundings through mechanical, electrical, or other means. In thermodynamics, work is expressed as a process that results in the change of a system's state or internal energy. Work is often represented by the letter ”W” and can be positive (work done by the system on the surroundings) or negative (work done on the system by the surroundings).

The work done on or by a system can be calculated using various mathematical expressions, depending on the specific work transfer mechanism. In this discussion, we will focus on the most common work transfer mechanisms in thermodynamics.

1. Mechanical Work

Mechanical work is perhaps the most familiar form of work transfer. It occurs when a force is applied to an object, causing it to move a certain distance. The work done by a constant force over a distance can be calculated using the formula:

$W_{mechanical}$ =F·d

Where:

$W_{mechanical}$ is the mechanical work done (measured in joules, J).

F is the applied force (measured in newtons, N).

d is the displacement over which the force is applied (measured in meters, m).

In thermodynamics, mechanical work is often associated with processes like the expansion or compression of gases in pistons, which is essential in heat engines. The work done in these processes can also be expressed as:

$W_{mechanical}$ =P·ΔV

Where:

P is the pressure of the gas.

ΔV is the change in volume.

Mechanical work is a key component of many thermodynamic cycles, including the Carnot cycle and the Rankine cycle, which are fundamental in power generation and refrigeration.

2. Electrical Work

Electrical work is related to the transfer of energy through the movement of charged particles, typically electrons, in an electrical circuit. When electrical current flows through a resistance, electrical work is done. The work done in an electrical circuit can be calculated using the formula:

$W_{electrical} = Q \cdot V$

Where:

$W_{electrical}$ is the electrical work done (measured in joules, J).

Q is the charge moved (measured in coulombs, C).

V is the potential difference (voltage) across the circuit (measured in volts, V).

In thermodynamics, electrical work is relevant in various applications, such as powering electronic devices, electric motors, and generators. For example, in a generator, mechanical work is converted into electrical work by rotating a coil of wire in a magnetic field, inducing an electromotive force (EMF).

3. Chemical Work

Chemical work is associated with chemical reactions and the transfer of energy during the breaking and forming of chemical bonds. When a chemical reaction occurs at constant pressure, the work done can be calculated as the product of the pressure (P) and the change in volume (ΔV) of the system:

$W_{chemical} = -P \cdot \Delta V$

In this formula, chemical work is considered negative if the volume increases during the reaction and positive if the volume decreases.

Chemical work is significant in the field of thermodynamics, particularly in the study of gases and chemical reactions. It has practical applications in various processes, including combustion, where chemical energy is converted into thermal energy and mechanical work, and in biological systems, where chemical reactions are crucial for energy production.

4. Pneumatic and Hydraulic Work

Pneumatic and hydraulic systems are based on the use of gases (pneumatics) or liquids (hydraulics) to transmit power and perform work. In both systems, a change in pressure is used to transfer mechanical work. The work done in a pneumatic or hydraulic system is given by:

$W_{pneumatic/hydraulic}$ =P·ΔV

Where:

$W_{pneumatic/hydraulic}$ is the work done in pneumatic or hydraulic systems (measured in joules, J).

P is the pressure change.

ΔV is the change in volume.

These systems are widely used in applications such as heavy machinery, vehicle brakes, and industrial automation, where the transfer of mechanical work over distance is critical.

5. Thermal Work

Thermal work is related to heat transfer and the expansion or compression of gases due to temperature changes. In processes involving gases, the thermal work can be calculated using the ideal gas law and the change in pressure and volume:

$W_{thermal} = \int_{V_1} V^2 PdV$

Where:

$W_t hermal$ is the thermal work done (measured in joules, J).

P is the pressure.

V_1 and V_2 are the initial and final volumes, respectively.

This equation represents the work done as a gas expands or is compressed. In isothermal processes (constant temperature), the work can be calculated as:

$$W_{thermal,isothermal} = nRT \cdot ln(\frac{V_2}{V_1}$$

Where:

n is the number of moles of the gas.

R is the ideal gas constant.

T is the absolute temperature.

Thermal work is essential in various thermodynamic processes, such as the expansion and compression of gases in heat engines and refrigeration systems. The work done during these processes contributes to the overall efficiency and performance of these systems.

6. Electromagnetic Work

Electromagnetic work involves the transfer of energy through electromagnetic fields, particularly electromagnetic radiation, such as light. When electromagnetic radiation interacts with matter, it can transfer energy to the material, leading to various effects, including mechanical work, the movement of charged particles, and changes in temperature.

Electromagnetic work has numerous applications, including solar panels, which convert sunlight into electricity, and microwave ovens, which use electromagnetic radiation to heat and cook food. In these applications, the work transfer involves the conversion of electromagnetic energy into other forms of energy.

7. Nuclear Work

Nuclear work is related to nuclear reactions and the release of energy from atomic nuclei. In nuclear reactors, for example, the energy generated by nuclear fission is harnessed to produce electricity. The work done in these systems involves the controlled release of nuclear energy.

Nuclear work is crucial in nuclear power plants, where it plays a central role in generating electrical power through the conversion of nuclear energy into mechanical work, which is then transformed into electrical work.

2.6.1 Applications of Work Transfer Mechanisms in Thermodynamics

The various work transfer mechanisms in thermodynamics have wide-ranging applications in science, engineering, and everyday life:

- ✧ **Heat Engines:** Work transfer mechanisms, particularly mechanical and thermal work, are essential in heat engines like steam engines, internal combustion engines, and gas turbines. These engines convert thermal energy into mechanical work, which can be used to generate power and propel vehicles.
- ✧ **Refrigeration and Air Conditioning:** Refrigeration systems rely on work transfer mechanisms, such as mechanical and thermal work, to transfer heat from a lower-temperature space (the interior of a refrigerator or air-conditioned room) to a higher-temperature space (the environment). This process is essential for cooling and preserving food and maintaining comfortable indoor temperatures.
- ✧ **Power Generation:** Electrical work is at the heart of power generation in power plants, including coal-fired, natural gas, and nuclear power plants. These facilities use various work transfer mechanisms to convert heat energy into electrical work, which is then distributed for various applications.
- ✧ **Chemical Reactions:** Chemical work is significant in chemical reactions, where the formation and breaking of chemical bonds are associated with changes in energy. It is a fundamental concept in thermodynamics, and understanding chemical work is crucial in the fields of chemistry and material science.

- **Transportation:** Work transfer mechanisms are essential in various forms of transportation. In automobiles, internal combustion engines convert chemical energy into mechanical work to propel the vehicle. Electric vehicles use electrical work to drive electric motors, while trains and airplanes use different forms of work transfer for propulsion.

- **Renewable Energy:** Work transfer mechanisms play a role in renewable energy sources like wind turbines and solar panels. Wind turbines convert mechanical work from the wind into electrical work, and solar panels convert electromagnetic work from sunlight into electrical work.

- **Aerospace:** In aerospace engineering, work transfer mechanisms are vital in the operation of rockets and spacecraft. Rocket propulsion systems rely on the expulsion of high-speed exhaust gases to generate mechanical work, propelling spacecraft into space.

- **Energy Storage:** Work transfer mechanisms are involved in various energy storage systems, including batteries, where electrical work is stored for later use, and pumped hydro storage, which converts electrical work into gravitational potential energy for storage and retrieval.

- **Manufacturing and Industrial Processes:** Work transfer mechanisms are integral to the operation of manufacturing equipment and industrial machinery. Mechanical work is used in cutting, shaping, and assembling materials, while electrical work powers a wide range of automated processes and systems.

- **Environmental Engineering:** Environmental engineers use work transfer mechanisms in processes like wastewater treatment, where pumps and compressors transfer mechanical work to move fluids and gases through treatment facilities.

2.7 Applications of the First Law

- **Heat Engines and the Carnot Cycle:** One of the most prominent and practical applications of the First Law of Thermodynamics is in the study of heat engines. Heat engines are devices that convert thermal energy into mechanical work. These engines are widely used in various applications, from internal combustion engines in automobiles to steam turbines in power plants. The First Law explains how the heat input and work output are related, and it helps in optimizing the efficiency of these engines. The Carnot cycle, which is based on the principles of the First Law, sets the theoretical limit for the efficiency of a heat engine, allowing engineers to design more efficient engines.

- **Refrigeration and Air Conditioning:** The principles of the First Law are vital in understanding refrigeration and air conditioning systems. These systems are designed to transfer heat from a lower-temperature region to a higher-temperature one. By accounting for the energy input and output, the First Law enables us to design efficient cooling systems for various applications, from household refrigerators to large industrial HVAC systems. This application is crucial for maintaining comfortable living conditions and preserving perishable goods.

- **Chemical Reactions and Thermochemistry:** In the field of chemistry, the First Law of Thermodynamics plays a central role in understanding the energy changes associated with chemical reactions. It allows chemists to calculate the heat absorbed or released during a chemical reaction, which is crucial for the design and optimization of chemical processes and industrial applications. Thermochemistry is a branch of chemistry dedicated to studying heat changes in chemical reactions, and it relies heavily on the principles of the First Law.
- **Phase Transitions and Calorimetry:** Phase transitions, such as the transition from a solid to a liquid (melting) or from a liquid to a gas (vaporization), are governed by the principles of the First Law. It helps in determining the energy required for these transitions and their effects on the surroundings. Calorimetry is a technique used to measure heat transfer in these processes and relies on the First Law for accurate measurements. Understanding phase transitions is essential in fields like materials science and environmental engineering, where knowledge of energy changes is crucial.
- **Electrical Circuits and Electrical Energy:** Electrical circuits involve the transfer of electrical energy in the form of current. The First Law is used to understand and analyze the distribution of energy in these circuits, helping engineers design efficient electrical systems for various applications, including power generation and distribution. Electrical engineers use the principles of the First Law to optimize the performance of electrical devices and systems, ensuring that electrical energy is used efficiently.
- **Geothermal Energy and Heat Transfer:** Geothermal energy harnesses the heat from the Earth's interior to generate electricity or provide heating and cooling. The First Law of Thermodynamics is crucial for calculating the efficiency of geothermal systems and understanding the transfer of heat from the Earth's core to the surface. By quantifying heat transfer in geothermal reservoirs, engineers can design sustainable and efficient energy systems that have a minimal environmental impact.
- **Environmental Engineering and Waste Heat Recovery:** The principles of the First Law are widely applied in environmental engineering to analyze and design systems for waste heat recovery, pollution control, and renewable energy production. Waste heat recovery systems capture and reuse heat that would otherwise be lost, improving overall energy efficiency. This is particularly important in industrial processes and power plants, where large amounts of waste heat are generated.
- **Material Science and Heat Transfer:** Understanding heat and energy transfer is vital in material science and engineering. The First Law aids in designing and developing materials with specific thermal properties, making it essential in industries such as aerospace, automotive, and construction. The behavior of

materials under different temperature conditions and their ability to conduct or insulate heat are important considerations in material selection and design.

- ✧ **Space Exploration and Thermal Management:** In the design and operation of spacecraft and space systems, the principles of the First Law of Thermodynamics are crucial. Engineers must carefully consider energy transfer and conservation in the harsh conditions of outer space, where temperature extremes can significantly impact the functionality of spacecraft and instruments. Effective thermal management systems are essential to ensure the survival of equipment and crew in space missions.

- ✧ **Food and Nutrition and Caloric Intake:** The First Law is also relevant in the study of food and nutrition. It helps in understanding the energy content of food and how the body utilizes this energy. This knowledge is used in dietary planning and health sciences. The caloric content of food is determined by measuring the energy released when food is burned, which is a direct application of the First Law.

- ✧ **Renewable Energy Systems:** The First Law plays a pivotal role in renewable energy systems, such as solar panels and wind turbines. It is used to calculate the energy conversion efficiency of these systems and optimize their performance. By understanding the principles of energy conversion and conservation, engineers can design more efficient and sustainable energy sources.

- ✧ **Biological Systems and Metabolism:** In biology, the First Law of Thermodynamics is applied to understand energy transfer and conversion in biological systems. It is fundamental in fields like physiology, biochemistry, and biophysics, helping researchers investigate various biological processes. The study of metabolism, which involves the conversion of energy within living organisms, relies heavily on the principles of the First Law.

- ✧ **Civil Engineering and Energy Efficiency:** In civil engineering, the First Law of Thermodynamics is used to analyze energy transfer and heat distribution in buildings and infrastructure. Engineers apply these principles to design energy-efficient structures that minimize energy losses through insulation, heating, and cooling systems. Sustainable building designs benefit from a thorough understanding of energy conservation.

- ✧ **Power Generation and Energy Production:** The First Law is the foundation for the design and operation of power generation systems, such as coal-fired power plants, nuclear reactors, and renewable energy facilities. It guides the optimization of energy conversion processes to ensure efficient electricity production. The study of thermodynamics is essential for engineers working in the power generation industry.

- ✧ **Transportation and Energy Efficiency:** Efficient transportation systems, from vehicles to aircraft, depend on the principles of the First Law. By understanding how energy is transformed and conserved in engines and propulsion systems, engineers can design more fuel-efficient and environmentally friendly transportation options. This is crucial for reducing energy consumption and greenhouse gas emissions.

- **Industrial Processes and Process Optimization:** The First Law is applied in various industrial processes to optimize energy usage and reduce waste. Industries such as chemical manufacturing, metallurgy, and petrochemicals benefit from a deep understanding of energy conservation. By minimizing energy losses and enhancing energy efficiency, these processes become more cost-effective and sustainable.
- **Solar Energy and Photovoltaic Cells:** Solar energy systems, including photovoltaic cells, depend on the principles of the First Law to capture and convert sunlight into electricity. The efficiency of these systems is determined by how effectively they convert solar energy into electrical energy while minimizing energy losses.
- **Wind Energy and Wind Turbines:** Wind energy is harnessed through wind turbines, which convert the kinetic energy of moving air into electricity. The First Law is essential in designing efficient wind turbines and understanding the energy conversion process in these systems.
- **Nuclear Energy and Nuclear Reactors:** Nuclear energy production relies on the principles of the First Law, particularly in the operation of nuclear reactors. These reactors generate heat through nuclear fission, which is then converted into electricity. The understanding of energy transfer and conversion is critical to ensure the safe and efficient operation of nuclear power plants.
- **Astrophysics and Stellar Energy:** In astrophysics, the First Law is used to understand the energy generation and transfer in celestial bodies, such as stars. Stellar energy production, including nuclear fusion in the sun, is a prime example of the application of the First Law to understand the energy balance in astronomical objects.
- **Environmental Impact Assessment:** The First Law plays a role in assessing the environmental impact of various processes and activities. It helps in quantifying energy consumption and waste generation, allowing environmental scientists and engineers to evaluate the sustainability of projects and make informed decisions to minimize ecological harm.
- **Nanotechnology and Thermal Properties:** Nanotechnology explores the behavior of materials at the nanoscale, where thermal properties become increasingly important. The First Law is applied to understand heat transfer and energy conservation at this level, guiding the development of new materials and technologies.
- **Energy Storage:** Efficient energy storage systems, such as batteries and capacitors, rely on the principles of the First Law to store and release energy as needed.

By understanding energy transfer and conversion in these systems, engineers can improve energy storage solutions for various applications.

- **Aerospace Engineering and Propulsion Systems:** Aerospace engineers apply the First Law in the design and optimization of propulsion systems for aircraft and spacecraft. It plays a crucial role in ensuring that propulsion systems are efficient and capable of delivering the required thrust and energy for successful missions.
- **Earth Sciences and Geothermal Gradients:** The First Law is used in the Earth sciences to understand the geothermal gradients and heat transfer within the Earth's crust. This knowledge is essential for geological and geophysical studies and has applications in geothermal energy exploration.
- **Oceanography and Heat Transfer in Oceans:** The First Law is applied in the study of heat transfer in the oceans, which affects ocean currents, climate patterns, and marine ecosystems. Oceanographers use these principles to understand how energy is distributed within the world's oceans.
- **Quantum Mechanics and Energy Levels:** In the realm of quantum mechanics, the First Law is used to understand the energy levels and transitions of particles and atoms. The quantization of energy levels in quantum systems is fundamental to our understanding of the behavior of particles at the quantum level.
- **Biomedical Engineering and Medical Devices:** Biomedical engineers use the First Law to design medical devices and equipment that involve energy transfer and conservation. Applications include the design of pacemakers, artificial organs, and medical imaging systems.
- **Energy Policy and Sustainability:** Energy policy decisions at the governmental and international levels are heavily influenced by the First Law of Thermodynamics. The principles of energy conservation and efficiency guide policies aimed at achieving sustainability, reducing energy consumption, and transitioning to renewable energy sources.
- **Weather and Climate Science:** Meteorologists and climate scientists apply the First Law to understand the energy balance of the Earth's atmosphere and how it influences weather patterns and climate change. The law is fundamental in modeling and predicting weather phenomena and their impacts.
- **Space Science and Astrophysical Phenomena:** Beyond Earth, the First Law is used to study a wide range of astrophysical phenomena, such as the behavior of black holes, the expansion of the universe, and the energy released in supernovae. Understanding the transfer and transformation of energy in space is crucial for advancing our knowledge of the cosmos.
- **Education and Research:** The First Law of Thermodynamics serves as a fundamental concept in science and engineering education. It is a cornerstone

of thermodynamics courses and textbooks and is essential for training future scientists and engineers.

CHAPTER 3

PROPERTIES OF PURE SUBSTANCES

A substance that has a fixed chemical composition throughout is called pure substance. Water, helium carbon dioxide, nitrogen are examples. It does not have to be a single chemical element just as long as it is homogeneous throughout, like air.

Pure substances are referred to objects that are made up of only one kind of particle. Pure substances are fixed structures in nature. The term pure substances are quite understandable and have a simple meaning. The classification of pure substances is as follows: compounds and elements. Only one single type of atom constitutes the body of a pure substance. The sole truth of pure substance is that it cannot be broken down. It also cannot be transformed, even if external means like chemical or physical means are applied. Metalloids, non-metals, or metals constitute the category of elements.

Compounds are also considered to be pure substances. It is so because; more than one pure substance is combined in a fixed ratio to give birth to a certain compound. These compounds can be broken down and still be considered pure substances as they were made with pure substances in the first place. From a young age, we were taught that matter is divided into gases, liquids, and solids. But growing up, as our

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knowledge expands; we get to know that matter further gets divided into mixtures and pure substances.

Pure substances have several characteristics and properties. They are as follows:

Temperature: is the first property of pure substances Kelvin and Celsius are the two most commonly used units for temperature. For converting Celsius into Kelvin, we need to add 273.15. For Example – if the temperature of a substance is 50 Celsius, then its temperature in Kelvin will be 50+273.15= 323.15. The lowest temperature ever achieved is 0 Kelvin.

Pressure: Force per unit area is called pressure. The formula for pressure is as follows: P=FA.

Volume and mass: People often confuse between volume and mass. But in reality, there are not many similarities between these two. It is an intensive property. There is a special term: specific volume (v). The value we get after dividing total volume by total mass is called specific volume, v=Vm. The inverse of specific volume is density.

Characteristics of pure substances The characteristics of pure substances are as follows: Pure substances are made of a single type of molecule or atom. It is so because they are mostly homogeneous. Pure substances are uniform and constant.Pure substances always have specific or fixed melting points and boiling points. Predictable subjects are formed when pure substances come under chemical reactions.

Important terms of a pure substance: Important terms when dealing with pure substances include: Vaporization is the point where a liquid changes into a vapor phase. Condensation, which is the point that a vapor changes into a liquid phase (and is the same point as for vaporization). Melting point is the point where a solid turns into a liquid. Freezing point is the point when a liquid turns into a solid. Sublimation is the point that a solid turns directly into a vapor. Desublimation means the point that a vapor turns directly into a solid (unusual, but it happens). A critical point occurs where the saturated liquid and saturated vapor curves meet and become the same. The triple point is the point where the gas, liquid, and solid phases exist at the same temperature.

3.1 Phase Diagrams

A phase diagram is a graph that shows the thermodynamic conditions of a substance at different pressures and temperatures. It uses temperature and pressure combinations to illustrate when a substance will occur as solid, liquid, or gas. A phase diagram in physical chemistry, engineering, mineralogy, and materials science is a type of chart used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium. Common components of a phase diagram are lines of equilibrium or phase boundaries, which refer to lines that mark conditions under which multiple phases can coexist at equilibrium. Phase transitions occur along lines of equilibrium. Metastable phases are not shown in phase diagrams as, despite their common occurrence, they are not equilibrium phases.

Triple points are points on phase diagrams where lines of equilibrium intersect. Triple points mark conditions at which three different phases can coexist. For example, the water phase diagram has a triple point corresponding to the single temperature and pressure at which solid, liquid, and gaseous water can coexist in a stable equilibrium (273.16 K and a partial vapor pressure of 611.657 Pa). The pressure on a pressure-temperature diagram (such as the water phase diagram shown) is the partial pressure of the substance in question. The solidus is the temperature below which the substance is stable in the solid state. The liquidus is the temperature above which the substance is stable in a liquid state. There may be a gap between the solidus and liquidus; within the gap, the substance consists of a mixture of crystals and liquid (like a ”slurry”). Working fluids are often categorized on the basis of the shape of their phase diagram.

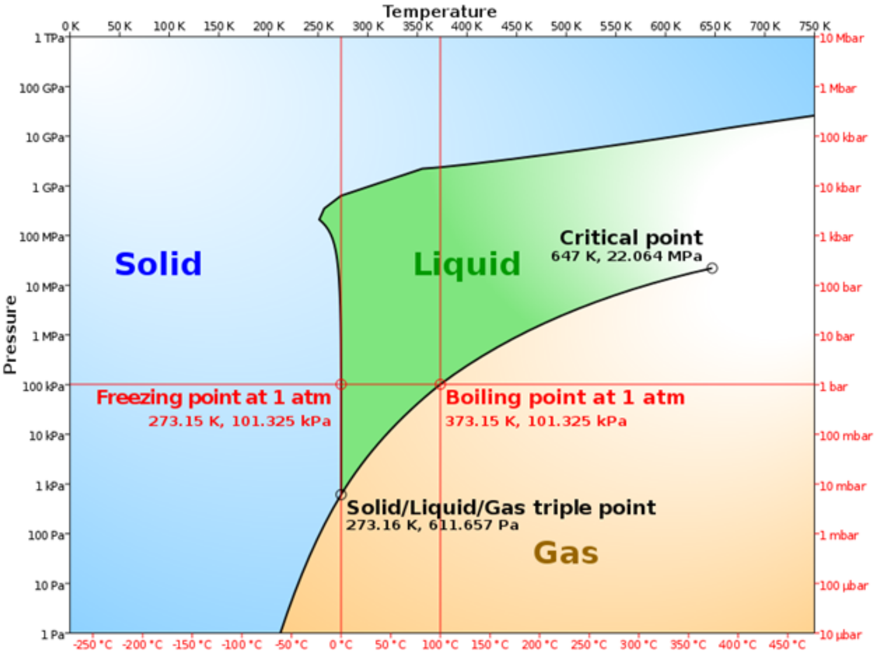


Figure 3.1 Simplified temperature/pressure phase change diagram for water. The pressure on a pressure-temperature diagram (such as the water phase diagram shown above) is the partial pressure of the substance in question.

3.1.1 Phase Diagrams Types

1. 2-dimensional diagrams

The simplest phase diagrams are pressure–temperature diagrams of a single simple substance, such as water. The axes correspond to the pressure and temperature. The phase diagram shows, in pressure–temperature space, the lines of equilibrium or phase boundaries between the three phases of solid, liquid, and gas.

The curves on the phase diagram show the points where the free energy (and other derived properties) becomes non-analytic: their derivatives with respect to the coordinates (temperature and pressure in this example) change discontinuously (abruptly). For example, the heat capacity of a container filled with ice will change abruptly as the container is heated past the melting point. The open spaces, where the free energy is analytic, correspond to single phase regions. Single phase regions are separated by lines of non-analytical behavior, where phase transitions occur, which are called phase boundaries.

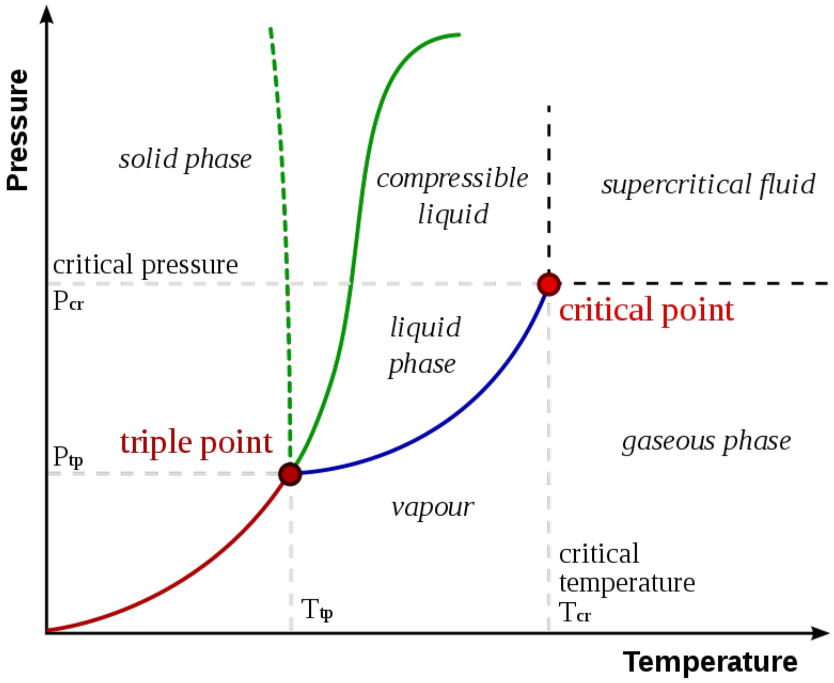


Figure 3.2 Simplified temperature/pressure phase change diagram for water. The pressure on a pressure-temperature diagram (such as the water phase diagram shown above) is the partial pressure of the substance in question.

In the diagram on the right, the phase boundary between liquid and gas does not continue indefinitely. Instead, it terminates at a point on the phase diagram called the critical point. This reflects the fact that, at extremely high temperatures and pressures, the liquid and gaseous phases become indistinguishable, in what is known as a supercritical fluid. In water, the critical point occurs at around T_c = 647.096 K (373.946 °C), p_c = 22.064 MPa (217.75 atm) and ρ_c = 356 kg/m3.

The existence of the liquid–gas critical point reveals a slight ambiguity in labelling the single phase regions. When going from the liquid to the gaseous phase, one usually crosses the phase boundary, but it is possible to choose a path that never crosses the boundary by going to the right of the critical point. Thus, the liquid and gaseous phases can blend continuously into each other. The solid–liquid phase boundary can only end in a critical point if the solid and liquid phases have the same symmetry group.

For most substances, the solid–liquid phase boundary (or fusion curve) in the phase diagram has a positive slope so that the melting point increases with pressure. This is true whenever the solid phase is denser than the liquid phase. The greater the pressure on a given substance, the closer together the molecules of the substance are brought to each other, which increases the effect of the substance's intermolecular forces. Thus, the substance requires a higher temperature for its molecules to have enough energy to break out of the fixed pattern of the solid phase and enter the liquid phase. A similar concept applies to liquid–gas phase changes.

Water is an exception which has a solid-liquid boundary with negative slope so that the melting point decreases with pressure. This occurs because ice (solid water) is less dense than liquid water, as shown by the fact that ice floats on water. At a molecular level, ice is less dense because it has a more extensive network of hydrogen bonding which requires a greater separation of water molecules. Other exceptions include antimony and bismuth. At very high pressures above 50 GPa (500 000 atm), liquid nitrogen undergoes a liquid-liquid phase transition to a polymeric form and becomes denser than solid nitrogen at the same pressure. Under these conditions therefore, solid nitrogen also floats in its liquid. The value of the slope dP/dT is given by the Clausius Clapeyron equation for fusion (melting)

$$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T \Delta V_{fus}}$$

where ΔHfus is the heat of fusion which is always positive, and ΔV_{fus} is the volume change for fusion. For most substances ΔV_{fus} is positive so that the slope is positive. However for water and other exceptions, ΔV_{fus} is negative so that the slope is negative. For multicomponent mixtures, like the ones naturally occurring in hydrocarbon reservoirs, the phase diagram turns into a phase envelope. Inside the envelope a liquid and a gas phase coexist while in the outside of the envelope the fluid occurs as a single phase gas or a single phase liquid. The images below correspond to the envelope of a mixture of Methane, Ethane, Propane, normal-Butane, iso-Butane, normal-Pentane, iso-Pentane, Hexane, and Heptane. Mol fraction compositions are shown on the plots.

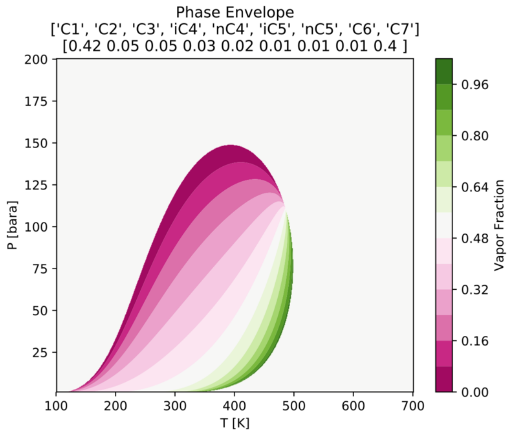


Figure 3.3 Hydrocarbon phase envelope 13 isochore lines

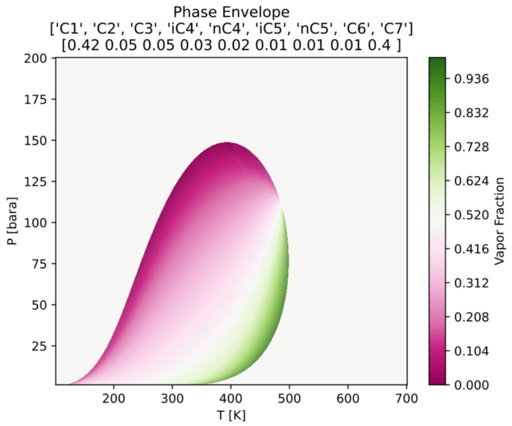


Figure 3.4 Hydrocarbon phase envelope 130 isochore lines

Thermodynamic properties

In addition to temperature and pressure, other thermodynamic properties may be graphed in phase diagrams. Examples of such thermodynamic properties include specific volume, specific enthalpy, or specific entropy. For example, single-component graphs of temperature vs. specific entropy (T vs. s) for water/steam or for a refrigerant are commonly used to illustrate thermodynamic cycles such as a Carnot cycle, Rankine cycle, or vapor-compression refrigeration cycle. Any two thermodynamic quantities may be shown on the horizontal and vertical axes of a two-dimensional diagram. Additional thermodynamic quantities may each be illustrated in increments as a series of lines curved, straight, or a combination of curved and straight. Each of these iso-lines represents the thermodynamic quantity at a certain constant value.

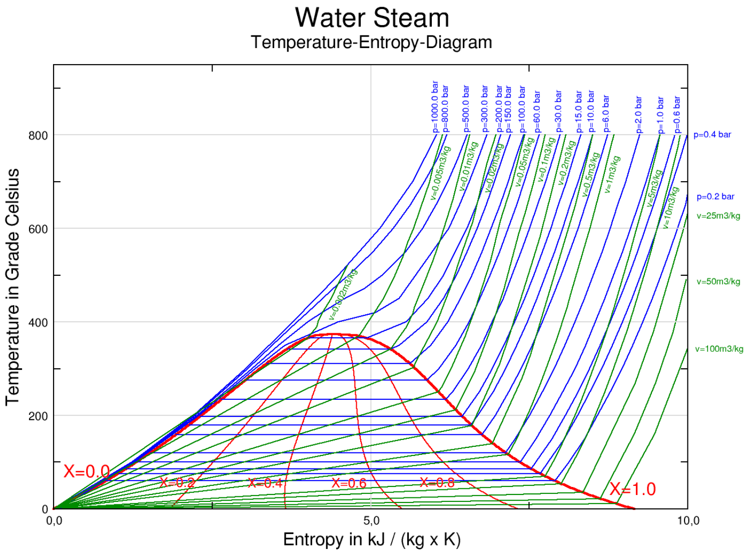


Figure 3.5 Temperature vs. specific entropy phase diagram for water/steam

Temperature vs. specific entropy phase diagram for water/steam In the area under the red dome, liquid water and steam coexist in equilibrium. The critical point is at the top of the dome. Liquid water is to the left of the dome. Steam is to the right of the dome. The blue lines/curves are isobars showing constant pressure. The green lines/curves are isochors showing constant specific volume. The red curves show constant quality

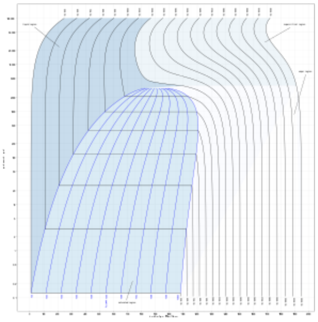


Figure 3.6 pressure{enthalpy (p{h) diagram for steam

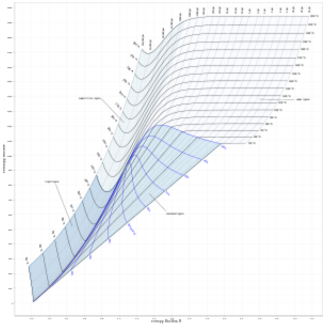


Figure 3.7 enthalpy{entropy (h{s) diagram for steam

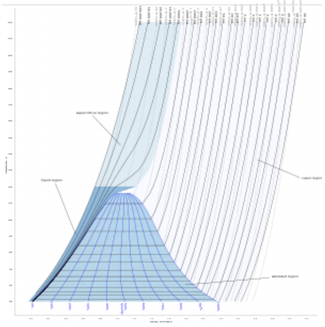


Figure 3.8 temperature{entropy (T{s) diagram for steam

2. 3-dimensional diagrams

It is possible to envision three-dimensional (3D) graphs showing three thermodynamic quantities. For example, for a single component, a 3D Cartesian coordinate type graph can show temperature (T) on one axis, pressure (p) on a second axis, and specific volume (v) on a third. Such a 3D graph is sometimes called a p–v–T diagram. The equilibrium conditions are shown as curves on a curved surface in 3D with areas for solid, liquid, and vapor phases and areas where solid and liquid, solid and vapor, or liquid and vapor coexist in equilibrium. A line on the surface called a triple line is where solid, liquid and vapor can all coexist in equilibrium. The critical point remains a point on the surface even on a 3D phase diagram.

An orthographic projection of the 3D p–v–T graph showing pressure and temperature as the vertical and horizontal axes collapses the 3D plot into the standard 2D pressure–temperature diagram. When this is done, the solid–vapor, solid–liquid, and liquid–vapor surfaces collapse into three corresponding curved lines meeting at the triple point, which is the collapsed orthographic projection of the triple line.

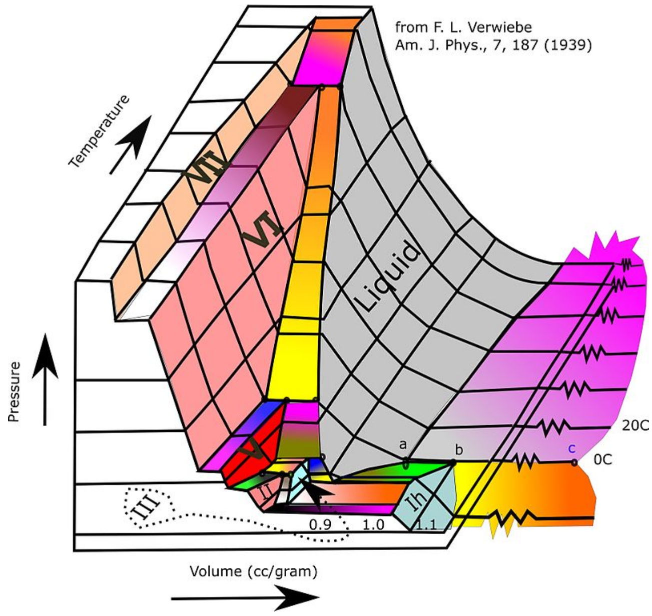

from F. L. Verwiebe
Am. J. Phys., 7, 187 (1939)

Figure 3.9 3D phase diagram of water fluids and selected ices

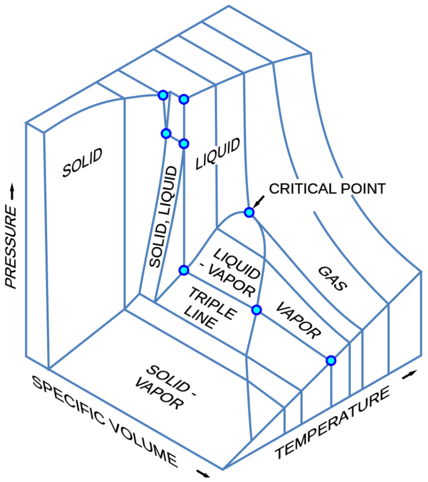


Figure 3.10 p{v{T 3D diagram for fixed amount of pure material

Binary mixtures

Other much more complex types of phase diagrams can be constructed, particularly when more than one pure component is present. In that case, concentration becomes an important variable. Phase diagrams with more than two dimensions can be constructed that show the effect of more than two variables on the phase of a substance. Phase diagrams can use other variables in addition to or in place of temperature, pressure and composition, for example the strength of an applied electrical or magnetic field, and they can also involve substances that take on

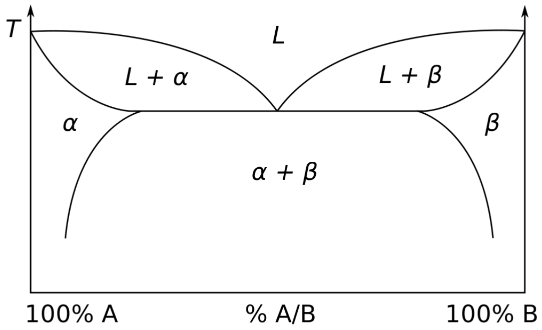


Figure 3.11 A phase diagram for a binary system displaying a eutectic point

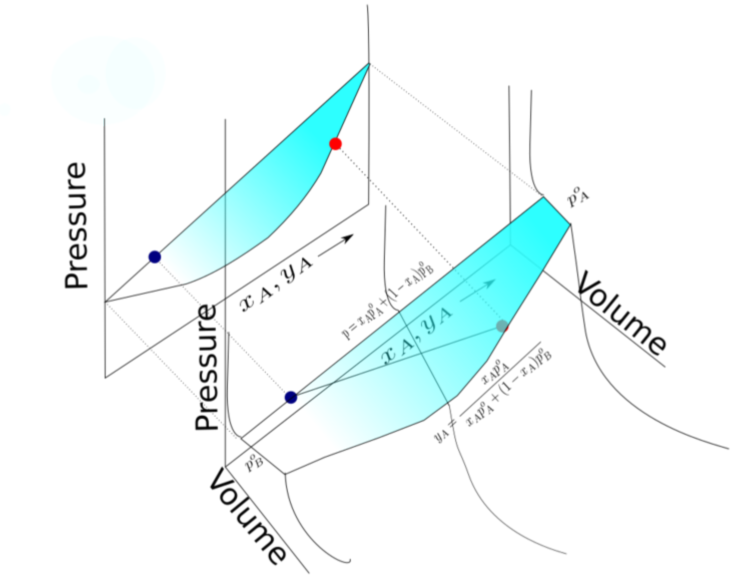


Figure 3.12 Two component ideal solution ideal gas phase diagram construction in p-v-x coordinates

One type of phase diagram plots temperature against the relative concentrations of two substances in a binary mixture called a binary phase diagram, as shown at right. Such a mixture can be either a solid solution, eutectic or peritectic, among others. These two types of mixtures result in very different graphs. Another type of binary phase diagram is a boiling-point diagram for a mixture of two components, i. e. chemical compounds. For two particular volatile components at a certain pressure such as atmospheric pressure, a boiling-point diagram shows what vapor (gas) compositions are in equilibrium with given liquid compositions depending on temperature. In a typical binary boiling-point diagram, temperature is plotted on a vertical axis and mixture composition on a horizontal axis.

A two component diagram with components A and B in an ”ideal” solution is shown. The construction of a liquid vapor phase diagram assumes an ideal liquid solution obeying Raoult’s law and an ideal gas mixture obeying Dalton’s law of partial pressure. A tie line from the liquid to the gas at constant pressure would indicate the two compositions of the liquid and gas respectively.

A simple example diagram with hypothetical components 1 and 2 in a non-azeotropic mixture is shown at right. The fact that there are two separate curved lines joining the boiling points of the pure components means that the vapor composition is usually not the same as the liquid composition the vapor is in equilibrium with. See Vapor–liquid equilibrium for more information.

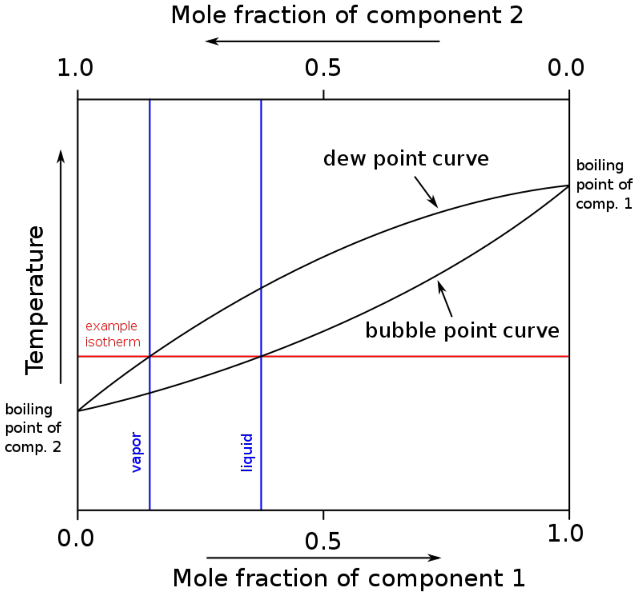


Figure 3.13 Boiling-point diagram

In addition to the above-mentioned types of phase diagrams, there are many other possible combinations. Some of the major features of phase diagrams include congruent points, where a solid phase transforms directly into a liquid. There is also the peritectoid, a point where two solid phases combine into one solid phase during cooling. The inverse of this, when one solid phase transforms into two solid phases during cooling, is called the eutectoid. A complex phase diagram of great technological importance is that of the iron–carbon system for less than 7% carbon (see steel).

The x-axis of such a diagram represents the concentration variable of the mixture. As the mixtures are typically far from dilute and their density as a function of temperature is usually unknown, the preferred concentration measure is mole fraction. A volume-based measure like molarity would be inadvisable.

3. Ternary phase diagrams

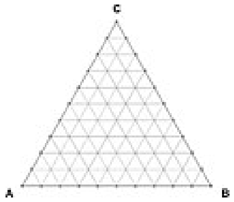


Figure 3.14 Gibbs triangle

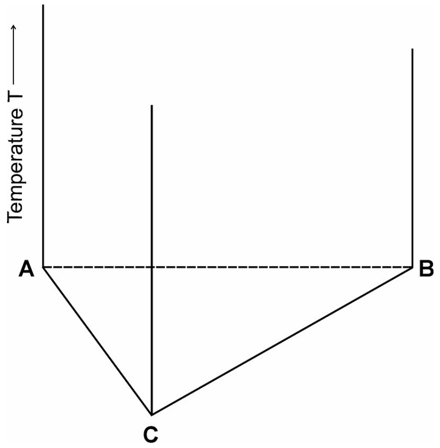


Figure 3.15 Space phase diagram of a ternary system

A system with three components is called a ternary system. At constant pressure the maximum number of independent variables is three – the temperature and two concentration values. For a representation of ternary equilibria a three-dimensional phase diagram is required. Often such a diagram is drawn with the composition as a horizontal plane and the temperature on an axis perpendicular to this plane. To represent composition in a ternary system an equilateral triangle is used, called Gibbs triangle (see also Ternary plot).

The temperature scale is plotted on the axis perpendicular to the composition triangle. Thus, the space model of a ternary phase diagram is a right-triangular prism. The prism sides represent corresponding binary systems A-B, B-C, A-C.

However, the most common methods to present phase equilibria in a ternary system are the following: 1) projections on the concentration triangle ABC of the liquidus, solidus, solvus surfaces; 2) isothermal sections; 3) vertical sections.

4. Crystals

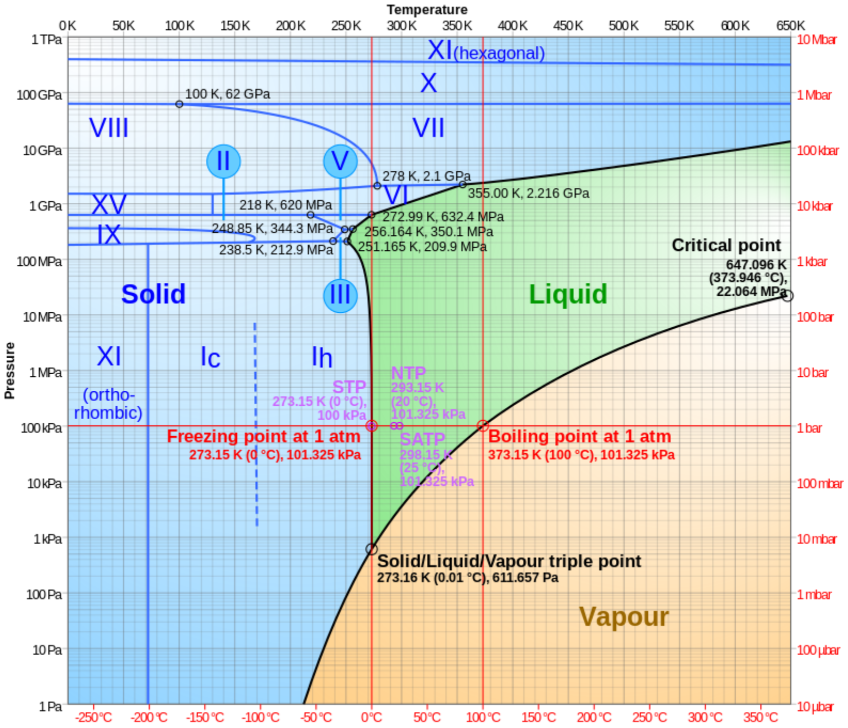


Figure 3.16 pressure{temperature phase diagram of water. The Roman numerals indicate various ice phases

Polymorphic and polyamorphic substances have multiple crystal or amorphous phases, which can be graphed in a similar fashion to solid, liquid, and gas phases.

5. Mesophases

Organic materials pass through intermediate states between solid and liquid; these states are called mesophases. Attention has been directed to mesophases because they enable display devices and have become commercially important through the so-called liquid-crystal technology. Phase diagrams are used to describe the occurrence of mesophases.

3.2 Phase Equilibria

Phase equilibria is the term used to describe with two or more phases co-exist (in equilibrium). The stability of phases can be predicted by the chemical potential, in that the most stable form of the substance will have the minimum chemical potential at the given temperature and pressure. Before delving into phase equilibria, it's important to understand the concept of phases. A phase is a region of a material that has uniform physical and chemical properties. In a solid phase, particles are closely packed and have fixed positions. They vibrate about their equilibrium positions but do not move significantly. In a liquid phase, particles are closely packed but have more freedom of movement. They can flow and take the shape of their container. Gas In a gas phase, particles are widely separated and have high kinetic energy. They move freely and occupy the entire volume of the container. Vapor is a term often used to describe the gas phase of a substance that is typically a liquid or solid at room temperature and pressure. For example, steam is the vapor phase of water.

3.2.1 Phase Equilibria Principles

Phase equilibria are governed by the Gibbs phase rule, which relates the number of phases, components, and degrees of freedom in a system at equilibrium. The Gibbs phase rule is expressed as

2F=C-P+2

Where:

F is the degrees of freedom (the number of intensive variables that can be independently varied while the system remains in equilibrium).

C is the number of components (the chemically distinct species in the system).

P is the number of phases in equilibrium.

This equation tells us how many variables (temperature, pressure, and composition) can be changed without disturbing the equilibrium of the system. Let's examine phase equilibria in different systems:

Binary Phase Diagrams: Binary phase diagrams involve systems with two components. These diagrams are widely used to study the phase equilibria of mixtures. The most common binary system is a solute (minor component) dissolved in a solvent (major component). The phase diagram typically consists of regions representing solid, liquid, and vapor phases and phase boundaries between them. Examples include the phase diagram for water and ethanol or the eutectic phase diagram for various alloys.

Ternary Phase Diagrams: Ternary phase diagrams deal with systems containing three components. These diagrams are more complex than binary diagrams, as they show the phase behavior of mixtures with three components. Ternary phase diagrams are often used in materials science, metallurgy, and geochemistry to understand the behavior of complex mixtures, such as alloys, minerals, and geological systems.

Multicomponent Systems: In systems with more than three components, the phase equilibria become highly intricate. These systems are prevalent in the chemical industry, where numerous chemical reactions and interactions occur. The study of multicomponent systems involves advanced thermodynamic models and computational methods to predict and analyze phase equilibria accurately.

3.2.2 Importance and Applications

Phase equilibria are essential in various fields, and their understanding has practical applications in several areas:

- Metallurgy and Materials Science: Phase diagrams of alloys help determine the microstructure of materials, such as steel or aluminum, which influences their mechanical and thermal properties. Heat treatment processes are designed based on phase equilibria to control the hardness and toughness of materials.
- Chemistry and Chemical Engineering: In the chemical industry, phase equilibria are crucial for designing separation processes like distillation, extraction, and crystallization. The solubility of compounds in solvents and the precipitation of products in chemical reactions are governed by phase equilibria.
- Geology and Earth Sciences: Understanding phase equilibria is essential in geology to study the formation and transformation of minerals and rocks under different temperature and pressure conditions. The stability of minerals and the behavior of magmatic systems are determined by phase equilibria.
- Environmental Science: Phase equilibria are relevant in environmental science to assess the behavior of pollutants and chemicals in natural systems, including soil and water. The mobility and bioavailability of contaminants depend on their phase behavior.
- Pharmaceutical and Food Industries: In drug formulation, knowledge of phase equilibria helps in solubility and stability studies of active pharmaceutical ingredients. The development of food products often requires an understanding of phase transitions, such as gelation or crystallization.
- Energy and Petrochemicals: The phase equilibria of hydrocarbons in reservoirs and pipelines are essential for the efficient extraction, transport, and processing of oil and natural gas. The design of separation units in refineries and the prediction of hydrate formation in gas pipelines rely on phase equilibria.
- Nanomaterials and Nanotechnology: In the development of nanomaterials, controlling phase transitions is critical for tailoring their properties and applications. Nanoparticle synthesis and self-assembly processes are governed by phase equilibria.

- ✧ Biotechnology and Pharmaceuticals: In biopharmaceuticals, phase equilibria affect protein crystallization, solubility, and stability. The formation of pharmaceutical polymorphs and cocrystals is guided by phase equilibria.

3.2.3 Experimental Methods and Techniques

The study of phase equilibria involves various experimental techniques and theoretical approaches:

Phase Diagrams: Experimental determination of phase diagrams involves observing phase transitions at different temperatures and pressures. Phase diagrams are constructed by plotting data points of phase boundaries, often represented graphically.

Thermal Analysis: Techniques like differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are used to study heat flows and mass changes during phase transitions. These methods provide information about phase changes and phase equilibria.

Spectroscopy: Infrared spectroscopy, nuclear magnetic resonance (NMR), and Raman spectroscopy are employed to study molecular-level interactions and phase behavior. Spectroscopic data offer insights into the composition and structure of phases.

Computational Modeling: Computational thermodynamics and molecular simulations, such as Monte Carlo and molecular dynamics, help predict phase equilibria. These methods provide valuable insights when experimental data are limited or difficult to obtain.

X-ray Diffraction: X-ray diffraction is used to determine the crystal structure of solid phases. It helps identify the arrangement of atoms or molecules in a crystal lattice.

Microscopy: Optical and electron microscopy techniques are used to observe phase transitions and microstructures in materials. These methods provide visual information about the size and distribution of phases.

Equations of State: Equations of state, such as the Van der Waals equation, help describe the behavior of gases and predict phase transitions. They are essential in thermodynamic modeling and process design.

3.2.4 Phase Transitions and Critical Points

Phase transitions represent the transformations between different phases in a material. Some of the most common types of phase transitions include:

1. Melting (Fusion): The transition from a solid phase to a liquid phase. This transition occurs at a specific temperature, known as the melting point.

2. Freezing (Solidification): The transition from a liquid phase to a solid phase. It also occurs at a specific temperature, which is the freezing point.

3. Vaporization (Boiling): The transition from a liquid phase to a gas phase. This transition takes place at the boiling point under standard pressure conditions.

4. Condensation: The transition from a gas phase to a liquid phase. Condensation occurs when a gas cools and loses energy.

5. Sublimation: The direct transition from a solid phase to a gas phase without passing through the liquid phase. Dry ice (solid carbon dioxide) sublimates at room temperature.

6. Deposition: The direct transition from a gas phase to a solid phase without becoming a liquid. Water vapor turning into frost on a cold surface is an example.

7. Critical Point: The critical point represents the conditions (temperature and pressure) at which the distinction between the liquid and gas phases disappears. Beyond this point, the substance is in a supercritical state, exhibiting properties of both liquid and gas phases.

3.2.5 Examples of Phase Equilibria

Water and Ice: The phase diagram for water shows the coexistence of solid (ice), liquid (water), and gas (vapor) phases. At standard atmospheric pressure, water freezes at 0°C and boils at 100°C.

Carbon Dioxide (CO2): Carbon dioxide exhibits sublimation behavior. At standard pressure, it sublimates directly from a solid (dry ice) to a gas (CO2 vapor) at -78.5°C.

Binary Alloy: The phase diagram of a binary alloy, such as lead-tin (Pb-Sn), illustrates the eutectic point where a mixture of the two elements forms a low-melting alloy. This eutectic alloy has applications in soldering.

Petrochemicals: The phase behavior of hydrocarbons in petroleum reservoirs and pipelines is crucial for oil and gas extraction. Understanding phase equilibria helps in preventing issues like gas hydrate formation, which can block pipelines.

Pharmaceuticals: In drug formulation, controlling the crystalline structure of an active pharmaceutical ingredient (API) is essential to optimize its properties. Polymorphs, solvates, and cocrystals of an API are determined by phase equilibria.

Geology and Minerals: Understanding the phase behavior of minerals at different pressures and temperatures helps geologists interpret the Earth's history. Knowledge of mineral phase equilibria is used to reconstruct geological processes.

3.2.6 Challenges and Future Developments

- The study of phase equilibria is a complex and multidisciplinary field that continues to advance with the help of modern experimental techniques and computational methods.

- Multicomponent Systems: The study of systems with numerous components, such as biological systems or complex chemical reactions, requires sophisticated models and computational tools.
- Nanomaterials: The design of advanced nanomaterials with specific properties depends on understanding and controlling phase transitions at the nanoscale.
- Environmental Impact: Phase equilibria research can contribute to addressing environmental challenges, such as the behavior of pollutants and contaminants in ecosystems.
- Advanced Materials: The development of new materials with tailored properties relies on precise control of phase equilibria.
- Energy and Sustainability: The optimization of processes in the energy sector and the reduction of environmental impacts require a deeper understanding of phase equilibria.

3.3 The P-v-T Surface

PVT Surface. The (pvT) surface shown opposite is for a material that contracts on freezing. The surface is described by the Equation of State of the material and is the locus of all equilibrium states of the material.

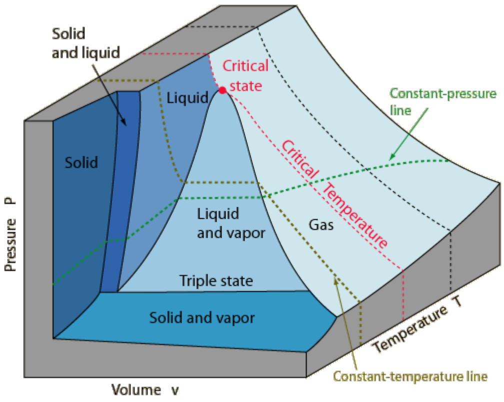


Figure 3.17 Caption

The equilibrium states of a simple, compressible substance can be specified in terms of its pressure, volume and temperature. If any two of these state variables is specified, the third is determined. This implies that the states of the substance can be represented as a surface in a three dimensional PvT space. The PvT surface above represents a substance which contracts upon freezing. Most substances do so, the notable exception being water which expands upon freezing. A considerable amount of information about the phases of matter can be illustrated with the PvT surface. The solid, liquid and gas(vapor) phases can be represented by regions on the surface. Note that there are regions on the surface which represent a single phase, and regions which are combinations of two phases. A point lying on a line between a single-phase and a two-phase region represents a ”saturation state”. The line between the liquid and the liquid-vapor regions is called the liquid-saturation line and any point on that line represents a saturated-liquid state. A point on the boundary between the vapor and the liquid-vapor regions is called a saturated-vapor state.

Note the critical state where the saturated-liquid and saturated-vapor lines meet. The state variables of this unique point are denoted by $P[c]$, $v[c]$ and T_c. If a substance is above the critical temperature Tc, it cannot condense into a liquid, no matter how high the pressure. This merging of the liquid and vapor states above the critical temperature is a characteristic of all known substances. While a pure vapor state can exist at a pressure lower than P_c, at pressures above P_c it is constrained to be a vapor. States with pressures above P_c are described as ”supercritical states”.

The remarkable ”triple state” of matter where solid, liquid and vapor are in equilibrium may be characterized by a temperature called the triple point. The triple state is represented by a line parallel to the Pv plane with a characteristic pressure for the substance but variable volume. The triple point temperature of water is assigned the value 273.16 K and the triple state of water is used as the reference for establishing the Kelvin temperature scale.

3.3.1 T-v and P-v diagrams

In many thermodynamic cycles, a working fluid experiences phase changes between liquid and vapour in the subcritical zone, such as water in a steam power plant and R134a in a vapour-compression refrigeration system. The liquid-vapour phase change can be illustrated in the T_v and P_v diagrams, as shown In these diagrams, we can clearly see the three regions: compressed liquid region, saturated liquid-vapour region, and superheated vapour region. The curve that separates the compressed liquid region and saturated liquid-vapour region is called the saturated liquid line. Any point on the saturated liquid line represents a saturated liquid state. In a similar fashion, the curve that lies between the saturated liquid-vapour region and the superheated vapour region is called the saturated vapour line. Any point on the saturated vapour line represents a saturated vapour state. The two saturation lines meet at the critical point.

It is important to note that the liquid state is commonly called compressed liquid or subcooled liquid, and the vapour state is commonly called superheated vapour. In the liquid-vapour, two-phase region, the corresponding isothermal and isobaric processes coincide and remain as horizontal lines. This indicates that, during the phase change process, both temperature and pressure remain constant, i.e., $T = T_{sat}$ and $P = P_{sat}$.

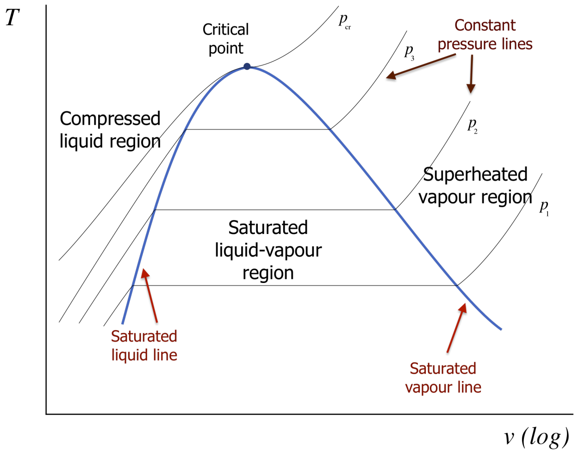


Figure 3.18 T-v diagram

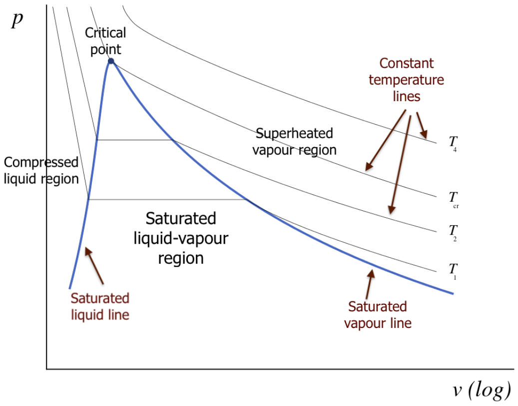


Figure 3.19 T-v diagram

3.4 Compressibility Factor

the compressibility factor (Z), also known as the compression factor or the gas deviation factor, describes the deviation of a real gas from ideal gas behaviour. It is simply defined as the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure. It is a useful thermodynamic property for modifying the ideal gas law to account for the real gas behaviour. In general, deviation from ideal behaviour becomes more significant the closer a gas is to a phase change, the lower the temperature or the larger the pressure. Compressibility factor values are usually obtained by calculation from equations of state (EOS), such as the virial equation which take compound-specific empirical constants as input. For a gas that is a mixture of two or more pure gases (air or natural gas, for example), the gas composition must be known before compressibility can be calculated. Alternatively, the compressibility factor for specific gases can be read from generalized compressibility charts that plot Z as a function of pressure at constant temperature. The compressibility factor should not be confused with the compressibility (also known as coefficient of compressibility or isothermal compressibility) of a material, which is the measure of the relative volume change of a fluid or solid in response to a pressure change.

Compressibility factor is a dimensionless quantity that characterizes the deviation of a real gas from ideal behavior. Ideal gases follow the ideal gas law, which relates pressure, volume, and temperature, and is given by the equation:

PV=nRT

Where:

P is the pressure of the gas.

V is the volume occupied by the gas.

n is the number of moles of the gas.

R is the universal gas constant.

T is the absolute temperature of the gas in Kelvin.

For an ideal gas, the compressibility factor (Z) is equal to 1 under all conditions of pressure and temperature. However, real gases do not always behave ideally, and their compressibility factor deviates from 1.

Calculating the Compressibility Factor

The compressibility factor is defined as the ratio of the molar volume of a real gas to the molar volume of an ideal gas under the same conditions of temperature and pressure:

$$Z = \frac{V_{idealgas}}{V_{realgas}}$$

For a given gas at a specific temperature and pressure, Z can be calculated using the following equation:

$$Z = \frac{nRT}{PV}$$

Where:

P is the pressure of the gas.

V is the volume occupied by the gas.

n is the number of moles of the gas.

R is the gas constant.

T is the absolute temperature.

By measuring the pressure, volume, and temperature of a real gas, you can determine its compressibility factor. Deviations of Z from 1 indicate non-ideal behavior.

compressibility factor calculator

Find the compressibility factor for air at 1 bar 1 bar and 293 K293 K having volume $1m^3$. Take the number of moles as $44 \cdot 6$ and gas constant R as 8.314 J/(K mol).

Step 1: Enter the gas pressure, P=1 bar.

Step 2: Give the gas volume, V=1 m3.

Step 3: Input the amount of substance in moles, n=44.6.

Step 4: The universal gas constant, R is set to 8.314 as default value.

Step 5: Fill in the temperature of gas, T=293 K.

Step 6: The calculator will now use the compressibility factor equation to return the value of the compressibility factor.

$$Z = \frac{P \cdot V}{n \cdot R \cdot T}$$

$$= \frac{10^5 \cdot 1}{44 \cdot 6.8 \cdot 314293} = 0.9204$$

3.4.1 Significance of the Compressibility Factor

The compressibility factor is of paramount importance in thermodynamics, fluid dynamics, and chemical engineering for several reasons:

Deviation from Ideal Behavior: The compressibility factor provides a quantitative measure of how a real gas deviates from ideal behavior. When Z is equal to 1, the gas behaves ideally. Deviations from 1 indicate non-ideal behavior, and the magnitude and direction of these deviations offer insights into the interactions between gas molecules.

Phase Behavior: Z is used to predict and understand the phase behavior of gases, including the conditions at which a gas may condense into a liquid or undergo phase transitions. For example, when Z is less than 1, it suggests the possibility of gas condensation.

Equation of State: Compressibility factors are often incorporated into equations of state (EOS) that describe the thermodynamic properties of real gases. One of the most well-known EOS is the Van der Waals equation:

$$P = \frac{nRT}{V_{nb}} - \frac{an^2}{V^2}$$

Where a and b are parameters that depend on the specific gas. By including compressibility factors in these equations, more accurate predictions of gas behavior can be made.

Chemical Process Design: In chemical engineering, understanding gas behavior is crucial for designing and optimizing chemical processes, especially those involving gases. Compressibility factors are used in process simulations and equipment design, ensuring safe and efficient operations.

Natural Gas Industry: In the natural gas industry, the behavior of gases is of utmost importance for the production, transportation, and storage of natural gas. Accurate predictions of gas properties, including Z, are vital for these operations.

Cryogenics and High-Pressure Physics: In extreme conditions, such as cryogenic temperatures or high pressures, gases often deviate significantly from ideal behavior. Accurate values of Z are essential for understanding these behaviors and developing technologies that operate under such conditions.

Environmental Sciences: Compressibility factors are used in the study of gas-phase reactions and environmental phenomena, such as air quality modeling and climate change research.

3.4.2 Factors Affecting the Compressibility Factor

The compressibility factor of a gas depends on several factors, including:

Type of Gas: Different gases have varying degrees of deviation from ideal behavior. For example, noble gases like helium and neon tend to behave more ideally than larger molecules like methane or carbon dioxide.

Temperature: As temperature increases, the compressibility factor tends to decrease. At high temperatures, gas molecules have greater kinetic energy, and the intermolecular forces become less significant.

Pressure: The compressibility factor typically increases with increasing pressure. At high pressures, the volume occupied by gas molecules becomes significant, causing deviations from ideal behavior.

Molecular Size and Shape: The size and shape of gas molecules play a crucial role in determining Z. For instance, long, flexible molecules may exhibit stronger deviations from ideal behavior.

Intermolecular Forces: The strength and nature of intermolecular forces (e.g., van der Waals forces or hydrogen bonding) between gas molecules affect the compressibility factor. Weaker forces tend to result in Z values closer to 1.

Chemical Composition: The presence of multiple gas species in a mixture can lead to interactions that affect the compressibility factor. Mixtures of gases can exhibit different behaviors compared to pure gases.

3.5 Departure Functions

In thermodynamics, a departure function is defined for any thermodynamic property as the difference between the property as computed for an ideal gas and the property of the species as it exists in the real world, for a specified temperature T and pressure P. Common departure functions include those for enthalpy, entropy, and internal energy.

Departure functions are used to calculate real fluid extensive properties (i.e. properties which are computed as a difference between two states). A departure function gives the difference between the real state, at a finite volume or non-zero pressure and temperature, and the ideal state, usually at zero pressure or infinite volume and temperature.

For example, to evaluate enthalpy change between two points h(v1,T1) and h(v2,T2) we first compute the enthalpy departure function between volume v1 and infinite volume at T = T1, then add to that the ideal gas enthalpy change due to the temperature change from T1 to T2, then subtract the departure function value between v2 and infinite volume. Departure functions are computed by integrating a function which depends on an equation of state and its derivative.

General expressions

$$\frac{H^{ig} - H}{RT} = \int_{\infty}^{V} \left[T\left(\frac{\partial Z}{\partial T}\right)_V)\right] \frac{dV}{V} + 1 - Z$$

$$\frac{S^{ig} - S}{R} = \int_{\infty}^{V} \left[T\left(\frac{\partial Z}{\partial T}\right)_V - 1 + Z)\right] \frac{dV}{V} - ln - Z$$

$$\frac{G^{ig} - G}{RT} = \int_{\infty}^{V} (1 - Z)\frac{dV}{V} + lnZ + 1 - Z$$

Departure functions for Peng–Robinson equation of state

The Peng Robinson equation of state relates the three interdependent state properties pressure P, temperature T, and molar volume V_m. From the state properties (P, V_m, T), one may compute the departure function for enthalpy per mole (denoted h) and entropy per mole (s)

$$h_{T,P} - h_{T,P}^{ideal} = RT_c \left[T_r(Z-1) - 2.078(1-\kappa)\sqrt{\alpha} ln\left(\frac{Z+2.414B}{Z-0.414B}\right)\right]$$

$$s_{T,P} - s_{T,P}^{ideal} = R_c \left[ln(Z-B) - 2.078\kappa\left(\frac{1+\kappa}{\sqrt{T_r}}\right) ln\left(\frac{Z+2.414B}{Z-0.414B}\right)\right]$$

where α is defined in the Peng-Robinson equation of state, T_r is the reduced temperature, P_r is the reduced pressure, Z is the compressibility factor, and

κ = 0.37464 + 1.54226 ω -0.26992 ω^2

B = 0.07780 $\frac{P_r}{T_r}$

one knows two of the three state properties (P, V_m, T), and must compute the third directly from the equation of state under consideration. To calculate the third state property, it is necessary to know three constants for the species at hand: the critical temperature T_c, critical pressure P_c, and the acentric factor ω. But once these constants are known, it is possible to evaluate all of the above expressions and hence determine the enthalpy and entropy departures.

3.5.1 Departure Functions Types

Departure functions are mathematical functions that describe the difference between a real substance's property and the property of the corresponding ideal substance. These functions are typically defined as the difference between the real substance's property (Y_r) and the property of the ideal substance (Y_i):

D(Y)=Y_r-Y_i

Departure functions can be defined for various thermodynamic properties, including enthalpy, internal energy, entropy, and volume. Some common departure functions include:

1. Enthalpy Departure Function (h - h_{ig}): Describes the difference between the real enthalpy (h) of a substance and the enthalpy of the ideal gas (h_{ig}) at the same temperature and pressure.

2. Entropy Departure Function (s - s_{ig}): Quantifies the deviation of the real substance's entropy (s) from that of the ideal gas (s_{ig}) under the same conditions.

3. Internal Energy Departure Function (u - u_{ig}): Represents the difference between the internal energy (u) of the real substance and the internal energy of the ideal gas (u_{ig}) at a given temperature and pressure.

4. Volume Departure Function (v - v_{ig}): Describes the difference between the real substance's molar volume (v) and the molar volume of the ideal gas (v_{ig}) at the same temperature and pressure.

3.5.2 Significance of Departure Functions

Departure functions are crucial in several aspects of thermodynamics and chemical engineering

Real Substance Behavior: Departure functions provide a quantitative measure of how real substances deviate from ideal behavior. They help us understand the impact of intermolecular interactions, molecular size, and other factors on the thermodynamic properties of real substances.

Equations of State: Departure functions are often used to modify or extend equations of state (EOS), such as the Van der Waals equation, to account for non-ideal behavior. Modified EOS can predict properties of real substances more accurately.

Phase Equilibria: Departure functions play a significant role in predicting and understanding phase transitions and phase equilibria. They are used in phase diagrams to describe the behavior of real substances under different conditions of temperature and pressure.

Chemical Process Design: In chemical engineering, departure functions are used to design and optimize chemical processes that involve real substances. Accurate predictions of thermodynamic properties are essential for process efficiency and safety.

Material Selection: Materials scientists and engineers use departure functions to choose materials for specific applications. The thermodynamic properties of materials must meet the requirements of the intended use, and departure functions help in making informed decisions.

3.5.3 Applications of Departure Functions

- Chemical and Petrochemical Industry: Departure functions are used extensively in the design and optimization of processes involving chemical reactions, separation, and purification. They help in predicting how real substances will behave under specific conditions.

- Natural Gas Processing: The behavior of natural gas and its components is crucial in the oil and gas industry. Departure functions are used to model the behavior of natural gas mixtures under various pressures and temperatures.

- Pharmaceuticals and Food Industry: In pharmaceutical and food production, departure functions are used to ensure the stability and safety of products, especially in the design of storage and processing conditions.

- Environmental Sciences: Understanding the thermodynamic properties of gases and their deviations from ideal behavior is essential for modeling and predicting air quality, dispersion of pollutants, and climate change.

- Cryogenics: In cryogenic applications, where extremely low temperatures are encountered, departure functions help design and optimize equipment used in liquefying and storing gases like liquid nitrogen and liquid helium.

3.6 Ideal Gas

An ideal gas is a theoretical gas composed of many randomly moving point particles that are not subject to interparticle interactions. The ideal gas concept is useful because it obeys the ideal gas law, a simplified equation of state, and is amenable to analysis under statistical mechanics. The requirement of zero interaction can often be relaxed if, for example, the interaction is perfectly elastic or regarded as point-like collisions.

Under various conditions of temperature and pressure, many real gases behave qualitatively like an ideal gas where the gas molecules (or atoms for monatomic gas) play the role of the ideal particles. Many gases such as nitrogen, oxygen, hydrogen, noble gases, some heavier gases like carbon dioxide and mixtures such as air, can be treated as ideal gases within reasonable tolerances[2] over a considerable parameter range around standard temperature and pressure. Generally, a gas behaves more like an ideal gas at higher temperature and lower pressure,[2] as the potential energy due to intermolecular forces becomes less significant compared with the particles' kinetic energy, and the size of the molecules becomes less significant compared to the empty space between them. One mole of an ideal gas has a volume of 22.710 954 64 litres (exact value based on 2019 redefinition of the SI base units) at standard temperature and pressure (a temperature of 273.15 K and an absolute pressure of exactly 105 Pa).

The ideal gas model tends to fail at lower temperatures or higher pressures, when intermolecular forces and molecular size becomes important. It also fails for most heavy gases, such as many refrigerants, and for gases with strong intermolecular forces, notably water vapor. At high pressures, the volume of a real gas is often considerably larger than that of an ideal gas. At low temperatures, the pressure of a real gas is often considerably less than that of an ideal gas. At some point of low temperature and high pressure, real gases undergo a phase transition, such as to a liquid or a solid. The model of an ideal gas, however, does not describe or allow phase transitions. These must be modeled by more complex equations of state. The deviation from the ideal gas behavior can be described by a dimensionless quantity, the compressibility factor, Z.

The ideal gas model has been explored in both the Newtonian dynamics (as in "kinetic theory") and in quantum mechanics (as a "gas in a box"). The ideal gas model has also been used to model the behavior of electrons in a metal (in the Drude model and the free electron model), and it is one of the most important models in statistical mechanics. If the pressure of an ideal gas is reduced in a throttling process the temperature of the gas does not change. (If the pressure of a real gas is reduced in a throttling process, its temperature either falls or rises, depending on whether its Joule–Thomson coefficient is positive or negative.)

3.6.1 Types of ideal gas

the classical or Maxwell–Boltzmann ideal gas, the ideal quantum Bose gas, composed of bosons, and the ideal quantum Fermi gas, composed of fermions. The classical ideal gas can be separated into two types: The classical thermodynamic ideal gas and the ideal quantum Boltzmann gas. Both are essentially the same, except that the classical thermodynamic ideal gas is based on classical statistical mechanics, and certain thermodynamic parameters such as the entropy are only specified to within an undetermined additive constant. The ideal quantum Boltzmann gas overcomes this limitation by taking the limit of the quantum Bose gas and quantum Fermi gas in the limit of high temperature to specify these additive constants. The behavior of a quantum Boltzmann gas is the same as that of a classical ideal gas except for the specification of these constants. The results of the quantum Boltzmann gas are used in a number of cases including the Sackur–Tetrode equation for the entropy of an ideal gas and the Saha ionization equation for a weakly ionized plasma.

3.6.2 Ideal gas law

In thermodynamics, Ideal gas law is a well-defined approximation of the behavior of many gases under diverse conditions. Ideal Gas Equation is the combination of empirical laws like Charle’s law, Boyle’s law, Gay-Lussac’s law, and Avogadro’s law. Ideal Gas Equation is the equation defining the states of the hypothetical gases expressed mathematically by the combinations of empirical and physical constants. It is also called the general gas equation. It can be defined as:

The ideal gas law is the equation of state for an ideal gas, given by:

PV=nRT

where

P is the pressure

V is the volume

n is the amount of substance of the gas (in moles)

T is the absolute temperature

R is the gas constant, which must be expressed in units consistent with those chosen for pressure, volume and temperature. For example, in SI units R = 8.3145 J · K-1· mol-1 when pressure is expressed in pascals, volume in cubic meters, and absolute temperature in kelvin. The ideal gas law is an extension of experimentally discovered gas laws. It can also be derived from microscopic considerations. Real fluids at low density and high temperature approximate the behavior of a classical ideal gas. However, at lower temperatures or a higher density, a real fluid deviates strongly from the behavior of an ideal gas, particularly as it condenses from a gas into a liquid or as it deposits from a gas into a solid. This deviation is expressed as a compressibility factor.

This equation is derived from Boyle's law V α $\frac{1}{P}$

Charles's law V α T

Avogadro's law V α n

After combining three laws we get

V α $\frac{nT}{P}$

This is

$$V\alpha = R\left(\frac{nT}{P}\right)$$

PV=nRT

3.6.3 Ideal Gas Behavior

The gas molecules in an ideal gas move freely in all directions, and collisions between them are considered perfectly elastic, implying that no Kinetic energy is lost as a result of the collision. Answer: Because their molecules have forces of attraction between them, gases deviate from the ideal gas behaviour. The Ideal Gas Law is a simple equation demonstrating the relationship between temperature, pressure, and volume for gases. These specific relationships stem from Charles's Law, Boyle's Law, and Gay-Lussac's Law. Charles's Law identifies the direct proportionality between volume and temperature at constant pressure, Boyle's Law identifies the inverse proportionality of pressure and volume at a constant temperature, and Gay-Lussac's Law identifies the direct proportionality of pressure and temperature at constant volume. Combined, these form the Ideal Gas Law equation: PV = NRT. P is the pressure, V is the volume, N is the number of moles of gas, R is the universal gas constant, and T is the absolute temperature.

The universal gas constant R is a number that satisfies the proportionalities of the pressure-volume-temperature relationship. R has different values and units that depend on the user's pressure, volume, moles, and temperature specifications. Various values for R are on online databases, or the user can use dimensional analysis to convert the observed units of pressure, volume, moles, and temperature to match a known R-value. As long as the units are consistent, either approach is acceptable. The temperature value in the Ideal Gas Law must be in absolute units (Rankine [degrees R] or Kelvin [K]) to prevent the right-hand side from being zero, which violates the pressure-volume-temperature relationship. The conversion to absolute temperature units is a simple addition to either the Fahrenheit (F) or the Celsius (C) temperature: Degrees R = F + 459.67 and K = C + 273.15.

For a gas to be "ideal" there are four governing assumptions:

1. The gas particles have negligible volume.

2. The gas particles are equally sized and do not have intermolecular forces (attraction or repulsion) with other gas particles.
3. The gas particles move randomly in agreement with Newton's Laws of Motion.
4. The gas particles have perfect elastic collisions with no energy loss.

In reality, there are no ideal gases. Any gas particle possesses a volume within the system (a minute amount, but present nonetheless), which violates the first assumption. Additionally, gas particles can be of different sizes; for example, hydrogen gas is significantly smaller than xenon gas. Gases in a system do have intermolecular forces with neighboring gas particles, especially at low temperatures where the particles are not moving quickly and interact with each other. Even though gas particles can move randomly, they do not have perfect elastic collisions due to the conservation of energy and momentum within the system.

While ideal gases are strictly a theoretical conception, real gases can behave ideally under certain conditions. Systems with either very low pressures or high temperatures enable real gases to be estimated as "ideal." The low pressure of a system allows the gas particles to experience less intermolecular forces with other gas particles. Similarly, high-temperature systems allow for the gas particles to move quickly within the system and exhibit less intermolecular forces with each other. Therefore, for calculation purposes, real gases can be considered "ideal" in either low pressure or high-temperature systems.

The Ideal Gas Law also holds true for a system containing multiple ideal gases; this is known as an ideal gas mixture. With multiple ideal gases in a system, these particles are still assumed not to have any intermolecular interactions with one another. An ideal gas mixture partitions the total pressure of the system into the partial pressure contributions of each of the different gas particles. This allows for the previous ideal gas equation to be re-written: Pi·V = ni·R·T. In this equation, Pi is the partial pressure of species i and ni are the moles of species i. At low pressure or high-temperature conditions, gas mixtures can be considered ideal gas mixtures for ease of calculation.

When systems are not at low pressures or high temperatures, the gas particles are able to interact with one another; these interactions greatly inhibit the Ideal Gas Law's accuracy. There are, however, other models, such as the Van der Waals Equation of State, that account for the volume of the gas particles and the intermolecular interactions.

Ideal Gas Behaviour Conditions

Many of the properties or ideal behaviour of gases are very similar to those of real gases. The following are some of the properties that are unique to Ideal gases:

- Molecule collisions are elastic, and their motion is frictionless, which means that the molecules do not lose energy
- The overall volume of individual molecules is orders of magnitude smaller than the volume occupied by the gas

- Between the molecules and their surroundings, there are no intermolecular forces at work
- The molecules are constantly moving, and the distance between them is much greater than the size of an individual molecule
- According to Newton's Laws of Motion, the gas particles move at random
- Molecules are only exposed to external forces when they collide
- These collisions are elastomeric and last only a few seconds

3.6.4 Ideal Gas Scale

we suppose that we have a thermometer that we can use to measure the temperature of a gas. We suppose that this thermometer uses a liquid, and we define an increase in temperature by the increase in the volume of this liquid. Our statement of Charles' law asserts that the volume of a gas is a linear function of the volume of the liquid in our thermometer and that the same linear function is observed for any gas. As we note in Section 2.8, there is a problem with this statement. Careful experiments with such thermometers produce results that deviate from Charles' law. With sufficiently accurate volume measurements, this occurs to some extent for any choice of the liquid in the thermometer. If we make sufficiently accurate measurements, the volume of a gas is not exactly proportional to the volume of any liquid (or solid) that we might choose as the working substance in our thermometer. That is, if we base our temperature scale on a liquid or solid substance, we observe deviations from Charles' law. There is a further difficulty with using a liquid as the standard fluid on which to base our temperature measurements: temperatures outside the liquid range of the chosen substance have to be measured in some other way.

Evidently, we can choose to use a gas as the working fluid in our thermometer. That is, our gas-volume measuring device is itself a thermometer. This fact proves to be very useful because of further experimental observation. To a very good approximation, we find that if we keep the pressures in the thermometer and in some other gaseous system constant at low enough values, both gases behave as ideal gases, and we find that the volumes of the two gases are proportional to each other over any range of temperature. Moreover, this proportionality is observed for any choice of either gas. This means that we can define temperature in terms of the expansion of any constant-pressure gas that behaves ideally. In principle, we can measure the same temperature using any gas, so long as the constant operating pressure is low enough. When we do so, our device is called the ideal gas thermometer. In so far as any gas behaves as an ideal gas at a sufficiently low pressure, any real gas can be used in an ideal gas thermometer and to measure any temperature accurately. Of course, practical problems emerge when we attempt to make such measurements at very high and very low temperatures.

The (very nearly) direct proportionality of two low-pressure real gas volumes contrasts with what we observe for liquids and solids. In general, the volume of a given liquid (or solid) substance is not exactly proportional to the volume of a second liquid (or solid) substance over a wide range of temperatures.

In practice, the ideal gas thermometer is not as convenient to use as other thermometers—like the mercury-in-glass thermometer. However, the perfect gas thermometer is used to calibrate other thermometers. Of course, we have to calibrate the perfect gas thermometer itself before we can use it.

We do this by assigning a temperature of 273.16 K to the triple point of water. (It turns out that the melting point of ice isn't sufficiently reproducible for the most precise work. Recall that the triple point is the temperature and pressure at which all three phases of water are at equilibrium with one another, with no air or other substances present. The triple-point pressure is 611 Pa or 6.03×10^3 atm. From both theoretical considerations and experimental observations, we are confident that no system can attain a temperature below absolute zero. Thus, the size 3 of the kelvin (one degree on the Kelvin scale) is fixed by the difference in temperature between a system at the triple point of water and one at absolute zero. If our ideal gas thermometer has a volume of V at thermal equilibrium with some other constant-temperature system, the proportionality of V and T means that

$$\frac{T}{V} = \frac{273.16}{V_2 73.16}$$

With the triple point fixed at 273.16 K, experiments find the freezing point of air-saturated water to be 273.15 K when the system pressure is 1 atmosphere. (So the melting point of ice is 273.15 K, and the triple-point is 0.10 C. We will find two reasons for the fact that the melting point is lower than the triple point: In Section 6.3 we find that the melting point of ice decreases as the pressure increases. In Section 16.10 we find that solutes usually decrease the temperature at which the liquid and solid states of a substance are in phase equilibrium.)

If we could use an ideal gas in our ideal gas thermometer, we could be confident that we had a rigorous operational definition of temperature. However, we note in Section 2.8 that any real gas will exhibit departures from ideal gas behavior if we make sufficiently accurate measurements. For extremely accurate work, we need a way to correct the temperature value that we associate with a given real gas volume. The issue here is the value of the partial derivative

$$(\frac{\partial V}{\partial T})_P$$

For one mole of an ideal gas,

$$(\frac{\partial V}{\partial T})_P = \frac{R}{P} = \frac{V}{T}$$

is a constant. For a real gas, it is a function of temperature. Let us assume that we know this function. Let the molar volume of the real gas at the triple point of water be

$V_2 73.16$ and its volume at thermal equilibrium with a system whose true temperature is V be VT. We have

$$\int_{273.16}^{T} (\frac{\partial V}{\partial T})_P dT = \int_{273.16}^{VT} dV = VT - V_{273.16}$$

When we know the integrand on the left as a function of temperature, we can do the integration and find the temperature corresponding to any measured volume, VT.

When the working fluid in our thermometer is a real gas we make measurements to find $(\partial V/\partial T)_P$ as a function of temperature. Here we encounter a circularity: To find $(\partial V/\partial T)_P$ from pressure-volume-temperature data we must have a way to measure temperature; however, this is the very thing that we are trying to find.

In principle, we can surmount this difficulty by attractively correcting the temperature that we associate with a given real-gas volume. As a first approximation, we use the temperatures that we measure with an uncorrected real-gas thermometer. These temperatures are a first approximation to the ideal gas temperature scale. Using this scale, we make non-pressure-volume-temperature measurements that establish $(\partial V/\partial T)_P$ as a function of temperature for the real gas. [This function is

$$(\frac{\partial V}{\partial T})_P = \frac{V + \mu_{JT} CP}{T}$$

where C_P is the constant-pressure heat capacity and μ_{JT} is the Joule-Thomson coefficient. Both are functions of temperature. We introduce C_p in Section 7.9. We discuss the Joule-Thomson coefficient further in Section 2.10 below, and in detail in Section 10.14. Typically $V >> C_P$ and the value of $(\partial V/\partial T)_P$ is well approximated by $V/T = R/P$. With $(\partial V/\partial T)_P$ established using this scale, integration yields a second approximation to the ideal gas temperatures. We could repeat this process until successive temperature scales converge at the number of significant figures that our experimental accuracy can support.

In practice, there are several kinds of ideal gas thermometers, and numerous corrections are required for very accurate measurements. There are also numerous other ways to measure temperature, each of which has its own complications. Our development has considered some of the ideas that have given rise to concept 4 that temperature is a fundamental property of nature that can be measured using a thermodynamic temperature scale on which values begin at zero and increase to arbitrarily high values. This thermodynamic temperature scale is a creature of theory, whose real-world counterpart would be the scale established by an ideal-gas thermometer whose gas actually obeyed $PV = nRT$ at all conditions. We have seen that such an ideal gas thermometer is itself a creature of theory.

The current real world standard temperature scale is the International Temperature Scale of 1990 (ITS-90). This defines temperature over a wide range in terms of the pressure-volume relationships of helium isotopes and the triple points of several selected elements. The triple points fix the temperature at each of several conditions up to 1357.77 K (the freezing point of copper). Needless to say, the temperatures assigned at the fixed points are the results of painstaking experiments designed to give the closest possible match to the thermodynamic scale. A variety of measuring devices—thermometers—can be used to interpolate temperature values between different pairs of fixed points.

3.7 Equations of State

In physics and thermodynamics, an equation of state is a mathematical relationship that describes the behavior of a physical system in terms of its thermodynamic properties, such as pressure, volume, and temperature. This mathematical description allows scientists and engineers to predict and analyze the behavior of a system, and has applications in a variety of fields, from chemistry and materials science to aerospace engineering and energy production. An equation of state is a mathematical equation that describes the relationships between different thermodynamic properties of a substance under various conditions. These equations provide a way to model and predict the behavior of matter, particularly how it responds to changes in temperature, pressure, and composition. Equations of state are designed to represent the physical behavior of real substances, and they can be used to describe gases, liquids, and solids. The primary variables in an EOS are typically pressure (P), volume (V), and temperature (T). These equations help relate these variables to the state of a substance, allowing scientists and engineers to understand and manipulate the properties of matter.

3.7.1 Understanding the concept of an equation of state

In order to understand equations of state, it is important to first grasp the underlying principles of thermodynamics. The study of thermodynamics is concerned with how energy is transferred and transformed within physical systems, and equations of state are a fundamental tool in this field, serving as a means of relating macroscopic properties to the behavior of individual molecules. Thermodynamics is a branch of physics that deals with the relationships between heat, work, and energy. It is a fundamental science that is used to understand a wide range of physical phenomena, from the behavior of gases to the workings of engines. At its core, thermodynamics is concerned with how energy is transferred and transformed within physical systems. One of the key concepts in thermodynamics is the idea of a system. A system is simply a portion of the universe that is being studied. It can be anything from a simple gas in a container to a complex biological organism. The behavior of a system is determined by its thermodynamic properties, which include temperature, pressure, volume, and energy.

At its core, an equation of state is simply a mathematical description of the relationship between a system's thermodynamic properties. Ideally, this relationship would be a simple, exact function of pressure, volume, and temperature, that would allow for precise calculations and predictions. However, in reality, the relationship is often more complex and may require empirical or theoretical adjustments in order to ensure accuracy. Equations of state are used to describe the behavior of a system under different conditions. For example, they can be used to predict the behavior of a gas at different temperatures and pressures, or to determine the properties of a liquid as it is heated or cooled. They are a fundamental tool in the study of thermodynamics and are used extensively in the fields of physics, chemistry, and engineering.

Equations of state play a fundamental role in predicting and understanding the behavior of matter over a wide range of conditions. By providing a mathematical description of the relationship between thermodynamic properties, equations of state allow researchers to study a wide variety of physical phenomena, from phase transitions to chemical reactions. Equations of state are used in a wide range of applications, from designing engines and turbines to developing new materials and drugs. They are an essential tool in the study of thermodynamics and are used by researchers around the world to better understand the behavior of matter under different conditions.

Equation of state that accurately predicts the properties of all substances under all conditions. An example of an equation of state correlates densities of gases and liquids to temperatures and pressures, known as the ideal gas law, which is roughly accurate for weakly polar gases at low pressures and moderate temperatures. This equation becomes increasingly inaccurate at higher pressures and lower temperatures, and fails to predict condensation from a gas to a liquid.

The general form of an equation of state may be written as

$f\ (p,V,T) = 0$

where

p is the pressure, V the volume, and T the temperature of the system. Yet also other variables may be used in that form. It is directly related to Gibbs phase rule, that is, the number of independent variables depends on the number of substances and phases in the system.

An equation used to model this relationship is called an equation of state. In most cases this model will comprise some empirical parameters that are usually adjusted to measurement data. Equations of state can also describe solids, including the transition of solids from one crystalline state to another. Equations of state are also used for the modeling of the state of matter in the interior of stars, including neutron stars, dense matter (quark–gluon plasmas) and radiation fields. A related concept is the perfect fluid equation of state used in cosmology.

Equations of state are applied in many fields such as process engineering and petroleum industry as well as pharmaceutical industry.

Any consistent set of units may be used, although SI units are preferred. Absolute temperature refers to the use of the Kelvin (K), with zero being absolute zero.

n, number of moles of a substance

V_m, $\frac{V}{n}$, molar volume, the volume of 1 mole of gas or liquid

R, ideal gas constant ≈ 8.3144621 J/mol·K

p_c, pressure at the critical point

V_c, molar volume at the critical point

T_c, absolute temperature at the critical point

3.7.2 Types of equations of state

Equations of state are mathematical expressions that relate the physical properties of a substance, such as pressure, volume, and temperature, to each other. There are several different types of equations of state that are commonly used in a variety of applications. Each equation has its own unique strengths and limitations, and may be more or less appropriate depending on the physical system being studied.

1. Ideal gas law

One of the most fundamental equations of state is the ideal gas law, which describes the behavior of gases at low pressure and high temperature. The ideal gas law relates the pressure, volume, and temperature of a gas sample, and is often used to make approximations in a wide range of applications, from atmospheric science to engineering. For example, the ideal gas law can be used to estimate the volume of a gas at a given temperature and pressure, or to calculate the pressure of a gas at a given volume and temperature. It is also used in the design of engines and other machinery that involve the compression and expansion of gases.

2. Van der Waals equation

The Van der Waals equation is a modification of the ideal gas law that accounts for the attractive and repulsive forces between gas molecules. This equation is commonly used to describe the behavior of gases at moderate pressures and temperatures, and provides a more accurate description than the ideal gas law in many scenarios. The Van der Waals equation takes into account the volume of the gas molecules themselves, as well as the attractive forces between them. This makes it more accurate than the ideal gas law in situations where the gas molecules are relatively close together and interact with each other.

3. Virial equation of state

The Virial equation of state is a more complex equation that can be used to describe the behavior of gases and liquids over a wider range of pressures and temperatures. The Virial equation accounts not only for the pairwise interactions of gas molecules, but also considers the interactions between three or more molecules, making it a more accurate description for complex systems. The Virial equation is often used in the study of thermodynamics and statistical mechanics, and is particularly useful for understanding the behavior of gases and liquids at high pressures and low temperatures.

4. Redlich-Kwong equation

The Redlich-Kwong equation is a widely-used equation of state that can be used to describe the behavior of non-ideal gases and liquids. This equation accounts for intermolecular forces between molecules, as well as the behavior of polar molecules and other complicated interactions. The Redlich-Kwong equation is often used in the field of chemical engineering, particularly in the design and optimization of industrial processes involving gases and liquids.

5. Peng-Robinson equation

The Peng-Robinson equation is another popular equation of state that is widely used in the petroleum industry for modeling and simulating various hydrocarbon mixtures. This equation is particularly useful for predicting the phase behavior of complex mixtures at high pressures and temperatures. The Peng-Robinson equation takes into account the size and shape of the molecules in the mixture, as well as the intermolecular forces between them. It is often used in the design and optimization of processes for the production and transportation of oil and gas.

3.7.3 Applications of equations of state

Equations of state have a wide range of applications in many different fields, from chemistry and materials science to aerospace engineering and energy production.

- ✧ **Predicting phase behavior:** One of the most important applications of equations of state is in predicting the phase behavior of a system. Researchers can use equations of state along with other thermodynamic models to predict how a substance will behave under various conditions, such as temperature, pressure, and composition. Understanding the phase behavior of a system is critical for many industrial processes, such as chemical separation and distillation.

- ✧ **Calculating thermodynamic properties:** Equations of state can also be used to calculate a wide range of thermodynamic properties, such as entropy, enthalpy, and fugacity. These properties can be used to predict how a system will behave under different conditions, and can help scientists and engineers design and optimize a wide variety of processes.

- ✧ **Modeling chemical reactions:** Equations of state are a crucial tool in modeling and simulating chemical reactions, allowing researchers to predict how reactants will behave under different conditions. These models are important for many fields, such as pharmaceuticals, where researchers use them to model drug reactions and optimize drug design.

- ✧ **Engineering and industrial applications:** Equations of state are also used extensively in many engineering and industrial applications, from designing chemical reactors to developing new materials for energy storage. By providing a mathematical description of the behavior of a system, equations of state allow engineers to design and optimize processes while minimizing costs and maximizing efficiency.

3.7.4 Limitations and challenges

- **Accuracy and experimental data:** Equations of state rely on experimental data in order to make accurate predictions. However, the accuracy of these models can be limited by the availability and reliability of experimental data, as well as the accuracy of the model itself. In addition, equations of state may not be able to accurately predict the behavior of a system under conditions that are significantly different from the range of conditions used in the experiments that were used to develop the model. For example, if the experimental data used to develop the model was collected at room temperature and atmospheric pressure, the model may not accurately predict the behavior of the substance at high pressure and temperatures. This can lead to inaccurate predictions and potentially dangerous situations in real-world applications.
- **Complex systems and mixtures:** Equations of state may struggle to describe the behavior of complex systems and mixtures, particularly when the physical system contains polar or charged molecules. These types of molecules can interact in ways that are difficult to predict using simple equations of state, which can lead to inaccurate predictions. For example, consider a mixture of water and ethanol. The behavior of this mixture can be difficult to predict using simple equations of state due to the complex interactions between the polar water molecules and the charged ethanol molecules. In these cases, more complex models may be necessary in order to accurately predict behavior.
- **High pressure and temperature conditions:** Equations of state may also struggle to accurately predict behavior under high pressure and temperature conditions, as the intermolecular interactions become more complex and the behavior of the substance may deviate significantly from what is predicted by the model. For example, consider a gas that is compressed to a very high pressure. At high pressures, the gas molecules are packed very closely together and the intermolecular interactions become stronger. This can lead to deviations from the predicted behavior, which can have important consequences in real-world applications.

CHAPTER 4

SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics states that the entropy of the universe will always increase over time. This means that the entropy of an isolated system will never decrease. The second law of thermodynamics is a physical law based on universal empirical observation concerning heat and energy interconversions. A simple statement of the law is that heat always flows spontaneously from hotter to colder regions of matter (or ’downhill’ in terms of the temperature gradient). The second law of thermodynamics establishes the concept of entropy as a physical property of a thermodynamic system. It predicts whether processes are forbidden despite obeying the requirement of conservation of energy as expressed in the first law of thermodynamics and provides necessary criteria for spontaneous processes. For example, the first law allows the process of a cup falling off of a table and breaking on the floor, as well as allowing the reverse process of the cup fragments coming back together and ’jumping’ back onto the table, while the second law allows the former and denies the latter. The second law may be formulated by the observation that the entropy of isolated systems left to spontaneous evolution cannot decrease, as they always tend toward a state of thermodynamic equilibrium where the entropy is highest at the given internal energy. An increase in the combined entropy of system and surroundings accounts for the irreversibility of natural processes, often referred to in the concept of the arrow of time.

the second law was an empirical finding that was accepted as an axiom of thermodynamic theory. Statistical mechanics provides a microscopic explanation of the law in terms of probability distributions of the states of large assemblies of atoms or molecules. The second law has been expressed in many ways. Its first formulation, which preceded the proper definition of entropy and was based on caloric theory, is Carnot's theorem, formulated by the French scientist Sadi Carnot, who in 1824 showed that the efficiency of conversion of heat to work in a heat engine has an upper limit.[7][8] The first rigorous definition of the second law based on the concept of entropy came from German scientist Rudolf Clausius in the 1850s and included his statement that heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time. The second law of thermodynamics allows the definition of the concept of thermodynamic temperature, but this has been formally delegated to the zeroth law of thermodynamics.

Second law of thermodynamics, statement describing the amount of useful work that can be done from a process that exchanges or transfers heat. The second law of thermodynamics can be precisely stated in the following two forms, as originally formulated in the 19th century by the Scottish physicist William Thomson (Lord Kelvin) and the German physicist Rudolf Clausius, respectively.

The two statements are in fact equivalent because, if the first were possible, then the work obtained could be used, for example, to generate electricity that could then be discharged through an electric heater installed in a body at a higher temperature. The net effect would be a flow of heat from a lower temperature to a higher temperature, thereby violating the second (Clausius) form of the second law. Conversely, if the second form were possible, then the heat transferred to the higher temperature could be used to run a heat engine that would convert part of the heat into work. The final result would be a conversion of heat into work at constant temperature—a violation of the first (Kelvin) form of the second law.

The concept of entropy was first introduced in 1850 by Clausius as a precise mathematical way of testing whether the second law of thermodynamics is violated by a particular process. The test begins with the definition that if an amount of heat Q flows into a heat reservoir at constant temperature T, then its entropy S increases by $\Delta S = Q/T$. (This equation in effect provides a thermodynamic definition of temperature that can be shown to be identical to the conventional thermometric one.) Assume now that there are two heat reservoirs R1 and R2 at temperatures T1 and T2. If an amount of heat Q flows from R1 to R2, then the net entropy change for the two reservoirs is

$$\Delta = \frac{Q}{T_1} - \frac{Q}{T_2}$$

ΔS is positive, provided that T1 ¿ T2. Thus, the observation that heat never flows spontaneously from a colder region to a hotter region (the Clausius form of the second law of thermodynamics) is equivalent to requiring the net entropy change to be positive for a spontaneous flow of heat. If T1 = T2, then the reservoirs are in equilibrium and ΔS = 0.

The condition ΔS ≥ 0 determines the maximum possible efficiency of heat engines. Suppose that some system capable of doing work in a cyclic fashion (a heat engine) absorbs heat Q1 from R1 and exhausts heat Q2 to R2 for each complete cycle. Because the system returns to its original state at the end of a cycle, its energy does not change. Then, by conservation of energy, the work done per cycle is W = Q1 - Q2, and the net entropy change for the two reservoirs is

$$\Delta = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

To make W as large as possible, Q2 should be kept as small as possible relative to Q1. However, Q2 cannot be zero, because this would make ΔS negative and so violate the second law of thermodynamics. The smallest possible value of Q2 corresponds to the condition ΔS = 0, yielding

$$\left(\frac{Q_2}{Q_1}\right)_{min} = \frac{T_2}{T_1}$$

This is the fundamental equation limiting the efficiency of all heat engines whose function is to convert heat into work (such as electric power generators). The actual efficiency is defined to be the fraction of Q1 that is converted to work (W/Q1).

The maximum efficiency for a given T1 and T2 is thus

$$\eta_{max} = 1 - \left(\frac{Q_2}{Q_1}\right)_{min} = 1 - \frac{T_2}{T_1}$$

A process for which ΔS = 0 is said to be reversible because an infinitesimal change would be sufficient to make the heat engine run backward as a refrigerator.

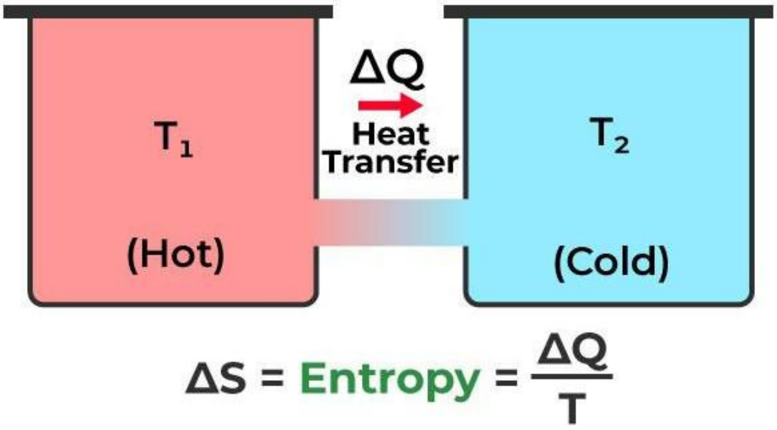
As an example, the properties of materials limit the practical upper temperature for thermal power plants to T1 ≅ 1,200 K. Taking T2 to be the temperature of the environment (300 K), the maximum efficiency is 1 - 300/1,200 = 0.75. Thus, at least 25 percent of the heat energy produced must be exhausted into the environment as waste heat to avoid violating the second law of thermodynamics. Because of various imperfections, such as friction and imperfect thermal insulation, the actual efficiency of power plants seldom exceeds about 60 percent. However, because of the second law of thermodynamics, no amount of ingenuity or improvements in design can increase the efficiency beyond about 75 percent.

The example of a heat engine illustrates one of the many ways in which the second law of thermodynamics can be applied. One way to generalize the example is to consider the heat engine and its heat reservoir as parts of an isolated (or closed) system—i.e., one that does not exchange heat or work with its surroundings. For example, the heat engine and reservoir could be encased in a rigid container with insulating walls. In this case the second law of thermodynamics (in the simplified form presented here) says that no matter what process takes place inside the container, its entropy must increase or remain the same in the limit of a reversible process. Similarly, if the universe is an isolated system, then its entropy too must increase with time. Indeed, the implication is that the universe must ultimately suffer a "heat death" as its entropy progressively increases toward a maximum value and all parts come into thermal equilibrium at a uniform temperature. After that point, no further changes involving the conversion of heat into useful work would be possible. In general, the equilibrium state for an isolated system is precisely that state of maximum entropy. (This is equivalent to an alternate definition for the term entropy as a measure of the disorder of a system, such that a completely random dispersion of elements corresponds to maximum entropy, or minimum information. See information theory: Entropy.)

So what exactly is the connection between entropy and the second law? Recall that heat at the molecular level is the random kinetic energy of motion of molecules, and collisions between molecules provide the microscopic mechanism for transporting heat energy from one place to another. Because individual collisions are unchanged by reversing the direction of time, heat can flow just as well in one direction as the other. Thus, from the point of view of fundamental interactions, there is nothing to prevent a chance event in which a number of slow-moving (cold) molecules happen to collect together in one place and form ice, while the surrounding water becomes hotter. Such chance events could be expected to occur from time to time in a vessel containing only a few water molecules. However, the same chance events are never observed in a full glass of water, not because they are impossible but because they are exceedingly improbable. This is because even a small glass of water contains an enormous number of interacting molecules (about 1024), making it highly unlikely that, in the course of their random thermal motion, a significant fraction of cold molecules will collect together in one place. Although such a spontaneous violation of the second law of thermodynamics is not impossible, an extremely patient physicist would have to wait many times the age of the universe to see it happen.

4.1 The Second Law of Thermodynamics Statement

Second law of thermodynamics defines that heat cannot move from a reservoir of lower temperature to a reservoir of higher temperature in a cyclic process. The second law of thermodynamics deals with the transfer of heat naturally from a hotter body to a colder body. Second Law of Thermodynamics is one of three Laws of Thermodynamics. The word "thermodynamics" comes from two root words: "thermo," meaning heat, and "dynamic," meaning power. Thus, the Laws of Thermodynamics are the Laws of "Heat Power. The First Law of Thermodynamics is commonly known as the Law of Conservation of Matter. While the Second Law of Thermodynamics is commonly known as the Law of Increased Entropy. According to the second law of thermodynamics, any naturally occurring process will always cause the universe's entropy (S) to increase. The law simply states that the entropy of an isolated system will never diminish over time.



entropy of a system and its surroundings remains constant in some instances where the system is in thermodynamic equilibrium or going through a reversible process. The Law of Increased Entropy is another name for the second law.

4.1.1 Different Statements of Second Law of Thermodynamics

The second law of thermodynamics may be expressed in many specific ways, by different scientists at different times. Here are the Second Law of Thermodynamics statements:

1. Kelvin-Planck Statement of Second Law of Thermodynamics

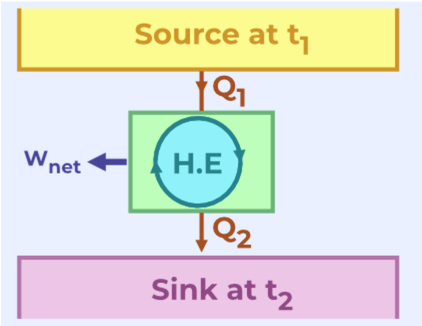


Figure 4.1 Kelvin-Planck Statement

It is impossible for a heat engine to produce a network in a complete cycle, if it exchanges heat only with bodies at a single fixed temperature. If Q2 =0 (i.e., Wnet = Q1, or efficiency=1.00), the heat engine produces work in a complete cycle by exchanging heat with only one reservoir, thus violating the Kelvin-Planck statement.

It's difficult to turn all of the heat emitted by a heated body into work. The working material of a heat engine absorbs heat from a hot body, transforms a portion of it into work, and returns the remainder to the cold body. No engine can transform all of the heat from the source into work without wasting any heat. This indicates that a sink is required to get continuous work. The following image shows the working of the heat engine.

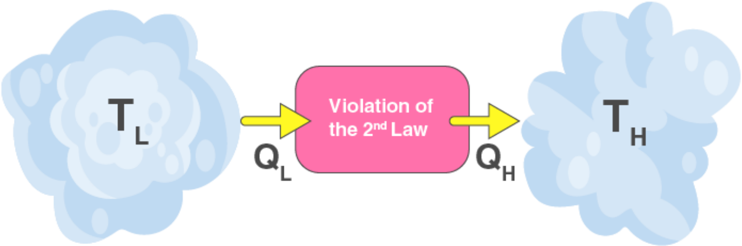
2. Clausius Statement of Second Law of Thermodynamics

It is impossible to construct a device operating in a cycle that can transfer heat from a colder body to a warmer one without consuming any work. Also, energy will not flow spontaneously from a low-temperature object to a higher-temperature object. It is important to note that we are referring to the net transfer of energy. Energy transfer can take place from a cold object to a hot object by the transfer of energetic particles or electromagnetic radiation. However, the net transfer will occur from the hot object to the cold object in any spontaneous process. And some form of work is needed to transfer the net energy to the hot object. In other words, unless the compressor is driven by an external source, the refrigerator won't be able to operate. The heat pump and refrigerator work on Clausius's statement.

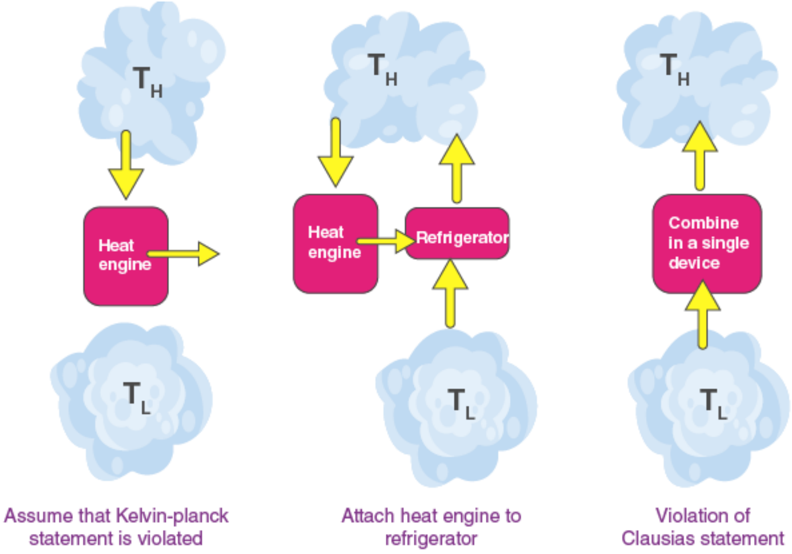
It is impossible to build a technology that can transmit heat from a colder body to a warmer body without wasting any energy. In other words, the refrigerator will not work unless the compressor is powered by an external source. Clausius's assertion is used by heat pumps and refrigerators.

A refrigerator, for example, can transfer a certain amount of heat from a cold body to a hot one without requiring any external energy. As a result, Clausius' assertion is violated. Assume that an engine operating between the same hot and cold bodies absorbs heat from the hot body, transforms a portion W into work, and then transfers the remaining heat to the cold body.

The engine does not break the second law of thermodynamics on its own. When the engine and the refrigerator operate together, they create a mechanism that absorbs all of the heat from the hot body and transforms it into work without sacrificing any of the cold body's heat. The Kelvin-Planck assertion is violated. As a result, we may conclude that the two versions of the second law of thermodynamics are equivalent in every way.



Both Clausius's and Kelvin's statements are equivalent, i.e., a device violating Clausius's statement will also violate Kelvin's statement and vice versa.

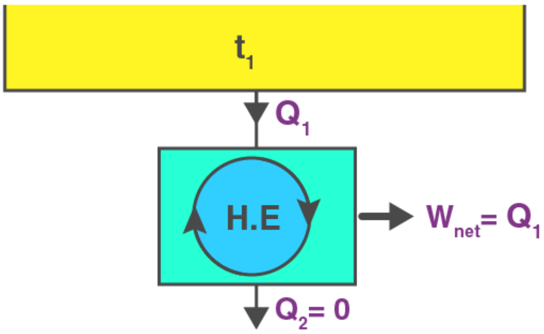


In addition to these statements, a French physicist named Nicolas Léonard Sadi Carnot, also known as the "father of thermodynamics", introduced the second law of thermodynamics. However, as per his statement, he emphasised the use of caloric theory for the description of the law. Caloric (self-repellent fluid) relates to heat, and Carnot observed that some caloric was lost in the motion cycle.

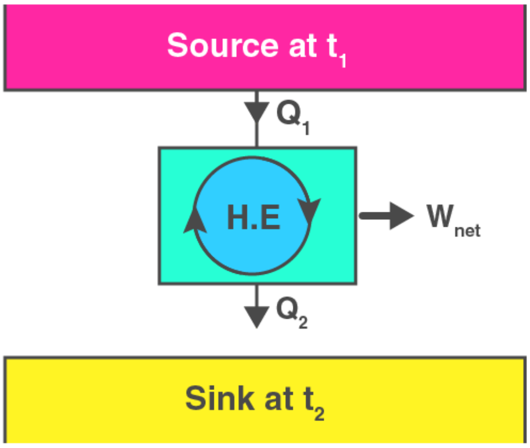
3. Perpetual Motion Machine of Second Kind

Perpetual motion machines are defined as devices that work while connecting with only one heat reservoir. These devices are considered to violate the second law of thermodynamics. These machines do not exist in the real life and only exist theoretically. We know that a heat engine interacts with two heat reservoirs at different temperatures to produce work in a cycle. The differences in the temperature of the two reservoirs result in the work being produced until the temperature in both reservoirs is equalized.

The device that produces work while interacting with a single heat reservoir is known as a perpetual motion machine of the second kind (PMM2). Also, a device that violates the second law of thermodynamics is a perpetual motion machine of the second kind.



Thus, a heat engine has to interact with at least two thermal reservoirs at different temperatures to produce work in a cycle. So long as there is a difference in temperature, motive power (i.e., work) can be produced. If the bodies with which the heat engine exchanges are of finite heat capacities, work will be produced by the heat engine until the temperature of the two bodies is equalised.



4.1.2 The Concept of Entropy

To fully understand the implications of the Second Law of Thermodynamics, it is crucial to introduce the concept of entropy. Entropy (S) is a measure of the degree of disorder or randomness in a system. It quantifies the thermal energy unavailable for performing useful work. In essence, it is a measure of the energy's quality, with lower entropy corresponding to higher quality or more concentrated energy.

The Second Law of Thermodynamics is often linked to the increase in entropy. Specifically, it can be stated as: ”The total entropy of an isolated system always increases over time and never decreases.” In this context, an isolated system refers to a closed system that does not exchange matter or energy with its surroundings. As energy is transferred or converted in the system, the entropy of the system and its surroundings increases. This principle embodies the idea that natural processes tend to move towards a state of greater disorder and randomness. Consider, for instance, the example of a cup of hot tea cooling down in a room. As the tea loses heat to its surroundings, the entropy of the tea decreases, but the overall entropy of the system (tea + room) increases. This increase in entropy is an expression of the Second Law of Thermodynamics.

4.1.3 Implications and Significance

The Second Law of Thermodynamics has profound implications in various fields and applications:

Energy Efficiency: The Second Law places fundamental limits on the efficiency of heat engines, including internal combustion engines and power plants. It guides the development of more efficient technologies and drives the pursuit of renewable and sustainable energy sources.

Entropy and Disorder: The concept of entropy provides a measure of disorder or randomness in a system. It has applications in fields as diverse as information theory, statistical mechanics, and even philosophy.

Chemical Reactions: The Second Law helps explain the spontaneity of chemical reactions. Reactions that lead to a decrease in free energy and an increase in entropy are more likely to occur without the input of external energy.

Environmental Science: The Second Law contributes to our understanding of environmental processes, including the dispersion of pollutants, climate change, and the flow of energy in ecosystems.

Refrigeration and Cooling: In the design of refrigeration and air conditioning systems, the Second Law is essential. It defines the limitations of refrigeration cycles and cooling processes.

Biological Systems: Biological processes, such as metabolism, are governed by the Second Law. Organisms must continually expend energy to maintain low entropy within their systems and counteract the natural increase in disorder.

Information Theory: The concept of entropy is fundamental in information theory, where it quantifies the uncertainty or randomness in a message or data.

Philosophy and Cosmology: The Second Law has inspired philosophical discussions and implications for the nature of time and the universe's ultimate fate, including the idea of the heat death of the universe.

4.1.4 Application of the Second Law of Thermodynamics

- ✧ The law states that heat always moves from a body that is warmer to a body that is colder. All heat engine cycles, including Otto, Diesel, etc., as well as all working fluids employed in the engines, are covered by this rule. Modern automobiles have advanced as a result of this law.

- ✧ Refrigerators and heat pumps that use the Reversed Carnot Cycle are other examples of how this concept is applied. You must provide external work if you want to transfer heat from a body with a lower temperature to a body with a greater temperature. Unlike the Reversed Carnot Cycle, which uses work to move heat from a lower-temperature reservoir to a higher-temperature reservoir, the original Carnot Cycle uses heat to produce work.

4.1.5 Limitations of Second Law of Thermodynamics

- ▪ The second law of thermodynamics is a concept that limits the occurrence of many processes that, despite being permitted by other physical laws, we know from experience does not occur. For instance, water in a glass that is at ambient temperature never spontaneously cools to create ice cubes, which would release energy into the environment.

- ▪ Suggesting that the universe will end in a state of "heat death," in which everything is the same temperature, the second rule also predicts the end of the universe. When everything is at the same temperature, there can be no work done and all of the energy is squandered as random atom and molecule motion, which is the most extreme level of disorder.

4.2 Reversible and Irreversible Processes

We see so many changes happening around us every day, such as boiling water, rusting of iron, melting ice, burning of paper, etc. In all these processes, we observe that the system in consideration goes from an initial state to a final state where some amount of heat is absorbed from the surroundings and some amount of work W is done by the system on the surrounding. Now, for how many such systems can the system and the surrounding be brought back to their initial state? With common examples such as rusting and fermentation, we can say that it is not possible in most cases. In this section, we shall learn about reversible and irreversible processes.

4.2.1 Reversible Processes

Reversible processes occur when a system returns to its original state after being disturbed. A classic example of this is the water cycle. A classic example is melting ice and vice versa. Water is originally in liquid condition, then freezes to produce ice, which melts again to give water when heated. Students should be aware that a reversible process involves two processes. While in the first process, particles change into another form, the reverse reaction occurs in the second process, with the results returning to the beginning stage. As a result, comprehending this will aid in further diving into the distinction between reversible and irreversible processes. For example, we can quickly push back the piston when the ideal gas expands in a vacuum or doubles its initial volume and restores its temperature and pressure by extracting some gas's heat.

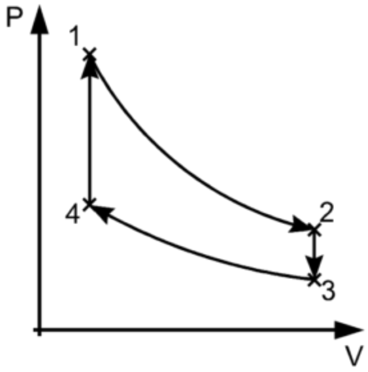
The reversible process is in contrast to the irreversible process. Heat flows to the object in two reversed directions. If the process ends, the object state can back to its initial state at the same conditions that the process happened within. It is an unspontaneous process, it happens only when there is thermodynamic equilibrium between the object and its surroundings, and making an infinitesimal change in the conditions of the object or its surroundings. For example, if you place a block of ice (at 0 °C) into a closed box (at 0 °C too), then you make a very small change in the temperature of the cubic ice or the closed box, the cubic ice will melt after a while. This kind of process doesn't influence the universe's entropy, it only happens at infinitesimal level.

Examples of Reversible Processes

- extension of springs
- slow adiabatic compression or expansion of gases
- electrolysis (with no resistance in the electrolyte)
- the frictionless motion of solids
- slow isothermal compression or expansion of gases
- A slow heat flow between two objects at 25 °C.
- A slow adiabatic compression of the air.
- Pushing an object on a frictionless surface.

A thermodynamic process is reversible if the process can return back in such a that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. It means both system and surroundings are returned to their initial states at the end of the reverse process.

In the figure above, the system has undergone a change from state 1 to state 2. The reversible process can reverse completely and there is no trace left to show that the system had undergone thermodynamic change. During the reversible process, all the



changes in state that occur in the system are in thermodynamic equilibrium with each other.

Internally reversible process: The process is internally reversible if no irreversibilities occur within the boundaries of the system. In these processes, a system undergoes through a series of equilibrium states, and when the process reverses, the system passes through exactly the same equilibrium states while returning to its initial state.

Externally reversible process: In externally reversible process no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the surface of contact between the system and reservoir is at the same temperature.

A process can be reversible only when its satisfying two conditions

1. Dissipative force must be absent.

2. The process should occur in infinite small time.

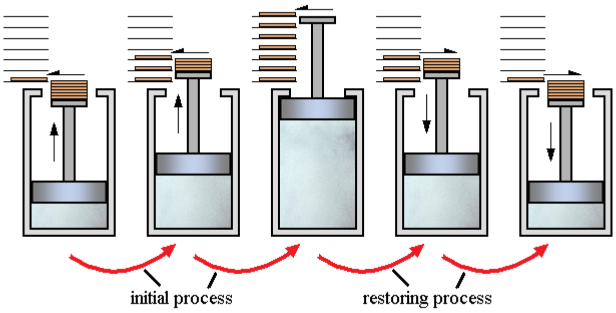


Figure 4.2 Reversible Processes

In words, the process which can reverse back completely is a reversible process. This means that the final properties of the system can perfectly reverse back to the original properties. The process can be perfectly reversible only if the changes in the process are infinitesimally small. In practical situations it is not possible to trace these extremely small changes in extremely small time, hence the reversible process is also an ideal process. The changes that occur during the reversible process are in equilibrium with each other.

4.2.2 Irreversible Process

An irreversible process is a spontaneous process that happens in all-natural processes. Heat spontaneously flows from the hot object to the cool object without going back to the hot object, which means this process walks in one direction. Once the process begins, the object state changes. Melting milk foam above the coffee is considered as irreversible process. The heat flows from coffee to milk foam. Entering milk's foam, heat causes a disorder between milk's molecules leading to rearranging molecules' order. Thus, the milk foam is not being a foam anymore. Typically, this process makes a significant change in universe's entropy because it's more probable to happen.

An irreversible process can be defined as a process in which the system and the surroundings do not return to their original condition once the process is initiated. Take an example of an automobile engine that has travelled a distance with the aid of fuel equal to an amount 'x'. During the process, the fuel burns to provide energy to the engine, converting itself into smoke and heat energy. We cannot retrieve the energy lost by the fuel and cannot get back the original form. There are many factors due to which the irreversibility of a process occurs, namely. The friction that converts the energy of the fuel to heat energy The unrestrained expansion of the fluid prevents from regaining the original form of the fuel Heat transfer through a finite temperature, the reverse of which is not possible as the forward process, in this case, is spontaneous Mixing of two different substances that cannot be separated as the intermixing process is again spontaneous in nature, the reverse of which is not feasible. Thus, some processes are reversible while others are irreversible in nature, depending upon their ability to return to their original state from their final state.

Examples of Irreversible Processes

- Relative motion with friction
- Throttling
- Heat transfer
- Diffusion
- Electricity flow through a resistance
- Converting mechanical energy into heat to stop the car by car brakes.
- Crystallizing the hot magma on the earth surface to form fiery rocks.

- Soaking the vegetables into water and salt solution to ferment it.

Irreversible processes are a result of straying away from the curve, therefore decreasing the amount of overall work done. An irreversible process is a thermodynamic process that departs from equilibrium. In terms of pressure and volume, it occurs when the pressure (or the volume) of a system changes dramatically and instantaneously that the volume (or the pressure) do not have the time to reach equilibrium.

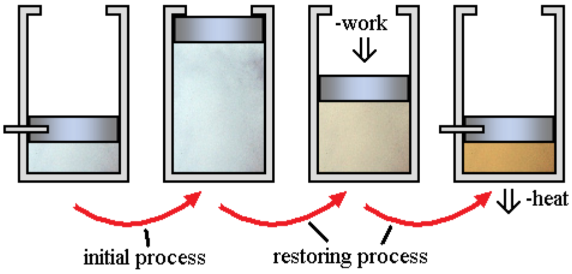


Figure 4.3 Irreversible Process

A classic example of an irreversible process is allowing a certain volume of gas to release into a vacuum. By releasing pressure on a sample and allowing it to occupy a large space, the system and surroundings are not in equilibrium during the expansion process. Here little work occurs. However, there is a requirement of significant work, with a corresponding amount of energy dissipation as heat flows to the environment. This is in order to reverse the process.

Irreversible Processes, and how do they work

Irreversible processes cannot be reversed or at least cannot be reversed without the great expense of time and money. Irreversible processes are controlled by economic considerations (costs), and these considerations usually eliminate one or more variables in the balanced equation. This is because if any of the variables were eliminated, it would destroy the balance of the reaction, and the system would be unable to sustain itself. For example, in an oil refinery plant where crude oil is converted into valuable products such as gasoline, kerosene, etc., many steps take place as each stage in the process consumes certain portions of the crude oil and turns out certain by-products. Each step in this process can never be reversed because if any one of these steps were eliminated, it would destroy the balance of the reaction.

Let's take another example. Consider the situation of a car engine that has travelled a particular distance while using a specific amount of fuel. The fuel burns to provide energy to the engine, producing smoke and heat energy in the process. We will never be able to regain the energy that the fuel has lost, nor will we ever be able to restore it to its former state and thus destroy what is called "economy". As a result, depending on their ability to return to their original form from their final state, specific processes are reversible while others are irreversible. Relative motion with friction, heat transfer throttling, diffusion and irreversible processes include the flow of electricity across a resistance.

Practically every situation is an example of an irreversible process since the system and its nature cannot be restored to their initial states simultaneously. Because it is considered a natural phenomenon, the small gradient between the states in the natural process indicates that the process is irreversible. When heat travels from one substance to another, the temperature difference between the two is finite. More importantly, at no point during the process is the system likely to be in equilibrium or a well-defined state. This is known as irreversibility.

4.3 Heat Engines and Refrigerators

Heat engines and refrigerators are thermodynamic devices designed to control the flow of heat and energy, and they play essential roles in various aspects of our lives. Understanding how these devices work is crucial in fields ranging from engineering and physics to environmental science and everyday household applications. The heat engine that operates most efficiently between a given high temperature reservoir and a given low temperature reservoir is a Carnot engine named after Sadi Carnot who first proposed it. It uses reversible processes to complete a thermodynamic cycle and produce the most useful work possible.

4.3.1 Heat Engines

In thermodynamics and engineering, a heat engine is a system that converts heat to usable energy, particularly mechanical energy, which can then be used to do mechanical work. While originally conceived in the context of mechanical energy, the concept of the heat engine has been applied to various other kinds of energy, particularly electrical, since at least the late 19th century. The heat engine does this by bringing a working substance from a higher state temperature to a lower state temperature. A heat source generates thermal energy that brings the working substance to the higher temperature state. The working substance generates work in the working body of the engine while transferring heat to the colder sink until it reaches a lower temperature state. During this process some of the thermal energy is converted into work by exploiting the properties of the working substance. The working substance can be any system with a non-zero heat capacity, but it usually is a gas or liquid. During this process, some heat is normally lost to the surroundings and is not converted to work. Also, some energy is unusable because of friction and drag.

In general, an engine is any machine that converts energy to mechanical work. Heat engines distinguish themselves from other types of engines by the fact that their efficiency is fundamentally limited by Carnot's theorem. Although this efficiency limitation can be a drawback, an advantage of heat engines is that most forms of energy can be easily converted to heat by processes like exothermic reactions (such as combustion), nuclear fission, absorption of light or energetic particles, friction, dissipation and resistance. Since the heat source that supplies thermal energy to the engine can thus be powered by virtually any kind of energy, heat engines cover a wide range of applications. Heat engines are often confused with the cycles they attempt to implement. Typically, the term "engine" is used for a physical device and "cycle" for the models.

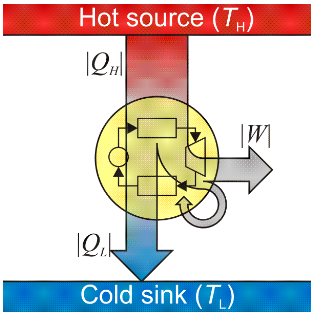


Figure 4.4 Heat Engines

A heat engine is a device that converts heat energy into mechanical work. Heat engines are the backbone of various applications, from powering automobiles and aircraft to generating electricity in power plants. They operate on the principles described by the laws of thermodynamics, particularly the First and Second Laws.

Working Substance: A heat engine employs a working substance, typically a gas or a liquid, which undergoes a thermodynamic cycle of compression, heat addition, expansion, and heat rejection. The working substance is enclosed within the engine's system.

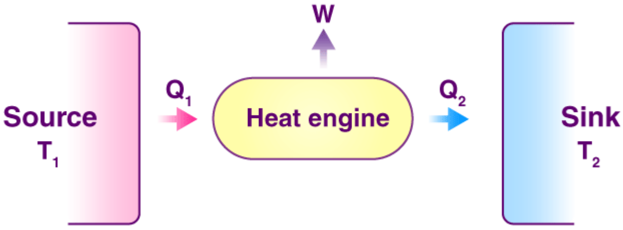
Heat Source: Heat engines require a high-temperature reservoir, often referred to as a heat source. This is where the working substance absorbs heat, increasing its internal energy.

Heat Sink: Heat engines also need a low-temperature reservoir or heat sink, where the working substance releases heat, lowering its internal energy.

Mechanical Work: The heat engine converts the energy transferred from the heat source into mechanical work that can be used to perform various tasks. This work typically involves moving a piston, turning a turbine, or performing other mechanical actions.

➥ Heat Engine Efficiency

A heat engine is a device that converts heat to work. It takes heat from a reservoir, then does some work like moving a piston, lifting weight etc. and finally discharges some heat energy into the sink.



Let us derive an expression for the efficiency of a heat engine. We can define heat engine efficiency as:

$\eta = WQ_1$

Where,

W = Work done by the engine

Q1 = Heat taken from the source

After each cycle, the engine returns to its initial state, so,

$\Delta U = 0$

So from the figure, it is clear that,

$W = Q_1 - Q_2$

Hence the heat engine efficiency is:

$\eta = \frac{Q_1 - Q_2}{Q_1}$

$\eta = 1 - \frac{Q_2}{Q_1}$

So for Q2 = 0 efficiency will be 100% but, in actual, this is not possible because there will be some loss of energy in the system. Hence, for every engine, there is a limit for its efficiency. The efficiency is maximum for a reversible engine such as Carnot heat engine.

➥ Types of Heat Engine

External combustion engine: In these heat engines, the fuel burns outside and away from the main engine, where force and motion are produced. A steam engine is an example of an external combustion engine.

Internal combustion engine: In these heat engines, the fuel burns inside the cylinder. A car engine is an example of an internal combustion engine. The internal combustion engine is more efficient than the external combustion engine as there is no energy wasted during heat transfer between the boiler and the cylinder.

➥ The Carnot Cycle

The idealized heat engine is represented by the Carnot cycle, a reversible cycle that defines the maximum possible efficiency of any heat engine operating between two temperature reservoirs. It consists of four processes:

Isothermal Expansion: The working substance expands isothermally (at a constant high temperature) while absorbing heat from the heat source. During this phase, the substance does work by moving a piston or turbine.

Adiabatic Expansion: The working substance continues to expand adiabatically (without heat exchange) while doing work, further lowering its temperature.

Isothermal Compression: In this phase, the working substance is compressed isothermally (at a constant low temperature) while rejecting heat to the heat sink.

Adiabatic Compression: The substance undergoes adiabatic compression back to its initial state, preparing it for the next cycle.

The Carnot cycle provides an upper limit to the efficiency of any heat engine operating between two temperature reservoirs. The efficiency of a Carnot engine is given by:

$$\text{Efficiency} = 1 - \frac{T_C}{T_H}$$

Where:

T_C is the absolute temperature of the heat sink (in Kelvin).

T_H is the absolute temperature of the heat source (in Kelvin).

The Carnot cycle is an idealized concept and is not achieved in real-world engines. However, it serves as a benchmark for the maximum possible efficiency.

Real Heat Engines: Real heat engines, such as internal combustion engines in cars, gas turbines in aircraft, and steam engines in power plants, operate based on principles similar to the idealized Carnot cycle but with losses due to friction, heat leakage, and other factors. These engines have efficiencies lower than the Carnot limit but are still highly efficient for many practical applications.

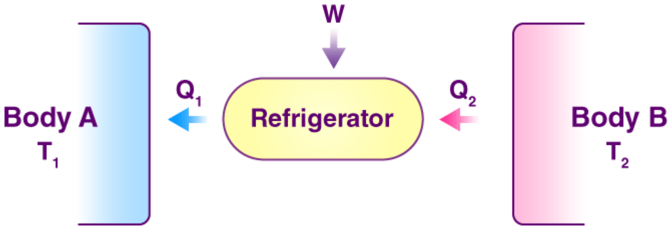
➥ Applications of Heat Engines

- ✧ Transportation: Internal combustion engines, whether gasoline or diesel, are commonly used in cars, trucks, and motorcycles. Jet engines, such as those in airplanes, are another example of heat engines.
- ✧ Power Generation: Heat engines play a vital role in generating electricity. Most power plants, whether fossil fuel-based (e.g., coal or natural gas) or nuclear, rely on steam turbines driven by heat engines to produce electrical power.

- ✧ Industrial Processes: Heat engines are used in various industrial processes, such as compressors in refrigeration and air conditioning systems, pumps, and many types of machinery.
- ✧ Household Appliances: Some household appliances, like refrigerators and air conditioners, employ heat engines to maintain temperature control.

4.3.2 Refrigerators

A refrigerator is a device that transfers heat from a cold environment (the inside of the refrigerator) to a warmer environment (the room or external surroundings). Refrigerators work on a similar thermodynamic principle as heat engines, but they reverse the direction of heat transfer. They are crucial for preserving food, cooling beverages, and a wide range of other applications.



A heat pump is a device that extracts heat from one piece and transfers it to another. Heat pumps transfer heat by circulating a substance known as refrigerant through a cycle of evaporation and condensation. Refrigerators and air conditioners are examples of heat pumps. A refrigerator is essentially an insulated box with a heat pump system connected to it. The evaporator coil is located inside the box, usually in the freezer compartment. Heat is absorbed from this location and transferred outside, usually behind or underneath the condenser coil's unit. A refrigerator takes out heat from a lower temperature T2 and releases it to a higher temperature T1. For this process to occur, work must be done on the system. Below is the schematic representation of the process:

- ➥ **Components of a Refrigerator**

In this case, we define the coefficient of performance as:

$\alpha = \frac{Q_2}{W}$

Where,

Q2 is the heat taken from the system

W is the work done on the refrigerator

Similar to heat engines after a cycle, the refrigerator returns to its original state hence ΔU = 0. So from the figure, W = $Q_1 - Q_2$

Therefore,

$$\alpha = \frac{Q_2}{Q_1 - Q_2}$$

A refrigerator cannot function without external work so its coefficient of performance can never be infinite.

Working Substance: Like heat engines, refrigerators also employ a working substance, typically a volatile gas or liquid, which undergoes a thermodynamic cycle. This working substance circulates within the system to facilitate heat transfer.

Evaporator: The evaporator is the part of the refrigerator located inside the appliance, where the working substance evaporates and absorbs heat from the contents of the refrigerator. This process cools the inside of the refrigerator.

Compressor: The compressor is responsible for raising the pressure and temperature of the working substance, causing it to release the heat it absorbed in the evaporator.

Condenser: The condenser is located on the back or underneath the refrigerator and serves to dissipate the heat removed from the inside of the refrigerator. The working substance loses heat to the room or external environment and becomes a liquid.

Expansion Valve: The expansion valve allows the working substance to expand and return to the evaporator, completing the refrigeration cycle.

➥ The Refrigeration Cycle

Refrigerators operate on a thermodynamic cycle known as the vapor-compression cycle. This cycle involves four main processes:

Evaporation: The working substance evaporates in the evaporator, absorbing heat from the interior of the refrigerator and lowering its temperature.

Compression: The compressor raises the pressure and temperature of the vaporized working substance, making it a high-temperature, high-pressure gas.

Condensation: In the condenser, the high-temperature gas releases heat to the surrounding environment and becomes a high-pressure liquid.

Expansion: The liquid working substance passes through the expansion valve, where it undergoes a sudden drop in pressure, becoming a low-temperature, low-pressure liquid-gas mixture. It then returns to the evaporator to begin the cycle anew. The refrigeration cycle continues, transferring heat from the inside of the refrigerator to the outside, thus maintaining a cooler temperature inside.

➥ Efficiency and Coefficient of Performance

The efficiency of a refrigerator is typically expressed in terms of its Coefficient of Performance (COP). The COP is defined as the ratio of the heat energy removed from the inside of the refrigerator to the work done by the compressor. In other words, it represents the amount of cooling produced per unit of work input.

COP= $\frac{Q_c}{W}$

Where:

COP is the Coefficient of Performance.

Q_c c is the heat removed from the inside of the refrigerator (cooling effect).

W is the work input to the compressor.

Refrigerators are designed to have a high COP, which indicates their efficiency in providing cooling. A higher COP means the refrigerator can remove more heat from the interior with less work input.

➥ **Environmental Considerations**

Refrigeration and air conditioning systems use various working substances, including hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). These substances have raised environmental concerns due to their potential to contribute to ozone depletion and global warming. As a result, there has been a shift towards developing more environmentally friendly refrigerants, such as hydrofluoroolefins (HFOs).

➥ **Applications of Refrigerators**

✧ Food Preservation: Refrigerators are a staple appliance in households and are used to store perishable food items, extending their shelf life.

✧ Commercial Refrigeration: Businesses, such as restaurants, grocery stores, and food production facilities, rely on large-scale refrigeration systems to store and display food products.

✧ Air Conditioning: Air conditioning systems, found in homes, offices, and vehicles, utilize refrigeration cycles to provide cooling and maintain comfortable indoor temperatures.

✧ Medical and Laboratory Applications: Refrigeration is essential for preserving medications, vaccines, and laboratory samples.

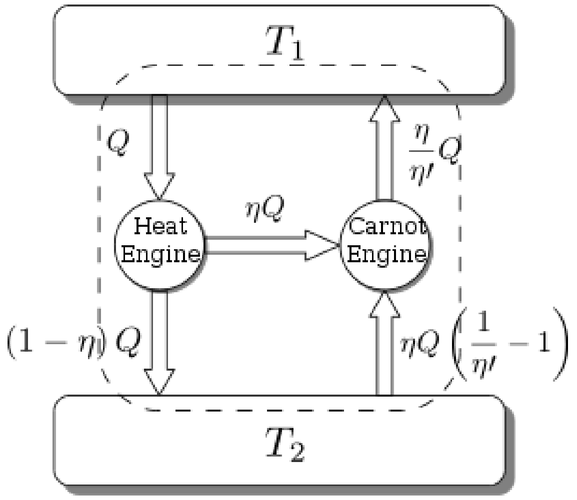
✧ Industrial Cooling: In industrial settings, refrigeration is used to cool machinery, equipment, and processes to prevent overheating and ensure optimal operation.

✧ Transportation: Refrigerated trucks and containers are used to transport temperature-sensitive goods, including food and pharmaceuticals.

4.4 Carnot Cycle

Carnot cycle, in heat engines, ideal cyclical sequence of changes of pressures and temperatures of a fluid, such as a gas used in an engine, conceived early in the 19th century by the French engineer Sadi Carnot. It is used as a standard of performance of all heat engines operating between a high and a low temperature. In the cycle the working substance of the engine undergoes four successive changes: expansion by heating at a constant high temperature; reversible adiabatic expansion; compression by cooling at a constant low temperature; and reversible adiabatic compression. The engine receives heat (from the heat source) during the expansion at high temperature, delivers work during the reversible adiabatic expansion, rejects heat (to the heat sink) during the compression at low temperature, and receives work during the reversible adiabatic compression. The ratio of the net work output to the heat input is equal to the ratio of the difference between the temperatures of the heat source and the heat sink divided by the temperature of the heat source. It represents Carnot's principle in that it is the largest such ratio of any engine operating between the two temperatures. The Carnot cycle was first developed in the year 1824 by a French physicist named Sadi Carnot. It is an ideal cycle that basically laid the foundation for the second law of thermodynamics. The Carnot cycle also brought up the concept of reversibility.

Carnot's Theorem

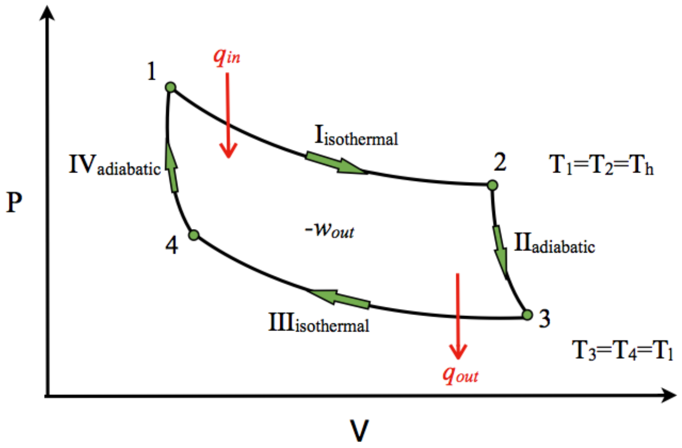


This theorem states that no engine working between two given temperatures can be more efficient than a reversible engine working between the same two temperatures and that all the reversible engines working between the same two temperatures have the same efficiency, whatever the working substance may be. According to the Carnot theorem, the reversible engine will always have a greater efficiency than the irreversible one. The reversible heat engine operates on a reverse cycle and functions as a heat pump (or refrigerator).

The Carnot cycle is reversible representing the upper limit on the efficiency of an engine cycle. Practical engine cycles are irreversible and thus have inherently lower efficiency than the Carnot efficiency when operating at the same temperatures.One of the factors determining efficiency is the addition of to the working fluid in the cycle and its removal. The Carnot cycle achieves maximum efficiency because all the heat is added to the working fluid at the maximum temperature.

4.4.1 The Efficiency of Carnot's Cycle

The Carnot cycle is reversible representing the upper limit on the efficiency of an engine cycle. Practical engine cycles are irreversible and thus have inherently lower efficiency than the Carnot efficiency when operating at the same temperatures.One of the factors determining efficiency is the addition of to the working fluid in the cycle and its removal. The Carnot cycle achieves maximum efficiency because all the heat is added to the working fluid at the maximum temperature.



The Carnot engine cycle when acting as a heat engine consists of the following Reversible isothermal expansion of the gas at the "hot" temperature. Isentropic (reversible adiabatic) expansion of the gas. Reversible isothermal compression of the gas at the "cold" temperature. Isentropic compression of the gas.

4.4.2 Carnot's Ideal Heat Engine

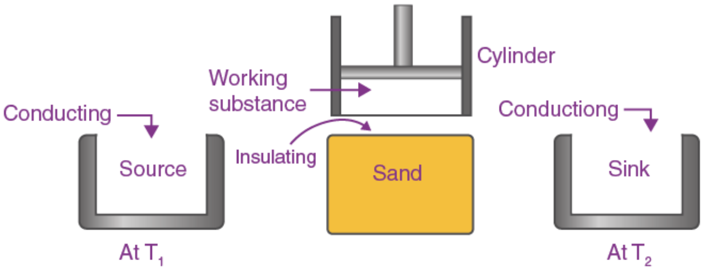


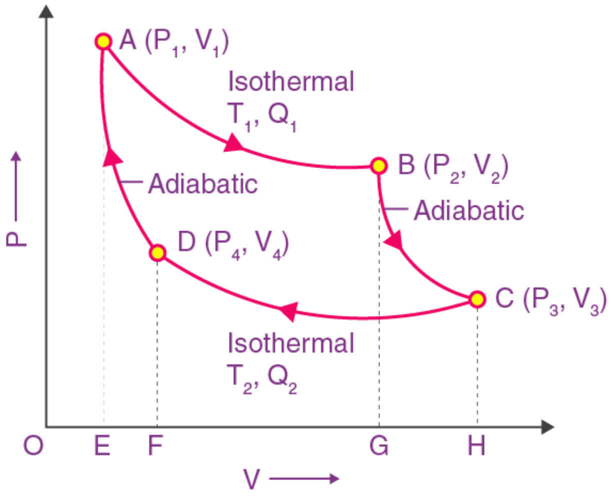
Figure 4.5 Carnot's Ideal Heat Engine

In 1824, the French engineer Sadi Carnot conceived a theoretical engine which is free from all practical imperfections. Such an engine cannot be realised in practice. It has maximum efficiency, and it is an ideal heat engine.

1. A cylinder having perfectly non-conducting walls, a perfectly conducting base, and is provided with a perfectly non-conducting piston which moves without friction in the cylinder. The cylinder contains one mole of perfect gas as the working substance.
2. Source A reservoir maintained at a constant temperature T1 from which the engine can draw heat by perfect conduction. It has an infinite thermal capacity, and any amount of heat can be drawn from it at constant temperature T1.
3. Heat insulating stand A perfectly non-conducting platform acts as a stand for adiabatic processes.
4. Sink A reservoir maintained at a constant lower temperature T2 (T2 ¡ T1) to which the heat engine can reject any amount of heat. The thermal capacity of the sink is infinite, so its temperature remains constant at T2, no matter how much heat is given to it.

4.4.3 Carnot’s Cycle and Its Stages

In order to obtain a continuous supply of work, the working substance is subjected to a cycle of quasi-static operations known as the Carnot cycle. The cycle, when it acts as a heat engine, consists of various steps, which are as follows.



1. Isothermal Expansion

The cylinder is first placed on the source so that the gas acquires the temperatures T_1 of the source. It is then allowed to undergo quasi-static expansion. As the gas expands, its temperature tends to fall. Heat passes into the cylinder through the perfectly conducting base, which is in contact with the source. The gas, therefore, undergoes slow isothermal expansion at the constant temperature T_1.

the working substance during isothermal expansion go from its initial state A (P_1, V_1, T_1) to state B (P_2, V_2, T_1) at constant temperature T1 along AB. In this process, the substance absorbs heat Q_1 from the source at T_1 and does work W1 given by,

$$Q_1 = W_1 = \int_{V1}^{V_2} PdV = RT1log_e \frac{V_2}{V_1} = areaABGEA$$

2. Adiabatic Expansion

The cylinder is now removed from the source and placed on the insulating stand. The gas is allowed to undergo slow adiabatic expansion, performing external work at the expense of its internal energy until its temperature falls to T_2, the same as that of the sink.

This operation is represented by the adiabatic BC, starting from state B (P_2, V_2, T_2) to state C (P_3, V_3, T_3). In this process, there is no transfer of heat, the temperature of the substance falls to T2, and it does some external work W2, given by,

$$W_2 = \int_{V1}^{V_2} P.dV = K \int_{V1}^{V_2} \frac{dV}{V^\gamma}$$

Because, during adiabatic process,

$$(PV^\gamma = constent = K)$$

$$= \frac{KV^{1-\gamma} - P_2V_2}{1-\gamma}$$

$$= \frac{P_3V_3 - P_2V_2}{1-\lambda}(P_2V_2^\gamma = P_3V_3^\gamma = K)$$

$$= \frac{RT_2 - RT_1}{1-\gamma}$$

$$= \frac{R(T_1 - T_2)}{\gamma - 1}$$

$$= AreaBCHGB$$

3. Isothermal Compression

The cylinder is now removed from the insulating stand and is placed on the sink, which is at a temperature of T_2. The piston is now very slowly moved inwards so that the work is done on the gas. The temperature tends to increase due to heat produced by compression since the conducting base of the cylinder is in contact with the sink, the heat developed passes to the sink, and the temperature of the gas remains constant at T_2. Thus, the gas undergoes isothermal compression at a constant temperature of T_2 and gives up some heat to the sink.

This operation is represented by the isothermal CD, starting from state (P_3, V_3, T_2) to state D (P_4, V_4, T_2). In this process, the substance rejects heat Q2 to the sink at T_2, and work W3 is done on the substance given by,

$$Q_2 = W_2 = \int_{V3}^{V_4} PdV = RT2log_e \frac{V_4}{V_3}$$

$$= -RTlog_e \frac{V_3}{V_4}$$

$$= areaCHFDC$$

(- ve sign indicates that work is done on the working substance)

4. Adiabatic Compression

The cylinder is now removed from the sink and again placed on the insulating stand. The piston is slowly moved inwards so that the gas in adiabatic compression is continued till the gas comes back to its original condition, i.e., state A (P_1, V_1, T_1), thus completing one full cycle.

This operation is represented by adiabatic DA, starting from D (P_4, V_4, T_2) to the final state A (P_1, V_1, T_1). In this process, work W4 is done on the substance and is given by,

$$W_4 = \int_{V4}^{V_1} P.dV$$

$$= -\frac{R(T_1 - T_2}{\gamma - 1}$$

$$AreaDFEAD$$

(- ve sign indicates that work is done on the working substance. Since W_2 and W_4 are equal and opposite, they cancel each other.)

4.4.4 Work Done by the Engine Per Cycle

During the above cycle, the working substance absorbs an amount of heat Q1 from the source and rejects Q2 to the sink.

Hence, the net amount of heat absorbed by the gas per cycle

$= Q_1 - Q_2$

The net amount of work done by the engine per cycle

$=W_{[}1] + W_2 + W_3 + W_{[}4]$

$= W_1 + W_3$ because

$= W_2 = -W_1$

From the graph, the net work done per cycle = area ABGEA + area BCHGB – area CHFDC – area DFEAD

= area ABCDA

Thus, the area enclosed by the Carnot's cycle consisting of two isothermals and two adiabatic gives the net amount of work done per cycle.

In the cyclic process,

Net heat absorbed = Net work done per cycle.

$Q_1 - Q_2 = W_1 + W_3$

$$RT_1 loge = \frac{V_2}{V_1} - RT_2 loge = \frac{V_3}{V_4}$$

Since the points A and D lie on the same adiabatic Da,

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)$$

Similarly, points B and C lie on the same adiabatic BC

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)$$

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

Or

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

Or

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting in equation, we get,

Net work done =

$$Q_1 - Q_2 = RT_1 log_e \frac{V_2}{V_1} - RT_2 log_e \frac{V_2}{V_1}$$

$$W = (Q_1 - Q_2) = R(T_1 - T_2) log_e \frac{V_2}{V_1}$$

Efficiency

The efficiency of the heat engine is the rate of the quantity of heat converted into work (useful output) per cycle to the total amount of heat absorbed per cycle.

$$Efficiency, \eta = \frac{Usefuloutput}{input} = \frac{W}{Q_1}$$

$$= \frac{(Q_1 - Q_2)}{Q_1}$$

$$\frac{R(T_1 - T_2) log_e \frac{V_2}{V_1}}{RT_1 log_e \frac{V_2}{V_1}}$$

$$\eta = \frac{(T_1 - T_2)}{T_1}$$

Or

$$\eta = 1 - \frac{(T_2}{T_1}$$

From the equation, we conclude that efficiency depends only upon the temperature of the source and sink, and is always less than unity. The efficiency is independent of the nature of the working substance.

From the equation,

$$\eta = 1 - \frac{(T_2}{T_1},$$

we get

$$\eta = 1, if T_2 = oK i.e.$$

the temperature of the sink is at absolute zero degrees. In practice, it is never possible to reach absolute zero, and hence 100% conversion of heat energy into mechanical work is not possible.

Again, the efficiency is minimum or zero, then $T_1 = T_2$, i.e., the temperature of the source is equal to the temperature of the sink, then $\eta = 0$, i.e., the engine does not work.

The Carnot heat engine is perfectly reversible. It can be operated in the reverse direction also. Then, it works like a refrigerator. The heat Q_2 is taken from the sink, and external work is done on the working substance and heat Q_2 is rejected to the source at a higher temperature (principle of a refrigerator).

the Carnot heat engine, the process of isothermal and adiabatic expansions and compressions are carried out very-very slowly, i.e., quasi-static. This is an ideal case. Any practical engine cannot satisfy these conditions. Therefore, all practical engines have an efficiency less than the Carnot engine.

4.5 Clausius Inequality

The Clausius Inequality is an extension of the Clausius statement of the Second Law of Thermodynamics, which asserts that heat does not spontaneously flow from a colder body to a hotter body. This statement highlights the concept of irreversibility in thermodynamic processes. The Clausius Inequality generalizes this principle to describe the behavior of heat exchanges in real-world, finite processes.

In mathematical terms, the Clausius Inequality can be expressed as follows:

$$\oint \frac{dQ}{T} \leq \Delta S_{total}$$

In this inequality:

$\oint$ represents the integral around a closed path in a thermodynamic cycle.

dQ is the incremental heat transfer.

T is the temperature at which heat is transferred.

ΔS_{total} is the total change in entropy of the system and its surroundings.

The Clausius Inequality reflects the fundamental tendency of natural processes to increase the total entropy of a system and its surroundings. It states that, during a real process, the sum of all the $\frac{dQ}{T}$ terms (representing the heat exchanges at various temperatures) is always less than or equal to the total change in entropy. In other words, the Clausius Inequality quantifies the irreversibility of processes and serves as a universal principle governing the flow of heat and energy.

4.5.1 Understanding the Components

To grasp the significance of the Clausius Inequality, it's essential to break down its components and explore how they contribute to our understanding of irreversible processes:

1. $\oint$ - Closed Path in a Thermodynamic Cycle: The integral $\oint$ represents the closed path taken in a thermodynamic cycle. This signifies that the Clausius Inequality can be applied to any cyclic process in which a working substance returns to its initial state. The integral allows for the assessment of the net effects on entropy during a complete cycle.

2. dQ - Incremental Heat Transfer: The dQ term represents incremental heat exchanges that occur during a process. Heat transfer (Q) is a fundamental component of thermodynamics, and dQ signifies small, incremental amounts of heat being transferred to or from a system. These transfers can occur at various temperatures.

3. T - Temperature at Which Heat Is Transferred: The T term in the Clausius Inequality is the absolute temperature at which heat is exchanged. Temperature is a crucial factor because it determines the quality of heat energy. Heat transfer at higher temperatures contributes more significantly to entropy changes.

4. ΔS_{total} - Total Change in Entropy: The ΔS_{total} term represents the total change in entropy of the system and its surroundings. It accounts for all entropy changes associated with the entire process, including those resulting from heat exchange, work done, and any other interactions.

4.5.2 Significance of the Clausius Inequality

Irreversibility: The Clausius Inequality quantifies the irreversibility of real-world processes. It acknowledges that, in most cases, processes are not fully reversible, and there is always a net increase in entropy.

Efficiency Analysis: The Clausius Inequality is used to assess the efficiency and performance of various thermodynamic devices and systems, including heat engines, refrigeration cycles, and chemical processes. It provides a tool for engineers and scientists to optimize these systems.

Heat Engines: In the analysis of heat engines, the Clausius Inequality highlights the limitations and irreversibility of these devices. It explains why no engine can have 100% efficiency and underscores the need for heat rejection to a lower-temperature reservoir.

Refrigeration and Air Conditioning: The Clausius Inequality is crucial in designing and optimizing refrigeration and air conditioning systems. It helps engineers assess the performance of these systems, particularly their coefficient of performance (COP).

Chemical Reactions: In chemistry, the Clausius Inequality is applied to assess the spontaneity and feasibility of chemical reactions. Reactions that lead to an increase in total entropy are more likely to occur.

Environmental Science: The Clausius Inequality plays a role in environmental science, particularly in the context of climate change and the dispersion of pollutants. It is used to model the behavior of greenhouse gases and assess the impact of human activities on global entropy and disorder.

Information Theory: The principles of entropy are also applicable in information theory, where entropy is used to measure uncertainty and information content. The Clausius Inequality can be related to the transmission of information and data loss in communication systems.

Philosophical and Cosmological Implications: The Second Law of Thermodynamics, with its associated concepts of entropy and the Clausius Inequality, has philosophical and cosmological implications. It raises questions about the nature of time, the ultimate fate of the universe, and the arrow of time.

4.5.3 Practical Applications

- ✧ Engineering: Engineers use the Clausius Inequality to assess the efficiency and performance of various energy systems, such as heat engines, refrigeration cycles, and power plants.
- ✧ Environmental Science: Environmental scientists apply the Clausius Inequality to model and predict the behavior of pollutants and greenhouse gases in the atmosphere. It is crucial in climate change research and air quality assessment.
- ✧ Information Technology: Information technologists use concepts related to entropy and the Clausius Inequality in data compression, error correction, and information security.
- ✧ Chemistry: In chemical kinetics, the Clausius Inequality is used to analyze the spontaneity of reactions and determine the conditions under which they will proceed.
- ✧ Astronomy and Cosmology: The Second Law of Thermodynamics, including the Clausius Inequality, is relevant in understanding the behavior of matter

in astrophysical environments and in cosmological models of the universe's evolution.

4.6 Entropy Change for Reversible and Irreversible Processes

In a reversible process, the entropy change of the system and surroundings are equal and opposite. In an irreversible process, we generate extra entropy. We can assign that ”extra” irreversible entropy either to the system or to the surroundings.

1. Reversible Process

In a reversible process, the system undergoes a series of infinitesimally small changes in a manner that it can return to its initial state by reversing these changes without leaving any trace. The entropy change (ΔS) for a reversible process is given by the formula:

$$\Delta S = \int \left(\frac{dQ_{rev}}{T}\right)$$

In this equation, ΔS represents the change in entropy, dQ_{rev} is the differential amount of heat exchanged during each infinitesimal step of the process, and T is the absolute temperature at which this heat exchange occurs. The integral sums up all these infinitesimal changes. Entropy change for a reversible process is path-independent, meaning it only depends on the initial and final states of the system.

2. Irreversible Process

In an irreversible process, the system undergoes changes that cannot be exactly reversed, and the system does not return to its initial state. The entropy change (ΔS) for an irreversible process can be determined by considering the actual heat transfer and temperature changes along the path. However, it's more challenging to calculate in many cases, as it depends on the specifics of the process and may require experimental data. For an idealized case where heat is transferred at constant temperature, you can calculate the entropy change using the formula:

$$\Delta S = \frac{Q_{irrev}}{T}$$

In this equation, ΔS is the change in entropy, Q_{irrev} is the heat transferred in the irreversible process, and T is the temperature at which the heat transfer occurs.

4.7 Entropy Principle and Applications

Entropy is a scientific concept that measures the disorder of a system. It's also a measure of how much energy in a system is not available to do work. As a system becomes more disordered, its energy becomes more evenly distributed and less able to do work. Entropy is an extensive property of a thermodynamic system, which means its value changes depending on the amount of matter that is present. In equations, entropy is usually denoted by the letter S and has units of joules per kelvin (J·K^{-1}).

Entropy, the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecular motion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system. The concept of entropy provides deep insight into the direction of spontaneous change for many everyday phenomena. Its introduction by the German physicist Rudolf Clausius in 1850 is a highlight of 19th-century physics. The idea of entropy provides a mathematical way to encode the intuitive notion of which processes are impossible, even though they would not violate the fundamental law of conservation of energy. For example, a block of ice placed on a hot stove surely melts, while the stove grows cooler. Such a process is called irreversible because no slight change will cause the melted water to turn back into ice while the stove grows hotter. In contrast, a block of ice placed in an ice-water bath will either thaw a little more or freeze a little more, depending on whether a small amount of heat is added to or subtracted from the system. Such a process is reversible because only an infinitesimal amount of heat is needed to change its direction from progressive freezing to progressive thawing. Similarly, compressed gas confined in a cylinder could either expand freely into the atmosphere if a valve were opened (an irreversible process), or it could do useful work by pushing a moveable piston against the force needed to confine the gas. The latter process is reversible because only a slight increase in the restraining force could reverse the direction of the process from expansion to compression. For reversible processes the system is in equilibrium with its environment, while for irreversible processes it is not.

4.7.1 Entropy Principle

Direction of Natural Processes: The increase in entropy is closely related to the directionality of natural processes. In a closed system, spontaneous processes tend to move towards a state of higher entropy. For example, ice melting into water is a process that increases the entropy of the system because the water molecules have greater freedom of movement and are more disordered than the solid ice.

Reversibility and Irreversibility: The concept of reversible and irreversible processes is connected to entropy. Reversible processes are those that can be undone without leaving any trace, and their entropy change is zero. Irreversible processes, on the other hand, result in an increase in entropy. For example, the expansion of a gas into a vacuum is an irreversible process, and it leads to an increase in entropy.

Entropy as a Measure of Energy Quality: The concept of entropy has been used to describe the quality of energy. High-quality energy has low entropy, meaning it is concentrated and can be easily converted into useful work. Low-quality energy, on the other hand, has high entropy, and it is less useful for performing work.

4.7.2 Applications of the entropy

- Second Law of Thermodynamics: The second law of thermodynamics states that the total entropy of an isolated system always increases over time. This law is often expressed as $\Delta S \geq 0$ for any spontaneous process, where ΔS is the change in entropy. It serves as a fundamental principle that defines the direction of natural processes, emphasizing the concept of irreversibility.

- Heat Transfer: Entropy is used to analyze and quantify heat transfer processes. In the context of heat transfer, the change in entropy is related to the heat exchanged. For an ideal reversible process, the change in entropy is given by $\Delta S = Q/T$, where ΔS is the change in entropy, Q is the heat transfer, and T is the temperature.

- Carnot Efficiency: The Carnot cycle, which consists of two reversible isothermal processes and two reversible adiabatic processes, represents the maximum efficiency that any heat engine operating between two temperature reservoirs can achieve. Entropy plays a crucial role in deriving the Carnot efficiency, which is equal to 1 - (T_c/T_h), where T_c and Th are the absolute temperatures of the cold and hot reservoirs, respectively.

- Phase Transitions: Entropy is used to describe phase transitions, such as the transition from a solid to a liquid or from a liquid to a gas. The change in entropy during a phase transition is related to the heat of fusion or vaporization. It helps determine the conditions under which phase changes occur.

- Chemical Reactions: In chemical thermodynamics, entropy is used to analyze chemical reactions. The change in entropy during a chemical reaction (ΔS_{rxn}) can indicate whether the reaction results in an increase or decrease in the disorder of the system. A positive ΔS_{rxn} suggests an increase in disorder (entropy) in the system.

- Entropy in Heat Engines: Entropy is used to analyze the efficiency and performance of heat engines, such as steam engines, gas turbines, and internal combustion engines. The efficiency of these engines is limited by the second law of thermodynamics, which relates to the increase in entropy during energy conversion.

- Entropy Generation: Entropy generation is a concept used to quantify the irreversibilities in real processes. It is related to the increase in entropy due to dissipative effects, like friction, heat conduction, and fluid viscosity. Minimizing entropy generation is a key consideration in engineering and design.

- Refrigeration and Heat Pumps: The performance of refrigeration and heat pump systems is analyzed using the concept of entropy. Entropy changes in the refrigerant during the various stages of the cycle are crucial in determining the efficiency and capacity of these systems.

CHAPTER 5

GASES AND GAS MIXTURES

the properties of gases is that they mix with each other. When they do so, they become a solution a homogeneous mixture. Some of the properties of gas mixtures are easy to determine if we know the composition of the gases in the mix. In gas mixtures, each component in the gas phase can be treated separately. In thermodynamics, the mixing of real gases at constant temperature and pressure is similar to the mixing of ideal gases. The fundamental result is an expression for the Gibbs energy of mixing, ΔmixG. From this, expressions for the entropy, enthalpy, and volume of mixing can be derived.

Gases are a state of matter characterized by their low density and ability to fill the volume of their container. In thermodynamics, gases are often described using the ideal gas law, which relates pressure (P), volume (V), the number of moles (n), the gas constant (R), and temperature (T) through the equation PV = nRT. Ideal gases follow this law precisely at low pressures and high temperatures, but real gases may deviate from ideal behavior, especially at high pressures and low temperatures.

Gas Mixtures Many real-world applications involve gas mixtures rather than pure gases. Gas mixtures consist of multiple gas components, each contributing to the overall properties of the mixture. Dalton's law of partial pressures states that the total pressure of a gas mixture is the sum of the partial pressures of its individual components. Amagat's law deals with the volume properties of gas mixtures. The behavior of gas mixtures can vary from ideal to non-ideal, and thermodynamics provides tools to analyze their properties and interactions.

5.1 Ideal Gas Law

The ideal gas law also called the general gas equation, is an equation that provides the relation among the various parameters of the gas i.e. they provide the relation among pressure(P), temperature(T), and Volume(V) of the gas. It is a combination of Charles's law, Boyle's Law, Avogadro's law, and Gay-Lussac's law. This law was first stated by the French physicist Benoit Paul Émile Clapeyron in 1834.

The Ideal Gas Law, often denoted as PV = nRT, is a fundamental equation in thermodynamics and the study of gases. It describes the behavior of ideal gases under a wide range of conditions and is a simplified model that provides valuable insights into how gases respond to changes in pressure, volume, temperature, and the number of gas particles.

The Ideal Gas Law Equation:

PV = nRT

Where:

P is the pressure of the gas.

V is the volume of the gas.

n is the number of moles of the gas.

R is the universal gas constant.

T is the absolute temperature of the gas in Kelvin.

Let's break down the components of this equation and delve into its significance:

Pressure (P): Pressure is a measure of the force exerted per unit area and is typically expressed in units such as Pascals (Pa), atmospheres (atm), or millimeters of mercury (mmHg). It represents the force that gas molecules exert on the walls of their container due to their random motion.

Volume (V): Volume represents the physical space occupied by the gas and is usually measured in liters (L) or cubic meters (m^3). The volume can vary depending on the container's size and shape.

Number of Moles (n): The number of moles is a measure of the quantity of gas and is expressed in moles (mol). A mole is a unit that contains approximately 6.022 x 10^{23} entities (Avogadro's number), which could be atoms, molecules, or ions.

Universal Gas Constant (R): The universal gas constant, denoted as ”R,” is a constant of proportionality that depends on the units used for pressure, volume, and temperature. The value of R varies with the unit system used. In the International System of Units (SI), it is approximately 8.314 J/(mol·K).

Absolute Temperature (T): Temperature is measured in Kelvin (K), an absolute temperature scale where 0 K represents absolute zero, the lowest theoretically possible temperature. In the Ideal Gas Law, temperature is always expressed in Kelvin to maintain consistency with other units. The Kelvin scale is defined as Celsius temperature plus 273.15.

Assumptions of the Ideal Gas Law

The Ideal Gas Law is based on several simplifying assumptions, and it is essential to understand these assumptions when using the equation: The equation assumes that the gas consists of a large number of tiny particles (atoms or molecules) that are in constant random motion. The size of these particles is negligible compared to the volume of the gas and the distance between them. It is assumed that the volume occupied by the gas particles is relatively small compared to the volume of the container. In other words, the volume of the gas particles themselves is considered negligible. Ideal gases do not experience intermolecular forces, such as attraction or repulsion between particles. This assumption simplifies calculations but doesn’t hold for real gases, especially at high pressures and low temperatures. The Ideal Gas Law works best at high temperatures and low pressures. Under these conditions, real gases tend to approximate ideal behavior. At lower temperatures or higher pressures, deviations from ideal behavior become more pronounced. The equation treats all gas particles as having the same molar mass. In reality, gas mixtures can have various gas species with different molar masses. However, this assumption is valid for many practical applications.

5.2 Real Gases

real gas usually refers to a gas that does not behave like an ideal gas. Their behaviour can be explained by the interactions between the gaseous molecules. These intermolecular interactions between the gas particles is the reason why real gases do not adhere to the ideal gas law. Real gases can be defined as non-ideal gases whose molecules occupy a given amount of space and have the ability to interact with each other.

It is important to understand that almost all gases can behave as real gases when they are placed in appropriate conditions. For example, under standard conditions of temperature and pressure (usually abbreviated as STP), the behaviour of air can be estimated with the help of the ideal gas law. This is because air behaves like an ideal gas under standard conditions for temperature and pressure. However, when the pressure applied to the air is increased to a very high magnitude, the same air starts to exhibit notable deviations from the ideal gas law and begins to exhibit the behaviour similar to that of a real gas.

Furthermore, any increase in the absolute temperature of the gas can also have a similar effect. This is because an increase in the absolute temperature of the gas results in an increase in the average kinetic energy of the molecules of the gas. This, in turn, results in an increase in the number of interactions between the molecules of the gas. Therefore, an increase in the absolute temperature of the air can also trigger notable deviations from ideal behaviour and make it a real gas.

Thus, almost all gas can behave like ideal gases as well as real gases. When the conditions are relatively ambient, most gases are known to exhibit almost ideal behaviour. However, under relatively extreme conditions in which either the temperature of the gas is raised to a very high value, the pressure on the gas is raised to a very high value, or both the temperature and the pressure associated with the gas is raised to extremely high values, most gases will deviate from ideal behaviour and become real gases.

Real gases are nonideal gases whose molecules occupy space and have interactions; consequently, they do not adhere to the ideal gas law. To understand the behaviour of real gases, the following must be taken into account:

- compressibility effects
- variable specific heat capacity
- van der Waals forces
- non-equilibrium thermodynamic effects

issues with molecular dissociation and elementary reactions with variable composition For most applications, such a detailed analysis is unnecessary, and the ideal gas approximation can be used with reasonable accuracy. On the other hand, real-gas models have to be used near the condensation point of gases, near critical points, at very high pressures, to explain the Joule–Thomson effect, and in other less usual cases. The deviation from ideality can be described by the compressibility factor Z

5.2.1 Characteristics of Real Gases

Intermolecular Forces: Real gases consist of molecules or atoms that interact with each other through intermolecular forces, such as van der Waals forces (London dispersion forces), dipole-dipole interactions, and hydrogen bonding. These forces are responsible for the deviations from ideal behavior.

Molecular Volume: Unlike the assumption of ideal gases, real gas molecules have finite volumes that occupy space. In high-density conditions, the actual volume occupied by gas molecules becomes significant and affects gas behavior.

Compressibility: Real gases exhibit compressibility, which means they can be compressed to a smaller volume than predicted by the ideal gas law. At high pressures, intermolecular forces cause the gas to occupy less volume than expected.

Temperature and Pressure Dependencies: The deviations of real gases from ideal behavior are more pronounced at low temperatures and high pressures. These are the conditions where intermolecular forces have a stronger influence.

Specific Gases: Different gases exhibit different levels of deviation from ideal behavior. For example, noble gases like helium and neon show behavior that closely approximates ideal gases under most conditions, while other gases, such as water vapor and carbon dioxide, exhibit significant deviations.

5.2.2 Causes of Deviations from Ideal Behavior

The deviations of real gases from ideal behavior can be attributed to several factors:

Intermolecular Forces: Interactions between gas molecules are the primary cause of deviations. These forces lead to attraction and repulsion between molecules, affecting their behavior. At low temperatures and high pressures, these forces become more significant.

Volume Exclusion: Real gas molecules have finite volumes that occupy space. As the density of a gas increases (at higher pressures), the actual volume occupied by gas molecules becomes more substantial compared to the container's volume. This leads to a reduction in available space for gas particles to move freely.

Kinetic Molecular Theory: The kinetic molecular theory, which underlies the ideal gas law, assumes that gas molecules have zero volume and do not experience intermolecular forces. Deviations from this idealized model occur when these assumptions break down.

Critical Point: Each gas has a critical point, characterized by a critical temperature and a critical pressure. At temperatures and pressures above these critical values, gases behave more like ideal gases. Below the critical point, deviations from ideal behavior are more significant.

Real Gas Constants: Some gases, particularly those with a high molecular weight, exhibit deviations from ideal behavior even at low pressures and moderate temperatures. These gases require specific real gas constants to account for these deviations.

5.2.3 Equations of State for Real Gases

To account for the deviations of real gases from ideal behavior, several equations of state have been developed. These equations introduce correction factors that consider intermolecular forces, molecular volume, and other factors affecting real gas behavior.

1. Van der Waals Equation

Proposed by Johannes Diderik van der Waals, this equation of state accounts for the finite size of gas molecules and intermolecular forces. It is given by

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

P is the pressure.

V is the volume.

n is the number of moles.

T is the absolute temperature.

a and b are Van der Waals constants specific to each gas.

The term (an$^2/V^2$) corrects for the attractive forces, and the term nb corrects for the molecular volume.

Real gases are often modeled by taking into account their molar weight and molar volume

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

or alternatively:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Where p is the pressure, T is the temperature, R the ideal gas constant, and V_m the molar volume. a and b are parameters that are determined empirically for each gas, but are sometimes estimated from their critical temperature (T_c) and critical pressure (p_c) using these relations:

$$a = \frac{27R^2T_c^2}{64p_c}$$

$$b = \frac{RT_c}{8p_c}$$

The constants at critical point can be expressed as functions of the parameters a, b:

$$p_c = \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27bR}$$

$$V_{m,c} = 3b$$

$$z_c = \frac{3}{8}$$

With the reduced properties

$$P_r = \frac{P}{P_c}$$

$$V_r = \frac{V_m}{V_{m,c}}$$

$$T_r = \frac{T}{T_c}$$

the equation can be written in the reduced form:

$$p_r = \frac{8}{3}\frac{T_r}{V_r - \frac{1}{3}} - \frac{3}{V_r^2}$$

2. Redlich-Kwong Equation

The Redlich-Kwong equation is another equation of state that considers the finite size of gas molecules and intermolecular forces. It is given by:

$$P = \frac{nRT}{V - b} - \frac{a}{\sqrt{T}V(V + b)}$$

Where:

P is the pressure.

V is the volume.

n is the number of moles.

T is the absolute temperature.

a and b are Redlich-Kwong constants specific to each gas.

This equation incorporates temperature-dependent corrections to account for deviations from ideal behavior.

The Redlich–Kwong equation is another two-parameter equation that is used to model real gases. It is almost always more accurate than the van der Waals equation, and

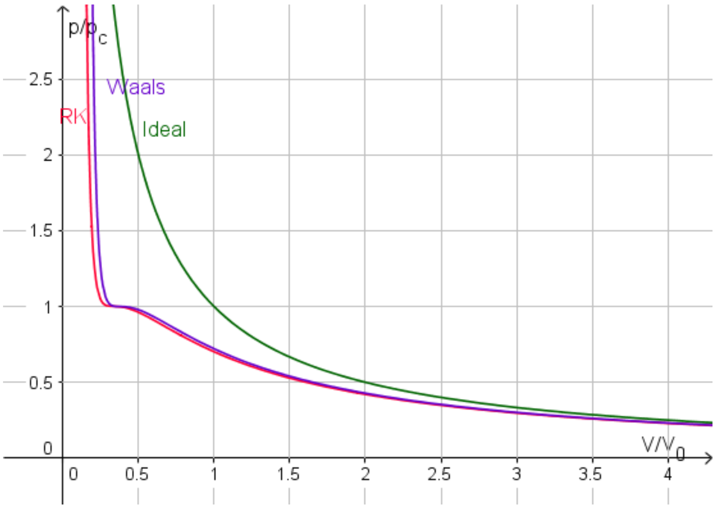


Figure 5.1 Critical isotherm for Redlich-Kwong model in comparison to van-der-Waals model and ideal gas (with V0=RT_c/p_c)

often more accurate than some equations with more than two parameters. The equation is

$$RT = \left(p + \frac{a}{\sqrt{T V_m}(V_m+b)}\right)(V_m + b)$$

or alternatively:

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T V_m}(V_m + b)}$$

where a and b are two empirical parameters that are not the same parameters as in the van der Waals equation. These parameters can be determined:

$$a = 0.42748\frac{R^2 T_c^{\frac{5}{2}}}{p_c}$$

$$b = 0.08664\frac{RT_c}{p_c}$$

The constants at critical point can be expressed as functions of the parameters a, b:

$$P_c = \frac{(\sqrt[3]{2} - 1)^{\frac{7}{3}}}{3^{\frac{1}{3}}} R^{\frac{1}{3}} \frac{a^{\frac{2}{3}}}{b^{\frac{5}{3}}}$$

$$T_c = 3^{\frac{2}{3}}((\sqrt[3]{2} - 1)^{\frac{4}{3}}(\frac{a}{bR})^{\frac{2}{3}}$$

$$V_{m,c} = \frac{b}{\sqrt[3]{2} - 1}$$

$$Z_c = \frac{1}{3}$$

Using

$$P_r = \frac{p}{P_c}$$

$$V_r = \frac{V_m}{P_{m,c}}$$

$$T_r = \frac{T}{T_c}$$

the equation of state can be written in the reduced form:

$$P_r = \frac{3T_r}{V_r - b_{\prime}} - \frac{1}{b_{\prime}\sqrt{T_r V_r}(V_r + b_{\prime}}$$

with

$$b_{\prime} = \sqrt[3]{2} - 1 \approx 0.26$$

3. Peng-Robinson Equation

The Peng-Robinson equation is a more complex equation of state that incorporates more accurate representations of molecular behavior. It accounts for the molecular size, shape, and intermolecular forces. It is often used in hydrocarbon systems. These equations, among others, provide more accurate representations of real gas behavior under a wide range of conditions. The specific equation chosen depends on the gas in question and the conditions of the system. Peng–Robinson equation of state has the interesting property being useful in modeling some liquids as well as real gases.

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(v_m - b)}$$

Gas	A0	a	B0	b	c
Air	131.8441	0.01931	0.04611	-0.001101	4.34×10^4
Argon, Ar	130.7802	0.02328	0.03931	0.0	5.99×10^4
Carbon dioxide, CO2	507.2836	0.07132	0.10476	0.07235	6.60×10^5
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, H2	20.0117	-0.00506	0.02096	-0.04359	504
Nitrogen, N2	136.2315	0.02617	0.05046	-0.00691	4.20×10^4
Oxygen, O2	151.0857	0.02562	0.04624	0.004208	4.80×10^4

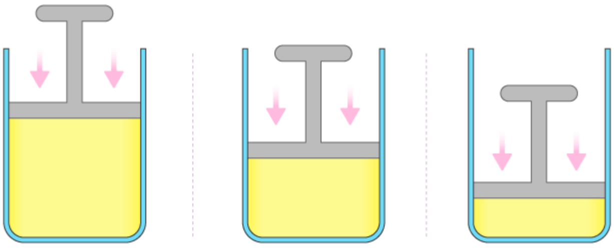
Table 5.1 Gas

5.3 Properties of Gases

Gasses do not possess any definite volume or shape. They totally fill all the space accessible to them. The characteristic or properties of gases to fill the available volume within a container is the result of the freedom that gas particles have to move everywhere in the accessible space. This autonomy of movement of gaseous molecules is because of the very weak binding forces amidst molecules. In other words, their intermolecular forces are very weak. Because of this, the molecules of a gas are in a continuous motion and are related to high velocity and therefore high kinetic energy.

1. Compressibility

Particles of gas have huge intermolecular spaces in the midst of them. By the exertion of pressure, much of this space can be diminished and the particles are brought closer. Thus, the volume of gas can be hugely reduced. This is termed as compressing the gas (Figure).



Compression of a gas by applying pressure

When we increase the pressure from 1 atmosphere to 2 atmospheres, the volume of gas gets compacted to half whereas if the volume of water was made to decrease similarly, it would reduce only by 0.00001 parts. Decreasing the temperature can also decrease the volume of a gas. When the temperature is reduced, there is a lesser amount of energy in the particles; their mobility is diminished and they move less away from each other. As a consequence, the intermolecular pull becomes more prominent and the particles come closer. This decreases the volume of the gas.

2. Expansibility

When pressure is exerted on gas, it contracts. On the other hand, when pressure is freed, the gas expands. When the temperature is augmented, the constituent particles gain more energy, travel faster and move away from each other. Consequently, the intermolecular pull becomes less prominent. The gas's volume increases.

3. Diffusibility

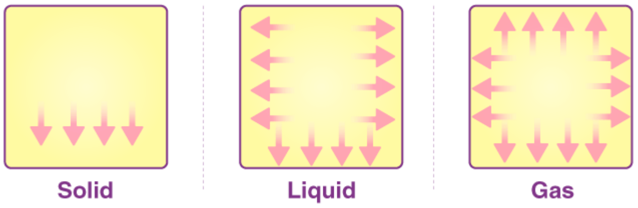
The molecules of the gas are in perpetual motion, at a very high velocity. There is a huge amount of intermolecular space amid the molecules. When two gases are mixed, particles of one gas can effortlessly pass through the intermolecular space of the other gas. As an outcome both the gases get completely and consistently mixed. Thus, a mixture of gases at all times remains homogeneous.

4. Low Density

Since gases have large intermolecular spaces, they have very large volumes when compared to their mass. Therefore, they have less densities. If 1 ml of water at 39.2oF is transformed into steam at 212oF and 1-atmosphere pressure, it will occupy a volume of 1700 ml.

5. Exertion of Pressure

Solids exert pressure only in the downward direction. Liquids apply pressure downward as well as to the sides. But gases apply pressure in all directions (a good sample is a balloon). This pressure is because of the bombardment of the particles against the walls of the vessel (Figure).



Exertion of pressure

5.4 Compressibility Factor Charts

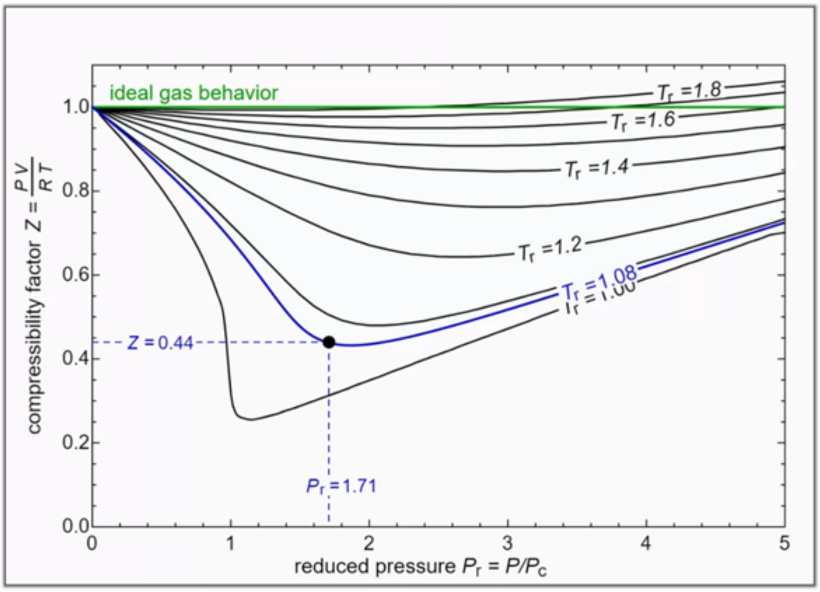


Figure 5.2 Compressibility Factor Charts

The compressibility factor chart plots the compressibility factor Z, equal to PV/RT, where V is the volume per mole, versus the reduced pressure P_r for several values of the reduced temperature T_r. The reduced pressure and temperature are defined by P_r = P/P_C and T_r = T/T_C, respectively, where P_C is the critical pressure and T_C is the critical temperature. Use buttons to select one of five molecules, and move the black dot to display the compressibility factor curve (blue) for any value of T_r between 1.0 and 1.8. The Z and Pr values for the location of the black dot are displayed on the chart. For an ideal gas, Z = 1 (green line).

5.5 Behavior of Gas Mixtures

In gas mixtures, each component in the gas phase can be treated separately. Each component of the mixture shares the same temperature and volume. (Remember that gases expand to fill the volume of their container; gases in a mixture do that as well.) However, each gas has its own pressure.

Dalton's Law of Partial Pressures

Dalton's Law is a fundamental concept that describes the behavior of gas mixtures. It states that in a mixture of gases, the total pressure is the sum of the partial pressures of each individual gas in the mixture. This law is named after the English chemist and physicist John Dalton, who formulated it in the early 19th century.

Mathematically, Dalton's Law can be expressed as follows:

$P_{total} = P_1 + P_2 + ... + P_n$

Where:

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

P_1, P_2, ..., P_n are the partial pressures of each gas component in the mixture.

The partial pressure of a specific gas component is the pressure that gas would exert if it occupied the entire volume by itself at the same temperature. This law is particularly useful when dealing with gas mixtures in various applications, such as in chemical reactions, industrial processes, and environmental science.

Mole Fraction

The mole fraction (X) of a specific gas component in a mixture is a crucial concept when dealing with gas mixtures. It represents the ratio of the number of moles of that gas to the total number of moles in the mixture. Mole fraction is a dimensionless quantity that provides insight into the composition of the mixture.

Mathematically, the mole fraction of a gas component is calculated as:

$\mathrm{X} = n_i / n_{total}$

Where:

X is the mole fraction of the gas component.

n_i is the number of moles of the specific gas component.

n_{total} is the total number of moles in the mixture.

Mole fractions are essential for determining the relative abundance of each gas component in the mixture. They are used in various thermodynamic calculations, such as calculating partial pressures, vapor-liquid equilibrium, and phase diagrams.

Partial Volume

The partial volume of a gas component in a mixture is the volume that the gas would occupy if it were isolated from the other gases in the mixture at the same temperature and pressure. It can be calculated using the mole fraction and the total volume of the gas mixture.

Mathematically, the partial volume (V_i) is given by:

$V_i = X_i * V_{total}$

Where:

V_i is the partial volume of the gas component.

X_i is the mole fraction of the gas component.

V_{total} is the total volume of the gas mixture.

Partial volumes are useful in various applications, such as in the design of gas storage systems, chemical reactions, and in understanding the behavior of gases in confined spaces.

Real Gas Behavior

While the ideal gas law is a useful approximation for many gases at low pressures and high temperatures, real gases deviate from ideal behavior under certain conditions. These deviations become more significant at high pressures and low temperatures. Real gas behavior is described by various equations of state, which take into account the finite size of gas molecules and the intermolecular forces between them. One of the most well-known equations of state for real gases is the Van der Waals equation, proposed by Johannes Diderik van der Waals in the late 19th century. The Van der Waals equation corrects for the volume occupied by gas molecules and the attractive forces between them. It is expressed as follows:

$[P + a(n/V)^2] * (V - nb) = nRT$

Where:

P is the pressure of the gas.

V is the volume of the gas.

n is the number of moles of gas.

T is the temperature.

a and b are constants specific to the gas.

The Van der Waals equation and similar equations of state provide a more accurate representation of gas behavior under non-ideal conditions, and they are essential for engineering applications involving high-pressure gases, such as in the oil and gas industry and chemical manufacturing.

Gas Mixtures in Chemical Reactions

Gas mixtures play a crucial role in chemical reactions. The stoichiometry of a chemical reaction, which describes the quantitative relationship between reactants and products, often involves gases. By using the principles discussed earlier, such as Dalton's Law, the ideal gas law, mole fractions, and partial pressures, it is possible to determine the behavior of gas mixtures in chemical reactions. For example, consider the combustion of methane (CH4) in oxygen (O2) to produce carbon dioxide (CO2) and water (H2O):

$CH4 + 2O2 \rightarrow CO2 + 2H2O$

In this reaction, methane and oxygen are both gases. The stoichiometry of the reaction tells us that one mole of methane reacts with two moles of oxygen to produce one mole of carbon dioxide and two moles of water. To calculate the volume of each gas involved in the reaction, we can use the ideal gas law, mole fractions, and the stoichiometry of the reaction. Let's assume we have 1 mole of methane and 2 moles of oxygen in a 1-liter container at a certain temperature and pressure. We can use the ideal gas law to calculate the partial pressures of each gas and determine the total pressure of the mixture. Then, by applying Dalton's Law, we can calculate the partial pressure of carbon dioxide and water vapor produced in the reaction. In this way, we can predict the behavior of gas mixtures in various chemical reactions, enabling us to design and optimize chemical processes and calculate reaction yields.

5.6 Psychrometrics

A psychrometric chart is an attempt to show the relationships in many of the properties of moist air. The chart shows all of the following properties: dry bulb temperature, wet bulb temperature, relative humidity, dew point temperature, humidity ratio, total heat (enthalpy) and specific volume.

5.6.1 The Importance of Psychrometrics

The properties of air, especially its moisture content, play a crucial role in many applications. Psychrometrics provides the tools and principles needed to understand and control these properties effectively. It is particularly important for several reasons:

Human Comfort: Achieving and maintaining indoor comfort in buildings is a primary application of psychrometrics. Understanding air temperature, humidity, and air movement is essential for creating spaces where people can work, live, and relax comfortably.

HVAC System Design: Heating, ventilation, and air conditioning (HVAC) systems are designed based on psychrometric principles. Proper design ensures efficient energy usage and the control of temperature and humidity levels in buildings.

Industrial Processes: Many industrial processes, such as food production, pharmaceuticals, and manufacturing, require precise control of air conditions. Psychrometrics helps in designing and optimizing these processes to ensure product quality and safety.

Energy Efficiency: Optimizing air properties can lead to significant energy savings. By understanding psychrometrics, engineers can design systems that use less energy to achieve the desired indoor conditions.

5.6.2 Psychrometric Properties

Psychrometrics deals with several key properties of moist air, which include:

Dry Bulb Temperature (DBT): This is the temperature of the air as measured with a standard thermometer.

Wet Bulb Temperature (WBT): WBT is the lowest temperature that can be reached by evaporatively cooling the air at constant pressure.

Dew Point Temperature (DPT): DPT is the temperature at which air becomes saturated with moisture, leading to the condensation of water vapor.

Relative Humidity (RH): RH is the ratio of the actual moisture content in the air to the maximum moisture content it can hold at a given temperature.

Specific Humidity (SH): SH is the mass of water vapor present in a unit mass of dry air.

Enthalpy (H): Enthalpy is a measure of the total energy content of the air, including sensible heat (temperature-related) and latent heat (moisture-related).

5.6.3 Psychrometric Processes

Psychrometric processes describe changes in air properties that occur during various HVAC and environmental control activities. Some common processes include:

Heating: When air is heated, its dry bulb temperature increases while its specific humidity remains constant.

Cooling and Dehumidification: Cooling air at constant pressure reduces both the dry bulb temperature and specific humidity, leading to an increase in relative humidity.

Humidification: Adding moisture to air increases its specific humidity and relative humidity while keeping the dry bulb temperature constant.

Mixing: When two air streams with different properties are mixed, the resulting state can be determined using psychrometric charts.

5.6.4 Comfort and Indoor Air Quality

In the context of human comfort, psychrometrics is vital. Several factors, including temperature, relative humidity, and air movement, contribute to how people perceive and experience their environment. The American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE) has defined specific comfort zones that take these factors into account, helping engineers design HVAC systems that maintain comfortable conditions. The comfort zone is typically represented on a psychrometric chart, showing the range of conditions where most people feel comfortable. Deviations from this zone can lead to discomfort, health issues, and decreased productivity.

5.6.5 Energy Efficiency and Sustainability

Psychrometrics also plays a significant role in enhancing energy efficiency and sustainability. By optimizing HVAC systems and controlling air properties effectively, energy consumption can be reduced. This is essential in a world where environmental concerns and rising energy costs are driving the demand for sustainable building design and operation. Advanced control strategies, such as demand-controlled ventilation and enthalpy-based cooling, rely on psychrometric principles to minimize energy consumption while maintaining indoor comfort and air quality.

5.6.6 Psychrometric Charts

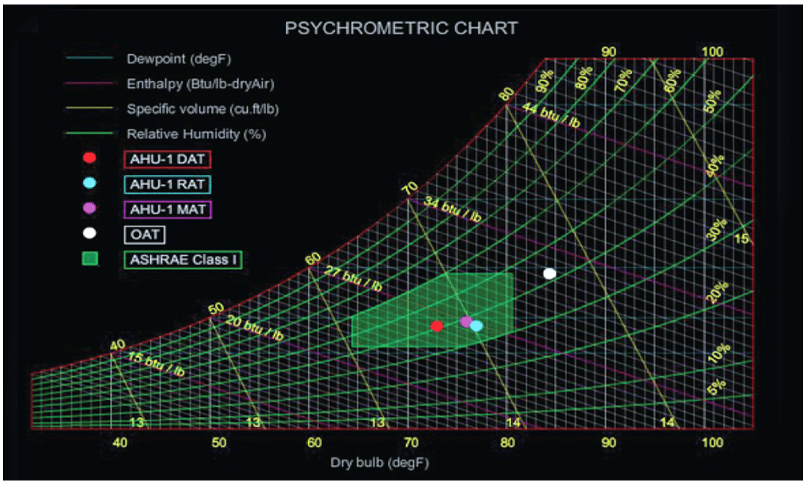


Figure 5.3 Psychrometric Charts

Psychrometric charts are graphical representations of air properties, making it easier to analyze and visualize changes in air conditions during different processes. These charts display relationships between dry bulb temperature, wet bulb temperature, dew point temperature, specific humidity, and enthalpy. Understanding a psychrometric chart allows engineers and designers to assess the impact of HVAC system changes, identify opportunities for energy savings, and select appropriate equipment and strategies to achieve desired indoor conditions.

5.7 Dalton's and Amagat's Laws

5.7.1 Dalton's Law

Dalton's Law Formula explains the behavior of gases and more precisely, for mixtures of gases. English chemist John Dalton first published it in the year 1802. Besides, the law state that when there is a blend of inactive gases (there is no reaction between them), the total pressure that it applies is equal to the amount of the partial pressure of each gas. We know this law by another name that is Dalton's law of partial pressures. Dalton's law, the statement that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual component gases. The partial pressure is the pressure that each gas would exert if it alone occupied the volume of the mixture at the same temperature. This empirical relation was stated by the English chemist John Dalton in 1801. It follows from the kinetic theory of gases under the assumption of an ideal (perfect) gas and assumes no chemical interaction between the component gases. It is approximately valid for real gases at sufficiently low pressures and high temperatures.

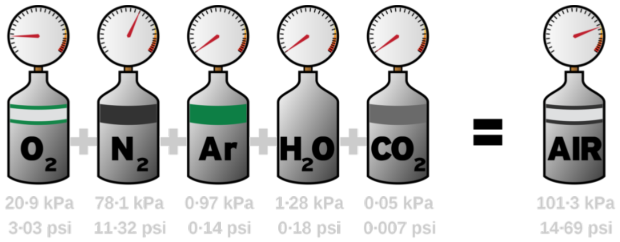


Figure 5.4 Dalton's Law

it is a mixture of non-reacting gases, the total pressure exercised is equal to the sum of the partial pressures of the individual gases. Also, this law is related to the ideal gas law.

Dalton's Law Formula

For a mixture of n number of gases the total pressure is:

$$p_{total} = \Sigma_{n=i}^{n} p_i$$

Or we can simply write it as:

$p_{total}=p_1+p_2+p_3+p_4+p_5....+p_n$

In this equation or formula, $p_1 + p_2 + p_3 + p_4 + p_5.... + p_n$ characterize the partial pressure of each gas in the mixture. Furthermore, we can relate the Dalton's law to the ideal gas law through the next equation:

$$p = \frac{nRT}{V} \to \frac{n_{total}RT}{v} = \frac{n_1RT}{v} + \frac{n_2RT}{v} + \frac{n_3RT}{v} + \frac{n_4RT}{v} + \frac{n_5RT}{v} ..... + \frac{n_nRT}{v}$$

In this the term $\frac{RT}{v}$ is common and the same for all the gases then we can reduce the expression to:

$n_{Total} = n_1 + n_2 + n_3 + n_4 + n_5 + ... + n_n$

In this way, the number of moles in a mixture of gases is equal to the sum of the moles of each gas.

Uses of Dalton's law

We can use it to calculate the mixtures of gases and the pressure and volume of each gas and are very important for the chemical industries. Nowadays, industries use sophisticated software for calculating these parameters. Still, Dalton's and Avogadro's law are the base of all these technologies.

5.7.2 Amagat's law

Amagat's law or the law of partial volumes describes the behaviour and properties of mixtures of ideal (as well as some cases of non-ideal) gases. It is of use in chemistry and thermodynamics. It is named after Emile Amagat.

Amagat's law states that the extensive volume V = N_v of a gas mixture is equal to the sum of volumes Vi of the K component gases, if the temperature T and the pressure p remain the same

$$N\,v(T,p) = \sum_{i=1}^{K} N_i\, v_i(T,p).$$

This is the experimental expression of volume as an extensive quantity.

According to Amagat's law of partial volume, the total volume of a non-reacting mixture of gases at constant temperature and pressure should be equal to the sum of the individual partial volumes of the constituent gases. So if

$$V_1, V_2, \ldots, V_n$$

are considered to be the partial volumes of components in the gaseous mixture, then the total volume V would be represented as

$$V = V_1 + V_2 + V_3 + \cdots + V_n = \sum_i V_i$$

Both Amagat's and Dalton's laws predict the properties of gas mixtures. Their predictions are the same for ideal gases. However, for real (non-ideal) gases, the results differ. Dalton's law of partial pressures assumes that the gases in the mixture are non-interacting (with each other) and each gas independently applies its own pressure, the sum of which is the total pressure. Amagat's law assumes that the volumes of the component gases (again at the same temperature and pressure) are additive; the interactions of the different gases are the same as the average interactions of the components.

The interactions can be interpreted in terms of a second virial coefficient B(T) for the mixture. For two components, the second virial coefficient for the mixture can be expressed as

$$B(T) = X_1B_1 + X_2B_2 + X_1X_2B_{1,2}$$

where the subscripts refer to components 1 and 2, the Xi are the mole fractions, and the Bi are the second virial coefficients. The cross term B1,2 of the mixture is given by

$B_{1,2} = 0$ for Dalton's law

and

$$B_{1,2} = \frac{B_1 + B_2}{2} \text{ for Amagat's law.}$$

When the volumes of each component gas (same temperature and pressure) are very similar, then Amagat's law becomes mathematically equivalent to Vegard's law for solid mixtures.