

Chapter 12

Laws of Thermodynamics

Learning Objectives

Syllabus:

Teaching Hour (TH): 4

First law of thermodynamics; First law of thermodynamics for a closed system; Internal and stored energy; Joule's law, enthalpy, specific heat; Applications of first law for a closed system; Related problems on a closed system; Second law of thermodynamics; Heat engine (four components of refrigerator and heat pump, COP of refrigerator and heat pumps); Kelvin-Planck and Clausius statement of the second law.

After studying this chapter, you will learn:

- To state and explain the first law of thermodynamics.
- To understand the concept of the first law of thermodynamics for a closed system.
- To understand the concept of internal and stored energy.
- To state and explain Joule's law.
- To understand the concept of enthalpy in thermodynamics.
- To understand the concept of specific heat in thermodynamics.
- To understand the main applications of the first law of thermodynamics for a closed system.
- To state and explain the second law of thermodynamics.
- To understand the concept of a heat engine.
- To explain the concept of the four components of a refrigerator and heat pump.
- To understand the concept of COP of refrigerators and heat pumps.
- To state and explain the Kelvin-Planck statement and Clausius statement of the second law of thermodynamics.
- To solve the numerical problems related to the first and second laws of thermodynamics.

A Chapter Opening Question

What are the significances of enthalpy in the field of engineering?

12.1 Introduction

The laws of thermodynamics are fundamental principles that govern the behavior of energy and matter in thermodynamic systems. These laws form the foundation of thermodynamics and are widely used in various fields such as mechanical engineering, electrical engineering, and chemical engineering. Understanding these laws is crucial for analyzing the behavior of thermodynamic systems and for designing and optimizing thermodynamic processes.

In this chapter, we will study the first law of thermodynamics for a closed system, internal energy and stored energy, Joule's law, enthalpy, and specific heat; applications of the first law for a closed system; related problems in a closed system; second law of thermodynamics; heat engine, four components of refrigerator and heat pump, coefficient of performance (COP) of refrigerator and heat pumps, Kelvin-Planck and Clausius statements of the second law of thermodynamics.

12.2 First Law of Thermodynamics

The *first law of thermodynamics* states that energy cannot be created or destroyed, only transformed from one form to another. In a thermodynamic system, the total energy is conserved, meaning that the energy added to the system plus the energy taken out of the system is equal to the total energy of the system. It is also known as the law of conservation of energy in thermodynamics.

When a system absorbs heat dQ and as a result, the internal energy of the system changes by dU and the system does an external work dW , then this law can be expressed mathematically as the energy balance equation as

$$dQ = dU + dW$$

This is the *mathematical form* of the first law of thermodynamics.

Here, dQ is positive for heat supplied while it is negative for heat extracted. dU is positive for an increase in internal energy and it is negative for a decrease in internal energy. dW is positive for the expansion of gas and negative for compression of the gas.

The first law of thermodynamics is a *basic principle of thermodynamics* and is widely used in various fields such as mechanical engineering, electrical engineering, and chemical engineering. It provides a fundamental understanding of the behavior of energy in thermodynamic systems and is the starting point for analyzing and designing thermodynamic processes.

Significance: It is based on the principle of *conservation of energy* and it signifies that heat can only be produced at the expenditure of *mechanical energy*.

Limitations: The main *limitations* of the first law of thermodynamics are

- (a) It does not tell about the necessary condition for the *conversion* of heat into mechanical work.
- (b) It does not tell about the *direction* of heat flow.
- (c) The first law of thermodynamics does not give to what extent the mechanical energy is obtained from the heat energy.
- (d) The first law of thermodynamics is silent about the *efficiency of conversion* of heat into mechanical work.

12.3 First Law of Thermodynamics for a Closed System

The *first law of thermodynamics for a closed system* states that the total energy of a closed system is conserved. In other words, the total energy of the system remains constant, and any change in the internal energy of the system must be due to heat transfer or work done on or by the system.

The first law of thermodynamics for a closed system is an important concept in thermodynamics as it provides a fundamental understanding of the behavior of energy in thermodynamic systems. It is widely used in the analysis and design of thermodynamic processes in various fields, including mechanical engineering, electrical engineering, and chemical engineering.

Example: Some *examples* of how this law applies to a closed system in thermodynamics are

- (a) A hot cup of coffee left on a table will eventually cool down to the same temperature as the surrounding air. The heat energy from the coffee is transferred to the air, and the total amount of energy in the closed system (the coffee and air) remains constant.
- (b) A car engine converts the energy stored in gasoline into mechanical energy to drive the car. The total energy in the closed system (the car and its surroundings) remains constant, but the energy is transformed from one form (chemical energy in gasoline) to another (mechanical energy in the car).
- (c) An insulated container filled with gas will experience a temperature change when heat is added or removed. The heat energy is transferred between the gas and the walls of the container, but the total energy in the closed system (the gas and the walls) remains constant.

4 Internal Energy and Stored Energy

Internal energy: Internal energy in thermodynamics refers to the total energy of a system, including its thermal energy, potential energy due to the positions of its particles, and other forms of energy that contribute to the system's overall energy. It is a state function, meaning that its value depends only on the state of the system and is independent of how the system arrived at that state.

Example: Some examples of internal energy in thermodynamics are

- (i) The internal energy of a gas, which is a combination of its kinetic energy (due to the motion of its particles) and its potential energy (due to the attraction and repulsion between its particles)
- (ii) The internal energy of a cup of hot coffee is a combination of its thermal energy, the potential energy of its particles, and the energy stored in any dissolved substances.

Stored energy: Stored energy in thermodynamics refers to the energy stored within a system due to its position, chemical composition, or other forms of energy. It is also a state function and is dependent on the state of the system.

Example: Some examples of stored energy in thermodynamics are

- (i) The chemical energy stored in a fuel cell
- (ii) The elastic potential energy stored in a compressed spring
- (iii) The gravitational potential energy is stored in a raised weight.

Difference: The main difference between internal energy and the stored energy is that internal energy is a more comprehensive term that includes all forms of energy within a system, while stored energy is a subset of internal energy that specifically refers to the energy that is being held in reserve, waiting to be used. For example, a hot cup of coffee has both internal energy and stored energy. The internal energy of the coffee includes its thermal energy, the potential energy of its particles, and any energy stored in dissolved substances. The stored energy of the coffee is specifically the thermal energy, which is being held in reserve waiting to be used.

12.5 Joule's Law of Thermodynamics

Joule's law of thermodynamics is a principle in thermodynamics that states that the amount of heat produced in a conductor is proportional to the square of the current and the resistance of the conductor. It is also known as Joule's first law or Joule-Lenz law. The law is expressed mathematically as

$$Q = I^2 R t$$

where Q is the *heat generated* in joules (J), I is the *current* flowing through the conductor in Amperes (A), R is the *resistance* of the conductor in Ohms (Ω) and t is the *time* over which the heat is generated in seconds (s).

Joule's law of thermodynamics is an important principle in electrical engineering and helps explain the heating effect in electrical circuits and the conversion of electrical energy into heat energy. It is one of the key principles that underlie the development of the electrical power grid and the efficient use of electrical energy.

Use: Joule's law of thermodynamics has many practical applications in various fields. Some of them are

- (a) Joule's law of thermodynamics is used in *electrical engineering* in the design and analysis of electrical circuits and the calculation of the heating effect in electrical components, such as resistors and transformers.

- (b) It can be used in *power generation* to determine the efficiency of electrical power generation and the conversion of electrical energy into heat energy in power plants.
- (c) It can be used in *energy conservation* to evaluate the energy efficiency of electrical appliances, including refrigerators, air conditioners, and other appliances that use electricity.
- (d) It can be used to design and analyze *heating systems*, including electric heating systems and radiant heating systems.
- (e) It can be used in the design of *medical devices*, such as diathermy machines, which use electrical currents to generate heat for medical purposes.
- (a) It can be used in *materials science* to evaluate the heating effect in conductive materials and to design materials with desired electrical and thermal properties.

12.6 Enthalpy

The thermodynamic quantity that represents the total energy of a thermodynamic system, including its internal energy and the energy required to change the volume of the system, is known as *enthalpy*. Mathematically, it is defined as the sum of the internal energy of the system and the product of its pressure and volume. The symbol for enthalpy is H .

Enthalpy is a state function, meaning that its value depends only on the state of the system and not on the path taken to reach that state. It is commonly used in thermodynamics to study energy transfer processes, such as heat transfer, and is often used in thermochemical calculations to predict the heat of reactions.

The change in enthalpy (ΔH) of a system is equal to the heat absorbed or released by the system during a process at constant pressure. This relationship is expressed by the equation as

$$\Delta H = Q_p$$

Where ΔH is the *change in enthalpy* of the system in joules (J) and Q_p is the *heat absorbed or released* by the system at constant pressure in joules (J).

Enthalpy is an important concept in thermodynamics and has numerous applications in engineering, chemistry, and energy science, including in the study of energy transfer processes like the design of power plants and the analysis of energy systems.

12.7 Specific Heat in Thermodynamics

The amount of heat required to raise the temperature of a unit mass of a substance by 1 degree Celsius (or Kelvin) is known as specific heat in thermodynamics. It is a measure of the heat capacity of a substance and is denoted by the symbol C_p or C_v . Specific heat is a property of a substance and is dependent on the temperature and pressure at which the substance is being heated. Different substances have different specific heat due to their molecular structures and how they absorb and release heat.

The equation for the heat required to raise the temperature of a substance is

$$Q = m C \Delta T$$

where Q is the heat absorbed or released in joules (J), m is the mass of the substance in kilograms (kg), C is the specific heat of the substance in joules per kilogram per degree Kelvin ($J \text{ kg}^{-1} \text{ K}^{-1}$) and ΔT is the change in temperature in degrees Kelvin (or Celsius).

Specific heat is an important concept in thermodynamics and has numerous applications in fields such as energy, materials science, and engineering. For example, it is used to determine the energy required to heat or cool a substance, to evaluate the performance of heat exchangers, and to design energy-efficient systems.

12.8 Application of the First Law in Thermodynamics for a Closed System

The first law of thermodynamics can be applied to a wide range of thermodynamic systems, including engines, power plants, and refrigeration systems, among others. For example, the first law of thermodynamics can be used to determine the efficiency of a heat engine by comparing the heat absorbed from a hot reservoir to the work performed by the engine.

In practice, the first law of thermodynamics is used to evaluate the energy balance of thermodynamic systems and to determine the changes in internal energy, heat, and work that occur during thermodynamic processes. It is a fundamental principle that underlies many areas of science and engineering, including energy, thermodynamics, and thermochemistry, among others.

12.9 Second Law of Thermodynamics

The second law of thermodynamics states that the total entropy of a closed system will always tend to increase over time. Entropy is a measure of the disorder or randomness of a system and is a measure of the energy that is unavailable for use. The second law of thermodynamics indicates that in any energy transfer or transformation, some energy will always be unavailable for use and will become dispersed as waste heat.

The second law of thermodynamics has several formulations, including the Clausius statement, the Kelvin-Planck statement, and the entropy production statement. The Clausius statement states that a thermodynamic process can't occur in which a system goes from a high-entropy state to a low-entropy state without an external energy source. The Kelvin-Planck statement states that it is impossible to construct a device that will operate in a cycle and produce a net amount of work while only exchanging heat with a single thermal reservoir.

The second law of thermodynamics has important implications for energy systems and technologies. For example, it places an upper limit on the efficiency of heat engines and sets the maximum theoretical efficiency of the Carnot cycle. It also provides a basis for understanding the direction of thermodynamic processes and the availability of energy in systems.

Use: The second law of thermodynamics is a fundamental principle that has numerous applications across a wide range of fields, including energy, engineering, physics and thermodynamics. It provides important insights into the limitations of energy systems and the potential for sustainable energy use. Some of its key applications of the second law of thermodynamics are

- The Second Law of Thermodynamics places an upper limit on the efficiency of heat engines. This is important for the design and optimization of heat engines, such as those used in power plants and automobiles.
- It is used to analyze and optimize the efficiency of energy conversion systems, including thermal power plants, refrigeration and air conditioning systems and renewable energy systems.
- It is used to determine the direction and feasibility of thermodynamic processes, such as heat transfer, phase transitions, and chemical reactions.
- It provides a basis for understanding the principles of refrigeration and air conditioning systems and is used to design and optimize these systems.
- It is used to evaluate the efficiency of energy storage systems and to determine the maximum theoretical efficiency of energy storage technologies.
- It is used to analyze and optimize energy harvesting systems, including those based on solar, wind and geothermal energy.

12.10 Kelvin-Planck Statement

The Kelvin-Planck statement is one of the important laws of thermodynamics. It *states* that it is impossible for any device that operates on a cycle to receive heat from a single temperature reservoir and produce a net amount of work. In other words, the Kelvin-Planck statement *implies* that it is not possible to convert heat completely into work. Some of the heat will always be wasted as unusable energy. This is because the second law of thermodynamics states that the total *entropy* of a closed system cannot decrease over time and the conversion of heat into work always increases the entropy of the system. It is also known as Kelvin's second law of thermodynamics or the Kelvin-Planck law of thermodynamics.

This statement has important implications for the design of heat engines and the development of sustainable energy sources. For example, it highlights the need for the development of more efficient heat engines that can convert more of the heat into usable energy.

Use: The Kelvin-Planck statement has several uses in thermodynamics and related fields. Some of the *applications* are

- The Kelvin-Planck statement sets the theoretical limit on the *efficiency of heat engines*, which is used as a benchmark for the design and optimization of real-world heat engines.
- It highlights the importance of reducing waste heat in heat engines and helps in the design of systems that can recover and reuse waste heat.
- It is used in the analysis and design of *energy conversion systems*, including power plants, engines and refrigeration systems.
- It provides a framework for *energy management* and helps in the identification of energy-saving opportunities in various industries and applications.
- It is widely taught in thermodynamics courses as part of the second law of thermodynamics, which sets the fundamental limits on the efficiency of energy conversion processes.

12.11 Clausius Statement

The Clausius statement is a formulation of the second law of thermodynamics. It states that heat cannot flow from a colder body to a hotter body without some other process occurring. In other words, the Clausius statement implies that heat always flows from high-temperature regions to low-temperature regions, and heat can't flow spontaneously from a cold body to a hot body without the presence of some other driving force. This driving force can be a heat engine, a refrigerator, or any other device that operates by exchanging heat with its environment. The Clausius statement is also known as the Clausius inequality or the Clausius law.

The Clausius statement is a fundamental principle of thermodynamics and has important implications for the design of thermal systems, such as heat engines, refrigerators and heat pumps. For example, it highlights the need for the development of more efficient thermal systems that can better control the flow of heat and increase the *efficiency* of energy conversion.

The Kelvin-Planck statement deals with the limits of *heat engines*, while the Clausius statement deals with the limits of *refrigerators*. Both statements are equivalent and together they form the second law of thermodynamics.

Use: The Clausius statement has several *applications* in thermodynamics and related fields. Some of them are

- The Clausius statement sets the theoretical limit on the efficiency of *refrigeration systems and air conditioning systems*, which is used as a benchmark for their design and optimization.
- It provides a framework for the analysis and design of *heat pumps*, which transfer heat from a cold body to a hot body and are used in heating and cooling applications.

- (c) It is widely taught in thermodynamics courses as part of the second law of thermodynamics, which sets the fundamental limits on the efficiency of energy conversion processes.
- (d) It is used in the analysis and design of *energy conversion systems*, including power plants, engines, and refrigeration systems.
- (e) It provides a framework for *energy management* and helps in the identification of energy-saving opportunities in various industries and applications.
- (f) It highlights the importance of reducing waste heat in *refrigeration systems* and helps in the design of systems that can recover and reuse waste heat.

12.12 Heat Engine

A device that converts heat energy into useful mechanical work is known as a *heat engine*. Heat engines operate based on the principles of thermodynamics, specifically the first and second laws of thermodynamics. Heat engines work by absorbing heat energy from a high-temperature source, typically a hot reservoir and then converting this energy into mechanical work by using a working fluid, such as a gas or liquid. The working fluid is then cooled and returns to the hot reservoir, completing the cycle. The mechanical work performed by the heat engine can be used to power machines or generate electricity.

There are several types of heat engines, including internal combustion engines, steam engines and Stirling engines. Suppose Q_H amount of heat takes the working substance from a high-temperature reservoir i.e., a source at high-temperature T_H , it converts some part of it into work done (W) and finally rejects the remaining part of heat Q_L to the low-temperature reservoir i.e., sink at the low-temperature T_L as shown in the block diagram. The *efficiency* of a heat engine is defined as the ratio of the useful work output to the heat input. Mathematically, the efficiency of the heat engine can be given by

$$\eta = \frac{\text{work output}}{\text{heat supplied}} = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \quad \dots \dots \dots \text{(i)}$$

In terms of the temperature of the source and sink reservoir, the efficiency of the ideal heat engine can be given by

$$\eta = 1 - \frac{T_L}{T_H} \quad \dots \dots \dots \text{(ii)}$$

For the reversible heat engine, we can write

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

$$\therefore \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0 \quad (\text{ideal heat engine}) \quad \dots \dots \dots \text{(iii)}$$

But, for the irreversible heat engine, eqⁿ (iii) can be modified as

$$\left(\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \right) < 0 \quad (\text{real heat engine}) \quad \dots \dots \dots \text{(iv)}$$

The efficiency of heat engines is limited by the second law of thermodynamics, which states that some heat energy will always be unavailable for use and will become dispersed as waste heat.

Heat engines play a crucial role in many areas of modern society, including transportation, power generation and industrial processes. They are also important in the field of energy conservation and sustainability, as they provide a way to convert waste heat into useful energy. In conclusion, heat engines are important in many areas of modern society and are used to convert waste heat into useful energy.

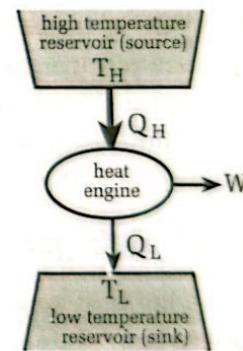


Fig: Block diagram of heat engine

12.13 Heat Pump

A device that transfers heat from a low-temperature source to a high-temperature sink, using mechanical energy is known as the *heat pump*. Heat pumps work on the principle of thermodynamics and are used for heating and cooling applications.

The coefficient of performance (COP) is a measure of the efficiency of a heat pump. It is defined as the ratio of the heat output to the energy input. The COP of the heat pump is important because it determines how much energy is required to transfer a given amount of heat. A high COP means that the system is more efficient and requires less energy to transfer heat. For a *heat pump*, the COP is defined as the ratio of the heating effect (the amount of heat added to the high-temperature space) to the energy input.

Suppose Q_L amount of heat takes the working substance from a low-temperature reservoir i.e. surroundings at low-temperature T_L , and it delivers to a high-temperature reservoir i.e. desired space at high-temperature T_H with the help of external work as shown in the block diagram. It maintains the temperature of the desired space higher than that of the surroundings.

The coefficient of performance (COP) of the heat pump is defined as the ratio of the desired effect to the work supplied i.e. work input. Mathematically, the coefficient of performance (COP) of the heat pump can be given by

$$\text{COP} = \frac{\text{desired effect}}{\text{work supplied}} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L} \quad \dots \dots \dots (\text{i})$$

In terms of the temperature of the hot and cold reservoir, the coefficient of performance (COP) of the ideal heat pump can be given by

$$\text{COP} = \frac{T_H}{T_H - T_L} \quad \dots \dots \dots (\text{ii})$$

For the reversible heat pump, we can write

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad (\text{ideal heat pump}) \quad \dots \dots \dots (\text{iii})$$

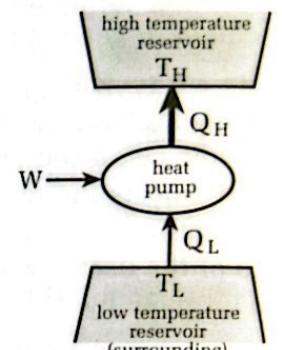


Fig: Block diagram of heat pump

The COP of a heat pump can be much higher than that of a refrigerator, typically ranging from 3 to 5. Heat pumps are widely used for heating and cooling applications, including residential and commercial heating and air conditioning systems, industrial processes and refrigeration. They play a crucial role in the field of energy conservation and sustainability, as they provide a way to use renewable energy sources, such as solar or geothermal energy, for heating and cooling.

12.14 Refrigerator

A device that removes heat from a low-temperature space and transfers it to a high-temperature space, to maintain the low-temperature space at a temperature below that of its surroundings is known as a *refrigerator*. Refrigerators work on the principle of thermodynamics and are widely used in households, commercial kitchens and industrial settings.

The coefficient of performance (COP) is a measure of the efficiency of a refrigeration system. It is defined as the ratio of the heat output to the energy input. The COP of a refrigerator is important because it determines how much energy is required to transfer a given amount of heat. A high COP means that the system is more efficient and requires less energy to transfer heat. For a *refrigerator*, the COP is defined as the ratio of the cooling effect (the amount of heat removed from the low-temperature space) to the energy input (the mechanical energy required to compress the refrigerant).

Suppose Q_L amount of heat takes the working substance from a low-temperature reservoir i.e. desired space at low-temperature T_L , and it delivers to a high-temperature reservoir i.e. surroundings at high-temperature T_H with the help of external work as shown in the block diagram. It maintains the temperature of the desired space lower than that of the surroundings.

The coefficient of performance (COP) of the refrigerator is defined as the ratio of the desired effect to the work supplied i.e. work input. Mathematically, the coefficient of performance (COP) of the refrigerator can be given by

$$\text{COP} = \frac{\text{desired effect}}{\text{work supplied}} = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L} \quad \dots \dots \dots \text{(i)}$$

In terms of the temperature of the hot and cold reservoir, the coefficient of performance (COP) of the ideal refrigerator can be given by

$$\text{COP} = \frac{T_L}{T_H - T_L} \quad \dots \dots \dots \text{(ii)}$$

For the reversible refrigerator, we can write

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad (\text{ideal refrigerator}) \quad \dots \dots \dots \text{(iii)}$$

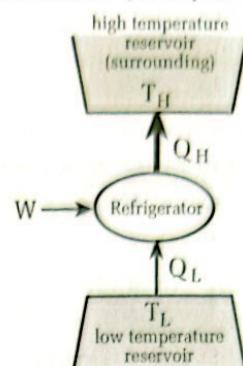


Fig: Block diagram of refrigerator

A typical COP for a refrigerator ranges from 1.5 to 3.5, depending on the design and operating conditions. Refrigeration plays a crucial role in many areas of modern society, including food preservation, air conditioning and medical applications. It is an important technology for reducing energy consumption and reducing the environmental impact of cooling systems.

Discussion: Both refrigerators and heat pumps typically consist of a refrigeration cycle, which includes a refrigerant that is used to absorb heat from the low-temperature space and transfer it to the high-temperature space. The refrigerant is typically circulated through a system of coils and compressors, which perform heat transfer. The refrigerant is then cooled and returns to the low-temperature space to absorb more heat, completing the cycle.

In conclusion, the efficiency of both the refrigerator and heat pump is defined as the ratio of the heat removed from the low-temperature space to the energy consumed by the refrigeration cycle. The second law of thermodynamics states that some energy will always be lost as waste heat in the refrigeration cycle.

12.15 Four Components of the Heat Pump and Refrigerator

The four main components of a refrigeration system or heat pump are the compressor, evaporator, condenser and expansion valve. These components work together to create a refrigeration cycle that is responsible for absorbing heat from a low-temperature space and transferring it to a high-temperature space.

Components: The four main components of a refrigeration system or a heat pump are

- (a) **Compressor:** The *compressor* is responsible for compressing the refrigerant gas and increasing its temperature, allowing it to transfer heat more efficiently.
- (b) **Evaporator:** The *evaporator* is where the refrigerant absorbs heat from the low-temperature space. As the refrigerant evaporates, it cools the space.
- (c) **Condenser:** The *condenser* is where the refrigerant releases heat to the high-temperature space. As the refrigerant condenses, it releases heat to the surrounding environment.

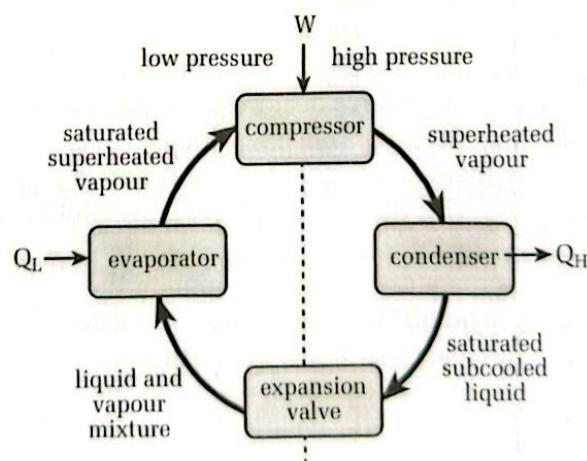


Fig: Four components of heat pump and refrigerator

- (d) **Expansion valve:** The *expansion valve* regulates the flow of refrigerant into the evaporator and reduces the pressure of the refrigerant, causing it to expand and cool. This cooling effect is what makes the evaporator effective at absorbing heat from the low-temperature space.

These four components work together to create a refrigeration cycle, which is responsible for absorbing heat from the low-temperature space, transferring it to the high-temperature space, and then returning it to the low-temperature space to be absorbed again.

Answer to Chapter Opening Question

Enthalpy is a measure of the total energy in a thermodynamic system. It is particularly important in the field of engineering because it can be used to determine the amount of heat that is transferred in a process. This is useful in many engineering applications, such as HVAC (heating, ventilation, and air conditioning) systems, power generation, and combustion engines. By understanding the enthalpy changes that occur in a system, engineers can design and optimize processes to be more energy efficient and cost-effective. Additionally, enthalpy can also be used to calculate the thermodynamic properties of materials, such as vapor pressure and saturation temperature, which are essential for the design and operation of many types of industrial equipment.

Review & Summary

1. The *first law of thermodynamics for a closed system* states that the total energy of a closed system is conserved.
2. Internal energy in thermodynamics refers to the total energy of a system, including its thermal energy, potential energy due to the positions of its particles, and other forms of energy that contribute to the system's overall energy.
3. Stored energy in thermodynamics refers to the energy stored within a system due to its position, chemical composition, or other forms of energy.
4. Stored energy in thermodynamics refers to the energy stored within a system due to its position, chemical composition, or other forms of energy.
5. Joule's law of thermodynamics is a principle in thermodynamics that states that the amount of heat produced in a conductor is proportional to the square of the current and the resistance of the conductor.
6. The thermodynamic quantity that represents the total energy of a thermodynamic system, including its internal energy and the energy required to change the volume of the system, is known as *enthalpy*.
7. The amount of heat required to raise the temperature of a unit mass of a substance by 1 degree Celsius (or Kelvin) is known as specific heat in thermodynamics.
8. The *second law of thermodynamics* states that the total entropy of a closed system will always tend to increase over time.
9. The Kelvin-Planck statement *indicates* that it is impossible for any device that operates on a cycle to receive heat from a single temperature reservoir and produce a net amount of work.
10. The Clausius statement indicates that heat cannot flow from a colder body to a hotter body without some other process occurring.
11. A device that converts heat energy into useful mechanical work is known as a *heat engine*.
12. A device that removes heat from a low-temperature space and transfers it to a high-temperature space, to maintain the low-temperature space at a temperature below that of its surroundings is known as a *refrigerator*.
13. A device that transfers heat from a low-temperature source to a high-temperature sink, using mechanical energy is known as the *heat pump*.
14. The *four main components* of a refrigeration system or a heat pump are the compressor, evaporator, condenser and expansion valve.
15. The coefficient of performance (COP) is defined as the ratio of the heat output to the energy input.

Key Formulae

First law of thermodynamics: $dQ = dU + dW$ and $\Delta U = Q - W$

Joule's first law or Joule-Lenz law: $Q = I^2 R t$

Change in enthalpy: $\Delta H = Q_p$

Specific heat in thermodynamics: $C = \frac{Q}{m \Delta T}$

Sample Conceptual Questions Answers

What is the significance of the first law of thermodynamics?

The first law of thermodynamics is a fundamental principle of physics that states that energy cannot be created or destroyed, but it can be transformed from one form to another. This law is also known as the law of conservation of energy, and it has far-reaching implications for many fields of study, including physics, chemistry, engineering, and environmental science. The significance of the first law of thermodynamics lies in its ability to help us understand and quantify the behavior of energy in a wide range of systems.

The first law of thermodynamics provides a way to balance the energy input and output of a system. It helps us understand how heat is transferred between different objects and systems. It also helps us understand the energy changes that occur during chemical reactions.

2. What are closed and open systems?

A closed system does not exchange matter with its surroundings but can exchange energy (in the form of heat or work) with its surroundings. The total energy of a closed system remains constant (by the First Law of Thermodynamics), but the system can change in other ways (such as temperature, pressure, or volume) as it exchanges energy with its surroundings. For example, a sealed container of gas and a piston-cylinder system are both examples of closed systems.

An open system can exchange both matter and energy with its surroundings. This means that the total energy of an open system can change as it exchanges both heat and work with its surroundings. Open systems are often found in nature, such as living organisms, rivers, or the Earth's atmosphere. In many engineering applications, open systems are used to convert energy from one form to another, such as power plants that generate electricity by converting heat energy from burning fuel.

3. What is the significance of enthalpy?

The thermodynamic property that is defined as the sum of the internal energy of a system and the product of its pressure and volume is called *enthalpy*. It is a useful and widely used concept in thermodynamics. It helps us understand the heat content of a system, quantify heat transfer and energy transfer, predict the direction of chemical reactions, and optimize the performance of various engineering systems.

4. What is the significance of specific heat in thermodynamics?

Specific heat is a fundamental property of a substance that describes how much energy is required to raise the temperature of a unit mass of the substance by a certain amount. In thermodynamics, the significance of specific heat lies in its relationship with the internal energy of a system. The internal energy of a system is the sum of the kinetic and potential energies of its particles. When heat is added to a system, its internal energy increases, and this energy can be used to do work.

5. What is the third law of thermodynamics?

The fundamental principle in thermodynamics that describes the behavior of matter at absolute zero temperature is called the *third law of thermodynamics*. It states that the entropy of a perfect crystal at absolute zero is zero.

In simpler terms, the third law of thermodynamics says that it is impossible to reach absolute zero temperature and that the entropy of a perfectly ordered crystal at absolute zero is zero. Therefore, the third law provides a framework for understanding the behavior of matter at very low temperatures.

6. What are the differences between the Kelvin-Planck Statement and the Clausius statement?

- » The Kelvin-Planck statement states that it is impossible to build a device that takes heat from a cold source and converts all of that heat into work without any heat being transferred to a hotter source. It focuses on the efficiency of heat engines and heat pumps, and it provides a limit on the maximum efficiency that can be achieved. On the other hand, the Clausius statement states that it is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a colder body to a hotter body. It focuses on the concept of entropy and provides a criterion for the direction of heat flow.

7. What are the differences between the heat engine and the heat pump?

- » A heat engine and a heat pump are both important thermodynamic devices that involve the transfer of heat energy, but they operate in opposite directions and have different purposes. A heat engine produces work output by extracting heat energy from a high-temperature source and releasing some of that energy to a low-temperature sink, while a heat pump moves heat energy from a low-temperature source to a high-temperature sink by consuming work input.

8. What are the physical meanings of the coefficient of performance (COP) of refrigerators and heat Pumps?

- » The coefficient of performance (COP) is a measure of the efficiency of refrigerators and heat pumps. It represents the ratio of the desired output to the required input energy. Here are the physical meanings of COP for refrigerators and heat pumps:

The COP of a refrigerator represents the ratio of the amount of heat removed from the refrigerated space to the amount of work required to remove that heat. In other words, it represents how much cooling can be achieved per unit of work input. A higher COP means that the refrigerator is more efficient in removing heat from the refrigerated space. For a refrigerator, the desired output is the cooling effect or the heat removed from the refrigerated space, and the required input is the work done by the compressor to remove that heat.

The COP of a heat pump represents the ratio of the amount of heat supplied to the heated space to the amount of work required to move that heat. In other words, it represents how much heating can be achieved per unit of work input. A higher COP means that the heat pump is more efficient in transferring heat from the heat source to the heated space. For a heat pump, the desired output is the heating effect or the heat supplied to the heated space, and the required input is the work done by the compressor or the pump to move that heat.

9. Can you do any kind of research work by studying about laws of thermodynamics?

- » Studying the laws of thermodynamics can provide a strong foundation in fundamental principles of energy and matter, which can be useful in many research endeavors. The laws of thermodynamics describe the fundamental principles of energy and matter, and how they interact with one another. These laws provide a basis for understanding many natural phenomena and technological systems, which can inspire creativity and innovation.

The principles of the first law of thermodynamics can be used to design renewable energy systems that make use of solar, wind, or geothermal energy sources. The second law of thermodynamics can be used to design more efficient heat engines or refrigeration systems.

Sample Examples

The density of a gas is 1.775 kg m^{-3} at 27°C and 10^5 N m^{-2} pressure and its specific heat capacity at constant pressure is $846 \text{ J kg}^{-1}\text{K}^{-1}$. Find the ratio of its specific heat capacity at constant pressure to that at constant volume.

Solution: Given;

$$\text{Density of gas } (\rho) = 1.775 \text{ kg m}^{-3} \quad \text{Pressure } (P) = 10^5 \text{ N m}^{-2}$$

$$\text{Temperature } (T) = 27^\circ\text{C} = (27 + 273) \text{ K} = 300 \text{ K}$$

$$\text{Specific heat capacity at constant pressure } (c_p) = 846 \text{ J kg}^{-1}\text{K}^{-1}$$

$$\text{Ratio of two specific heat capacities } (\gamma) = \frac{c_p}{c_v} = ?$$

For m kg of gas, the *ideal gas equation* is

$$PV = m rT$$

$$\therefore r = \frac{PV}{m T} = \frac{P}{(m/V) T} = \frac{P}{\rho T} = \frac{10^5}{1.775 \times 300} = 187.79 \text{ J kg}^{-1}\text{K}^{-1}$$

$$\text{So, } c_p - c_v = r, \quad \text{for one kg of gas.}$$

$$\therefore c_v = c_p - r = 846 - 187.79 = 658.21 \text{ J kg}^{-1}\text{K}^{-1}$$

$$\text{So, } \gamma = \frac{c_p}{c_v} = \frac{c_p}{c_p - r} = \frac{846}{846 - 187.79} = \frac{846}{658.21} = 1.29$$

Thus the ratio of specific heat capacity at constant pressure to that at constant volume is 1.29.

Determined the change in internal energy when 4 gm of air is heated from 0°C to 2°C .
(Given: specific heat of air at constant volume = $0.172 \text{ kcal kg}^{-1}\text{C}^{-1}$)

Solution: Given;

$$\text{Mass of air } (m) = 4 \text{ gm} = 4 \times 10^{-3} \text{ kg}$$

$$\text{Change in temperature } (dT) = 0^\circ\text{C} \text{ to } 2^\circ\text{C} = 2^\circ\text{C}$$

$$\text{Specific heat of air at constant volume } (C_v) = 0.172 \text{ kcal kg}^{-1}\text{C}^{-1}$$

$$\text{Change in internal energy } (dU) = ?$$

From the *first law of thermodynamics*, we have

$$dU = dQ - dW = m C_v dT - P dV = (4 \times 10^{-3} \times 0.172 \times 2) - 0 = 1.38 \times 10^{-3} \text{ kcal}$$

Hence, the value of change in internal energy of the given gas is 1.38×10^{-3} kcal.

- 1 gm of water becomes 1671 cc of steam when boiled at a pressure of 1 atm. If the heat of vapourization of water is 540 cal/gm, calculate the external work done and increase in the internal energy.**

Solution: Given;

$$\text{Mass of water } (m) = 1 \text{ gm}$$

$$\text{Initial volume of water } (V_1) = \frac{\text{mass of water}}{\text{density of water}} = \frac{1 \text{ gm}}{1 \text{ gm/cm}^3} = 1 \text{ cm}^3 = 10^{-6} \text{ m}^3$$

$$\text{Final volume of steam } (V_2) = 1671 \text{ cc} = 1671 \text{ cm}^3 = 1671 \times 10^{-6} \text{ m}^3$$

$$\text{Latent heat of vapourization of water } (L) = 540 \text{ cal/gm}$$

$$\text{Pressure } (P) = 1 \text{ atm} = 1.01 \times 10^5 \text{ N m}^{-2}$$

$$\text{External work done } (dW) = ? \quad \text{Increasing internal energy } (dU) = ?$$

For the *external work done*, we have

$$dW = P dV = P (V_2 - V_1) = 1.01 \times 10^5 (1671 \times 10^{-6} - 10^{-6}) = 169 \text{ J} = 40.2 \text{ cal}$$

From the *first law of thermodynamics*, we have

$$dU = dQ - dW = 540 - 40.2 = 499.8 \text{ cal}$$

Hence, the value of external work done is 40.2 cal and the increase in internal energy is 499.8 cal.

4. A motor car has a pressure of 3 atm at a room temperature of 27 °C. If the tyre suddenly bursts, calculate the resulting temperature. (Given, γ for air = 1.4)

Solution: Given;

$$\text{Initial temperature } (T_1) = 27^\circ\text{C} = 300 \text{ K}$$

$$\gamma = 1.4$$

$$\text{Final temperature } (T_2) = ?$$

For an *adiabatic process*, we have

$$T^\gamma P^{1-\gamma} = \text{constant}$$

$$\text{So, } T_1^\gamma P_1^{1-\gamma} = T_2^\gamma P_2^{1-\gamma}$$

$$\text{or, } T_2^\gamma = T_1^\gamma \left(\frac{P_1}{P_2}\right)^{1-\gamma} = (300)^{1.4} \times \left(\frac{3}{1}\right)^{1-1.4} = 1893$$

$$\therefore T_2 = (1893)^{1/\gamma} = (1893)^{1/1.4} = 219.2 \text{ K} = -53.8^\circ\text{C}$$

Hence, the value of the resulting temperature is -53.8°C .

5. A reversible engine takes in heat from a reservoir of heat at 527°C and gives out heat to the sink at 127°C . How many calories per second must it take from the reservoir to produce useful mechanical work at the rate of 750 W?

Solution: Given;

$$\text{Temperature of source reservoir } (T_H) = 527^\circ\text{C} = 800 \text{ K}$$

$$\text{Temperature of sink } (T_L) = 127^\circ\text{C} = 400 \text{ K}$$

$$\text{Mechanical work } (W) = 750 \text{ W}$$

$$\text{Rate of heat absorbed in calories } (Q_H) = ?$$

For the *efficiency* of the heat engine, we have

$$\eta = 1 - \frac{T_L}{T_H} = 1 - \frac{400}{800} = 0.5$$

$$\text{Now, } \eta = \frac{W}{Q_H}$$

$$\therefore Q_H = \frac{W}{\eta} = \frac{750}{0.5} = 1500 \text{ J/s} = 357.2 \text{ cal/s}$$

Hence, the value of the rate of heat absorbed by the heat reservoir is 357.2 cal/s.

6. A refrigerator has to transfer an average of 200 J of heat per second from the temperature -10°C to $+27^\circ\text{C}$. Calculate the average power consumed, assuming an ideal reversible cycle and no other losses.

Solution: Given;

$$\text{Temperature of source } (T_H) = -10^\circ\text{C} = 263 \text{ K}$$

$$\text{Temperature of sink } (T_L) = 27^\circ\text{C} = 300 \text{ K}$$

$$\text{Rate of heat rejected } (Q_L) = 200 \text{ J/s}$$

$$\text{Average power consumed } (W) = ?$$

For the *refrigerator*, we have

$$\eta = 1 - \frac{T_L}{T_H} = 1 - \frac{Q_L}{Q_H}$$

$$\therefore Q_H = Q_L \times \frac{T_H}{T_L} = 200 \times \frac{263}{300} = 228.1 \text{ J/s}$$

Now, the *average power consumption* is

$$W = Q_H - Q_L = 228.1 - 200 = 28.1 \text{ J/s}$$

Hence, the value of average power consumed by the given refrigerator is 28.1 J/s.

Calculate the change in entropy when 10 gm of ice at 0 °C is converted into water at the same temperature. Given latent heat of fusion of ice = 80 cal/gm.

Solution: Given;

$$\text{Mass of ice (m)} = 10 \text{ gm}$$

$$\text{Temperature (T)} = 0^\circ\text{C} = 273 \text{ K}$$

$$\text{Latent heat of fusion of ice (L)} = 80 \text{ cal/gm}$$

$$\text{Change in entropy (dS)} = ?$$

For the increase in entropy, we have

$$dS = \frac{dQ}{T} = \frac{m L}{T} = \frac{10 \times 80}{273} = 2.93 \text{ cal/K}$$

Hence, the value of change in entropy of the given ice on melting into the water at 0 °C is 2.93 cal/K.

A heat pump has a coefficient of performance (COP) that is 80% of the ideal heat pump. It maintains a hall at room temperature of 20 °C, which leaks energy 1000 W per degree temperature difference to the ambient. For a maximum of 1500 W of input power, estimate the minimum outside temperature for which the heat pump is sufficient.

Solution: Given;

$$\text{COP}_{\text{actual}} = 80\% \text{ of COP}_{\text{ideal}}$$

$$\text{Higher temperature (T}_H\text{)} = 20^\circ\text{C} = 293 \text{ K}$$

$$\text{Rate of leakage energy} = 1000 \text{ W/C}$$

$$\text{Input power (W)} = 1500 \text{ W}$$

$$\text{Lower temperature (T}_L\text{)} = ?$$

The heating rate of the heat pump is

$$Q_H = 1000 \times (T_H - T_L) = 1000 \times (293 - T_L) \text{ W} = (293,000 - 1000 T_L) \text{ W}$$

According to the question, we can write

$$\text{COP}_{\text{actual}} = 80\% \text{ of COP}_{\text{ideal}}$$

$$\text{or, } \frac{Q_H}{W} = 0.8 \times \frac{T_H}{T_H - T_L}$$

$$\text{or, } \frac{1000 \times (T_H - T_L)}{W} = 0.8 \times \frac{T_H}{T_H - T_L}$$

$$\text{or, } 1000 \times (T_H - T_L)^2 = 0.8 \times W \times T_H = 0.8 \times 1500 \times 293 = 3.51 \times 10^5$$

$$\text{or, } (T_H - T_L)^2 = 3.51 \times 10^2 = 351$$

$$\text{or, } T_H - T_L = \sqrt{351} = 18.7$$

$$\therefore T_L = T_H - 18.7 = 293 - 18.7 = 274.3 \text{ K}$$

Hence, the value of the outside temperature of the given heat pump is 274.3 K,

9. In inventor makes the following claims. Determine whether the claims are valid or not and exemplifying with logical reasons.

- (a) A Diesel engine operating between temperatures 500 °C and 2000 °C will produce 1.2 kW of power output consuming 0.15 kg/h of Diesel having a calorific value of $4.25 \times 10^4 \text{ kJ/kg}$.
- (b) A heat pump supplies heat to a room maintained at 22 °C at a rate of 50,000 kJ/h. The inventor claims a work input of 8,000 kJ/h is sufficient when the surrounding is at -2 °C.
- (c) A refrigerator maintains -5 °C in the refrigerator which is kept in a room where the temperature is 30 °C and has a COP of 8.

Solution: Given;

- (a) Temperature of source (T_H) = 2000 °C = 2273 K

Temperature of sink (T_L) = 500 °C = 773 K

Output power (W) = 1.2 kW

$$\text{Fuel consumption rate } (m_F) = 0.15 \text{ kg/h} = \frac{0.15}{3600} \text{ kg/s} = 4.17 \times 10^{-5} \text{ kg/s}$$

Calorific value of Diesel (CV) = 4.25×10^4 kJ/kg

For the *ideal engine*, we have

$$\eta_{\text{ideal}} = \left(1 - \frac{T_L}{T_H}\right) \times 100\% = \left(1 - \frac{773}{2273}\right) \times 100\% = 65.99\%$$

The *rate of heat supplied* to the Diesel engine is

$$Q_H = m_F \times CV = 4.17 \times 10^{-5} \times 4.25 \times 10^4 = 1.77 \text{ kW}$$

According to the *inventor's claim*, we have

$$\eta_{\text{inventor}} = \frac{W}{Q_H} \times 100\% = \frac{1.2}{1.77} \times 100\% = 67.8\%$$

Here, $\eta_{\text{inventor}} > \eta_{\text{ideal}}$, so the given statement is not possible.

- (b) Temperature of source (T_H) = 22 °C = 295 K

Temperature of sink (T_L) = -2 °C = 271 K

Rate of heating (Q_H) = 50,000 kJ/h

Input power (W) = 8,000 kJ/h

For the *ideal heat pump*, we have

$$\text{COP}_{\text{ideal}} = \frac{Q_H}{Q_H - Q_L} \times 100\% = \frac{295}{295 - 271} \times 100\% = 12.3\%$$

According to the *inventor's claim*, we have

$$\text{COP}_{\text{inventor}} = \frac{Q_H}{W} \times 100\% = \frac{50,000}{8,000} \times 100\% = 6.3\%$$

Here, $\text{COP}_{\text{inventor}} < \text{COP}_{\text{ideal}}$, so the given statement is possible.

- (c) Higher temperature (T_H) = 30 °C = 303 K

Lower temperature (T_L) = -5 °C = 268 K

COP claimed by the inventor ($\text{COP}_{\text{inventor}}$) = 8

For the *ideal refrigerator*, we have

$$\text{COP}_{\text{ideal}} = \frac{T_L}{T_H - T_L} \times 100\% = \frac{268}{303 - 268} \times 100\% = 7.65\%$$

Here, $\text{COP}_{\text{inventor}} > \text{COP}_{\text{ideal}}$, so the given statement is not possible.

Exercise and Problems

Short Answer Questions

1. State and explain the first law of thermodynamics.
2. Describe the first law of thermodynamics for a closed system.
3. Distinguish between internal and stored energies.

State and explain Joule's law.

What is meant by enthalpy in thermodynamics?

What is specific heat in thermodynamics?

What is meant by the heat engine?

What is meant by the COP of refrigerators and heat pumps?

Long Answer Questions

Mention the main applications of the first law of thermodynamics for a closed system.

State and explain the second law of thermodynamics.

What are the four components of a refrigerator and heat pump?

State and explain the Kelvin-Planck statement and Clausius statement of the second law of thermodynamics.

Numerical Problems

1. The temperature of 5 gm of air is raised from 0 °C to 1 °C at constant volume. Compute the increase in its internal energy. (Specific heat of air at constant volume = $0.172 \text{ cal gm}^{-1} \text{ }^{\circ}\text{C}^{-1}$)
[Ans: 3.6 J]
2. An engine of a car of power 42 kW is operating between 227 °C and 177 °C. Calculate:
 - (a) the efficiency of the engine and
 - (b) the amount of heat absorbed and the amount of heat rejected per second.*[Ans: (a) 10%, (b) $4.2 \times 10^5 \text{ J}$ & $3.78 \times 10^5 \text{ J}$]*
3. A heat engine takes 200 J of heat from the hot reservoir and delivers 120 J of heat to the cold reservoir in a cycle. If the temperature of a cold reservoir is 300 K, what could be the minimum temperature of the hot reservoir?
[Ans: 500 K]
4. A reversible engine converts one-sixth of input heat into work. When the temperature of the sink is reduced by 62 °C, its efficiency is doubled. Find the temperature of the source and the sink.
[Ans: 372 K and 310 K]
5. A reversible engine intakes 200 g of steam at 100 °C per minute and cools it down to 30 °C. Calculate the heat rejected by the steam engine per minute (Latent heat of vaporization of steam = 540 cal/g)
[Ans: $5.12 \times 10^5 \text{ J}$]
6. In a petrol engine, the rate of production of heat due to the combustion of petrol is $7.45 \times 10^5 \text{ cal h}^{-1}$. The efficiency of the engine is 30%. Calculate the power of the engine. (1 HP = 746 W)
[Ans: 0.35 HP]
7. A petrol engine consumes 10 kg of petrol in one hour. The calorific value of petrol is $11.4 \times 10^5 \text{ cal g}^{-1}$. The power of the engine is 30 kW. Calculate the efficiency of the engine.
[Ans: 22.6%]

