Course: Physics 1

Module 2: Thermodynamics

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Module 2: Thermodynamics

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Introduction

- Thermodynamics is a 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.

- In thermodynamics, one usually considers both thermodynamic systems and their environments. A typical thermodynamic system is a definite quantity of gas enclosed in a cylinder with a sliding piston that allows the volume of gas to vary, as shown in Figure 15.

- In other words, a thermodynamic system is a quantity of matter of fixed identity, around which we can draw a boundary (see Figure 15). The boundary may be fixed or moveable. Work or heat can be transferred across the system boundary. All things outside the boundary constitute the surroundings of the system.

- When working with devices such as engines it is often useful to define the system to be an identifiable volume with flow in and out. This is termed a control volume.

- A closed system is a special class of system with boundaries that matter cannot cross. Hence the principle of the conservation of mass is automatically satisfied whenever we employ a closed system analysis. This type of system is sometimes termed a control mass.

- In general, a thermodynamic system is defined by its temperature, volume, pressure, and chemical composition. A system is in equilibrium when each of these variables has the same value at all points.

- A system’s condition at any given time is called its thermodynamic state. For a gas in a cylinder with a movable piston, the state of the system is identified by the temperature, pressure, and volume of the gas. These properties are characteristic parameters that have definite values at each state.

- If the state of a system changes, then it is undergoing a process. The succession of states through which the system passes defines the path of the process. If, at the end of the process, the properties of the system return to their original values, the system undergoes a cyclic process or a cycle. Note that even if a system has returned to its original state and completed a cycle, the state of the surroundings may have changed.

- If the change in value of any property during a process depends only on the initial and final states of the system, not on the path followed by the system, the property is called a state function.

- In contrast, the work done as the piston moves and the gas expands, and the heat that the gas absorbs from its surroundings depend on the detailed way in which the expansion occurs; therefore, work and heat are not state functions.
2.1. States of macroscopic and microscopic

- In statistical mechanics, a **microstate** describes a specific detailed microscopic configuration of a system. In contrast, the **macrostate** of a system refers to its macroscopic properties such as its temperature and pressure. In statistical mechanics, a macrostate is characterized by a probability distribution on a certain ensemble (set) of microstates.

- In other words, the microscopic description of a system is the complete description of each particle in this system. In the example shown in Figure 15, the microscopic description of the gas would be the list of the state of each molecule: position and velocity. It would require a great deal of data for this description; note that there are roughly $10^{19}$ molecules in one cm$^3$ of air at room temperature and pressure.

- The macroscopic description, which is in terms of a few properties is thus far more accessible and usable for engineering applications, although it is restricted to equilibrium states.

- For a given macroscopic system, there are many microscopic states. In statistical mechanics, the behavior of a substance is described in terms of the statistical behavior of its atoms and molecules. One of the main results of this treatment is that isolated systems tend toward disorder and entropy is a measure of this disorder (see section 2.2, this module).

- For example, consider the molecules of a gas in the air in your room. If half of the gas molecules had velocity vectors of equal magnitude directed toward the left and the other half had velocity vectors of the same magnitude directed toward the right, the situation would be very ordered. Such a situation is, however, extremely unlikely. If you could actually view the molecules, you would see that they move randomly in all directions, bumping into one another, changing speed upon collision, some going fast and others going slowly. This situation is highly disordered.

- The cause of the tendency of an isolated system toward disorder is easily explained. To do so, we again distinguish between microstates and macrostates of a system. A microstate is a particular description of the properties of the individual molecules of the system. For example, the description we just gave of the velocity vectors of the air molecules in your room being very ordered refers to a particular microstate, and the more likely random motion is another microstate—one that represents disorder. A macrostate is a description of the conditions of the system from a macroscopic point of view and makes use of macroscopic variables such as pressure, density, and temperature. For example, in both of the microstates described for the air molecules in your room as mentioned above, the air molecules are distributed uniformly throughout the volume of the room; this uniform density distribution is a macrostate. We could not distinguish between our two microstates by making a macroscopic measurement—both microstates would appear to be the same macroscopically, and the two macrostates corresponding to these microstates are equivalent.

- For any given macrostate of the system, a number of microstates are possible, or accessible. Among these microstates, it is assumed that all are equally probable. When all possible microstates are examined, however, it is found that far more of them are disordered than are ordered. Because all of the microstates are equally probable, it is highly likely that the actual macrostate is one resulting from one of the highly disordered microstates, simply because there are many more of them.

- Similarly, the probability of a macrostate’s forming from disordered microstates is greater than the probability of a macrostate’s forming from ordered microstates. All physical processes that take place in a system tend to cause the system and its surroundings to move toward more probable macrostates. The more probable macrostate is always one of greater disorder. If we consider a
system and its surroundings to include the entire Universe, then the Universe is always moving toward a macrostate corresponding to greater disorder.

2.2. General laws of thermodynamics

- The most important laws of thermodynamics are:

  The zeroth law of thermodynamics: When two systems are each in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other.

![Thermodynamic Equilibrium](image)

*Figure 16: Depicting the first law of thermodynamics (Courtesy of NASA).*

The first law of thermodynamics or the law of conservation of energy: The change in a system’s internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings.

The second law of thermodynamics: Heat does not flow spontaneously from a colder region to a hotter region, or, equivalently, heat at a given temperature cannot be converted entirely into work.

Consequently, the entropy of a closed system, or heat energy per unit temperature, increases over time toward some maximum value. Thus, all closed systems tend toward an equilibrium state in which entropy is at a maximum and no energy is available to do useful work.
The third law of thermodynamics: The entropy of a perfect crystal of an element in its most stable form tends to zero as the temperature approaches absolute zero. This allows an absolute scale for entropy to be established that, from a statistical point of view, determines the degree of randomness or disorder in a system.

1) THE ZEROTH LAW OF THERMODYNAMICS and TEMPERATURE

- Experimental observations show that:
  1. If two bodies are in contact through a thermally-conducting boundary for a sufficiently long time, they will reach an thermal equilibrium.
  2. Two systems which are individually in thermal equilibrium with a third are in thermal equilibrium with each other; all three systems have the same value of the property called temperature.

- These closely connected ideas of temperature and thermal equilibrium are expressed formally in the zeroth law of thermodynamics (the law of equilibrium):
  
  If objects 1 and 3 are separately in thermal equilibrium with object 2, then objects 1 and 3 are in thermal equilibrium with each other.

- Figure 16 depicts the first law of thermodynamics.

- The importance of this law is that it enables to define a universal standard for temperature. If two different systems cause the same reading on the same thermometer, they have the same temperature. A temperature scale on a new thermometer can be set by comparing it with systems of known temperature.

- We can think of temperature as the property that determines whether an object is in thermal equilibrium with other objects. Two objects in thermal equilibrium with each other are at the same temperature. Conversely, if two objects have different temperatures, then they are not in thermal equilibrium with each other.

2) THE FIRST LAW OF THERMODYNAMICS or THE LAW OF CONSERVATION OF ENERGY

a) MACROSCOPIC DESCRIPTION OF AN IDEAL GAS

- In this section we examine the properties of a gas of mass m confined to a container of volume V at a pressure P and a temperature T. It is useful to know how these quantities are related. In general, the equation that interrelates these quantities, called the equation of state, is very complicated.

- An ideal gas is defined as one in which all collisions between atoms or molecules are perfectly elastic, and in which there are no intermolecular attractive forces. One can visualize it as a collection of perfectly hard spheres which collide but which otherwise do not interact with each other. In such a gas, all the internal energy is in the form of kinetic energy, and any change in internal energy is accompanied by a change in temperature.

- In reality, an ideal gas does not exist. If the gas is maintained at a very low pressure (or low density), the equation of state is quite simple and can be found experimentally. However, such a low-density gas is commonly referred to as an ideal gas. The concept of an ideal gas is very useful in view of the fact that real gases at low pressures behave as ideal gases do. The concept of an ideal gas implies that the gas molecules do not interact except upon collision, and that the molecular volume is negligible compared with the volume of the container.
• For an ideal gas, the relationship between three state variables: absolute pressure (P), volume (V), and absolute temperature (T) may be deduced from kinetic theory and is called the ideal gas law

\[ PV = nRT \]  

(4)

where \( n \) is number of moles of the gas sample; \( R \) is a universal constant that is the same for all gases; \( T \) is the absolute temperature in kelvins \( (T = 273.15 + t \, ^\circ C, \text{where } t \, ^\circ C \text{ is the temperature in Celsius degrees}) \).

• Equation (4) is also called the equation of state of ideal gas.

• If the equation of state is known, then one of the variables \((V, P, T)\) can always be expressed as some function of the other two.

• It is convenient to express the amount of gas in a given volume in terms of the number of moles \( n \). As we know, one mole of any substance contains the Avogadro’s number of constituent particles (atoms or molecules), \( N_A = 6.0221 \times 10^{23} \) particles/mol.

• The number of moles \( n \) of a gas is related to its mass \( m \) through the expression

\[ n = \frac{m}{M} \]  

(5)

where \( M \) is the molar mass of the gas substance, which is usually expressed in grams per mole \((g/mol)\). For example, the molar mass of oxygen \((O_2)\) is 32.0 g/mol. Therefore, the mass of one mole of oxygen is 32.0 g.

• Experiments on numerous gases show that as the pressure approaches zero, the quantity \( PV/nT \) approaches the same value \( R \) for all gases. For this reason, \( R \) is called the universal gas constant.

In SI units, in which pressure is expressed in pascals \((1 \text{ Pa} = 1 \text{ N/m}^2)\) and volume in cubic meters, the product \( PV \) has units of newton.meters, or joules, and \( R \) has the value

\[ R = 8.315 \text{ J/mol.K} \]

If the pressure is expressed in atmospheres and the volume in liters \((1 \text{ L} = 10^{-3} \text{ m}^3)\), then \( R \) has the value

\[ R = 0.08214 \text{ L.atm/mol.K} \]

• Using this value of \( R \) and Equation (4), we find that the volume occupied by one mole of any gas at atmospheric pressure and at 0°C \((273 \text{ K})\) is 22.4 L.

• Now that we have presented the equation of state, we can give a formal definition of an ideal gas, as follow:

\textit{An ideal gas is one for which } PV/nT \text{ \it is constant at all pressures.}

• The ideal gas law states that if the volume and temperature of a fixed amount of gas do not change, then the pressure also remains constant.

• The ideal gas law is often expressed in terms of the total number of molecules \( N \). Because the total number of molecules equals the product of the number of moles \( n \) and Avogadro’s number \( N_A \), we can write equation (4) as

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\[ PV = nRT = \frac{N}{N_A}RT \quad (6) \]

or

\[ PV = Nk_B T \quad (7) \]

where \( k_B \) is Boltzmann’s constant, which has the value

\[ k_B = \frac{R}{N_A} = 1.38066 \times 10^{-23} \text{ J/K} = 8.617385 \times 10^{-5} \text{ eV/K} \]

Example: An ideal gas occupies a volume of 100 cm\(^3\) at 20°C and 100 Pa. Find the number of moles of gas in the container. (Ans. \(4.1 \times 10^{-6}\) mol)

b) HEAT AND INTERNAL ENERGY

- Until about 1850, the fields of thermodynamics and mechanics were considered two distinct branches of science, and the law of conservation of energy seemed to describe only certain kinds of mechanical systems.

- However, mid-19th century experiments performed by the Englishman James Joule and others showed that energy may be added to (or removed from) a system either by transferring heat or by doing work on the system (or having the system do work). Today we know that internal energy, which we define formally later, can be transformed to mechanical energy.

- Once the concept of energy was broadened to include internal energy, the law of conservation of energy emerged as a universal law of nature.

- This section focuses on the concept of internal energy, the processes by which energy is transferred, the first law of thermodynamics, and some of the important applications of the first law. The first law of thermodynamics is the law of conservation of energy. It describes systems in which the only energy change is that of internal energy, which is due to transfers of energy by heat or work.

- Furthermore, the first law makes no distinction between the results of heat and the results of work. According to the first law, a system’s internal energy can be changed either by an energy transfer by heat to or from the system or by work done on or by the system.

- HEAT

- Heat is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings. When you heat a substance, you are transferring energy into it by placing it in contact with the surroundings that have a higher temperature.

  This is the case, for example, when you place a pan of cold water on a stove burner—the burner is at a higher temperature than the water, and so the water gains energy.

- We shall also use the term heat to represent the amount of energy transferred by this method.
Internal energy

It is important to make a major distinction between internal energy and heat. Internal energy is all the energy of a system that is associated with its microscopic components—atoms and molecules—when viewed from a reference frame at rest with respect to the system. The last part of this sentence ensures that any bulk kinetic energy of the system due to its motion through space is not included in its internal energy.

Internal energy includes kinetic energy of translation, rotation, and vibration of molecules, potential energy within molecules, and potential energy between molecules. It is useful to relate internal energy to the temperature of an object, but this relationship is limited—we shall find later that internal energy changes can also occur in the absence of temperature changes.

The internal energy of a monatomic ideal gas is associated with the translational motion of its atoms. This is the only type of energy available for the microscopic components of this system. In this special case, the internal energy is simply the total kinetic energy of the atoms of the gas; the higher the temperature of the gas, the greater the average kinetic energy of the atoms and the greater the internal energy of the gas.

More generally, in solids, liquids, and molecular gases, internal energy includes other forms of molecular energy. For example, a diatomic molecule can have rotational kinetic energy, as well as vibrational kinetic and potential energy.

Internal energy is defined as the energy associated with the random, disordered motion of molecules. It is separated in scale from the macroscopic ordered energy associated with moving objects; it refers to the invisible microscopic energy on the atomic and molecular scale.

For example, on the macroscopic scale a room temperature glass of water sitting on a table has no apparent energy, either potential or kinetic. But on the microscopic scale it is a seething mass of high speed molecules (H₂O) traveling at hundreds of meters per second. If the water were tossed across the room, this microscopic energy would not necessarily be changed when we superimpose an ordered large scale motion on the water as a whole. Figure 15 depicts what we have just mentioned.

U is the most common symbol used for internal energy. Note that in the textbook of Halliday et al (1999), E_int is used in place of U, and the authors reserved U for potential energy.
THE EQUIPARTITION OF ENERGY

• The theorem of equipartition of energy states that *molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion and that this energy is \( \frac{1}{2} k_B T \) per degree of freedom.*

• In other words, at equilibrium, each degree of freedom contributes \( \frac{1}{2} k_B T \) energy.

• We have assumed that the sole contribution to the internal energy of a gas is the translational kinetic energy of the molecules. However, the internal energy of a gas actually includes contributions from the translational, vibrational, and rotational motions of the molecules.

  The rotational and vibrational motions of molecules can be activated by collisions and therefore are “coupled” to the translational motion of the molecules. The branch of physics known as statistical mechanics has shown that, for a large number of particles obeying the laws of Newtonian mechanics, the available energy is \( \frac{1}{2} k_B T \), on the average, shared equally by each independent degree of freedom, in agreement with the equipartition theorem, as mentioned above.

• A diatomic gas such as O\(_2\) has five degrees of freedom: three associated with the translational motion and two associated with the rotational motion, so the number of degrees of freedom is \( f = 5 \). Because each degree of freedom contributes, on the average, \( \frac{1}{2} k_B T \) of energy, the total internal energy for a system of \( N \) molecules of a diatomic gas is \( U = N \frac{5}{2} k_B T = n \frac{5}{2} RT \).

• Generally, the total internal energy for a system of polyatomic ideal gas is

\[
U = N \frac{f}{2} k_B T = n \frac{f}{2} RT
\]  

(8)

where \( f \) is the number of degrees of freedom of the ideal gas of interest. For monatomic gases \( f = 3 \); for diatomic gases \( f = 5 \); for polyatomic gases \( f = 6 \).

• From (8), we see that the internal energy of an ideal gas is a function of temperature only. If the temperature of a system changes by an amount of \( \Delta T \), the system’s internal energy change is

\[
\Delta U = N \frac{f}{2} k_B \Delta T = n \frac{f}{2} R \Delta T
\]  

(9)

THE FIRST LAW OF THERMODYNAMICS

• The first law of thermodynamics is the application of the conservation of energy principle to heat and thermodynamic processes:
The sign conventions for $W$ and $Q$ are shown in the below table. We must be very careful and consistent in following the sign conventions.

<table>
<thead>
<tr>
<th>$Q &gt; 0$</th>
<th>The system gains heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q &lt; 0$</td>
<td>The system loses heat</td>
</tr>
<tr>
<td>$W &gt; 0$</td>
<td>Work done by the system</td>
</tr>
<tr>
<td>$W &lt; 0$</td>
<td>Work done on the system</td>
</tr>
</tbody>
</table>

The first law makes use of the key concepts of internal energy, heat, and work. It is used extensively in the discussion of heat engines.

The first law asserts that if heat is recognized as a form of energy, then the total energy of a system plus its surroundings is conserved; in other words, the total energy of the universe remains constant.

**Changing the state of a system with heat and work**

**Changing with heat**

Changes of the state of a system are produced by interactions with the environment or its surroundings through heat and work, which are two different modes of energy transfer. During these interactions, equilibrium (a static or quasi-static process) is necessary for the equations that relate system properties to one another to be valid.

Heat is energy transferred due to temperature differences only.

1. Heat transfer can alter system states;
2. Bodies do not ‘contain’ heat; heat is identified as it comes across system boundaries;
3. The amount of heat needed to go from one state to another is path dependent;
4. Adiabatic processes are ones in which no heat is transferred.

**Specific heats of gases**

The values of the specific heats of gases depend on how the thermodynamic process is carried out. In particular, the specific heats of gases for constant-volume processes can be very different from that for constant-pressure processes. To understand such difference, let us study the specific heats of an ideal gas with the help of the first law of thermodynamics.
(a) Specific heat of an ideal gas for constant-volume processes

Suppose heat flows into a constant-volume container which is filled with \( n \) moles of an ideal gas. Then the temperature of the gas rises by the amount \( \Delta T \), and its pressure increases as well. The heat added to the gas, \( Q_V \), is given by:

\[
Q_V = nC_V \Delta T
\]

(10)

where \( C_V \) is the molar specific heat of the gas at constant volume. Thus we can write

\[
C_V = \frac{Q_V}{n\Delta T}
\]

(11)

According to the first law of thermodynamics \( \Delta U = Q - W \), the change in internal energy \( \Delta U = Q_c \) in process (a) since \( W = P\Delta V = P \times 0 = 0 \). But \( \Delta U = \frac{1}{2} nR\Delta T \) for a polyatomic ideal gas. Hence we have

\[
C_V = \frac{Q_V}{n\Delta T} = \frac{f}{2} nR\Delta T / n\Delta T = \frac{f}{2} R
\]

(12)

(b) Specific heat of an ideal gas for constant-pressure processes

Similarly, the whole process can be carried out at constant pressure, but this time with the temperature and volume varies. If heat is added to the gas, then its temperature and volume increase. The molar specific heat of a gas at constant pressure \( C_P \) is related to the heat added \( Q_P \) by

\[
Q_P = nC_P \Delta T
\]

(13)

So we have

\[
C_P = \frac{Q_P}{n\Delta T}
\]

(14)

Again according to the first law of thermodynamics, for process (b), as heat is added to the container, the increasing volume involves a work \( W \) by the gas, where \( W = P\Delta V = nR\Delta T \) (here \( W > 0 \)). Using the relation \( \Delta U = Q - W \) again, we obtain

\[
Q_P = \Delta U + W = \frac{f}{2} nR\Delta T + nR\Delta T = \left(\frac{f}{2} + 1\right)nR\Delta T
\]

(15)

Plugging it into the expression of \( C_P \), we have

\[
C_P = \frac{Q_P}{n\Delta T} = \frac{f + 1}{2} nR\Delta T / n\Delta T = \left(\frac{f}{2} + 1\right)R
\]

(16)

• Hence, from (12) and (16) we have

\[
C_P - C_V = R
\]

(17)
Because \( R > 0 \) we conclude that \( C_p \) is greater than \( C_v \); extra work is required for expansion while increasing the temperature.

**Changing with work**

- As just mentioned, *heat* is a way of changing the energy of a system by virtue of a temperature difference only. Any other means for changing the energy of a system is called *work*. We can have push-pull work (e.g. in a piston-cylinder, lifting a weight), electric and magnetic work (e.g. an electric motor), chemical work, surface tension work, elastic work, etc.

- In defining work, we focus on the effects that the system (e.g. an engine) has on its surroundings. Thus we define work as being positive when the system does work on the surroundings (energy leaves the system). If work is done on the system (energy added to the system), the work is negative.

- Toward the middle of the 19th century, heat was recognized as a form of energy associated with the motion of the molecules of a body. Speaking more strictly, heat refers only to energy that is being transferred from one body to another. The total energy a body contains as a result of the positions and motions of its molecules is called its internal energy; in general, a body's temperature is a direct measure of its internal energy. All bodies can increase their internal energies by absorbing heat. However, mechanical work done on a body can also increase its internal energy; e.g., the internal energy of a gas increases when the gas is compressed. Conversely, internal energy can be converted into mechanical energy; e.g., when a gas expands it does work on the external environment. In general, the change in a body's internal energy is equal to the heat absorbed from the environment minus the work done on the environment. This statement constitutes the first law of thermodynamics, which is a general form of the law of conservation of energy.

- The first law is put into action by considering the flow of energy across the boundary separating a system from its surroundings. Consider the classic example of a gas enclosed in a cylinder with a movable piston, as shown in Figure 16. The walls of the cylinder act as the boundary separating the gas inside from the world outside, and the movable piston provides a mechanism for the gas to do work by expanding against the force holding the piston (assumed frictionless) in place. If the gas does work \( W \) as it expands, and absorbs heat \( Q \) from its surroundings through the walls of the cylinder, then this corresponds to a net flow of energy \( W - Q \) across the boundary to the surroundings. In order to conserve the total energy, there must be a counterbalancing change \( \Delta U = Q - W \) in the internal energy of the gas.

- The first law provides a kind of strict energy accounting system in which the change in the internal energy account \( \Delta U \) equals the difference between deposits \( Q \) and withdrawals \( W \).

- There is an important distinction between the quantity \( \Delta U \) and the related energy quantities \( Q \) and \( W \). Since the internal energy \( U \) is characterized entirely by the quantities (or parameters) that uniquely determine the state of the system at equilibrium, it is said to be a state function such that any change in internal energy is determined entirely by the initial \( (i) \) and final \( (f) \) states of the system: \( \Delta U = U_f - U_i \).

- However, as mentioned earlier, \( Q \) and \( W \) are not state functions because their values depend on the particular process (or path) connecting the initial and final states.

- From a formal mathematical point of view, the incremental change \( dU \) in the internal energy is an exact differential, while the corresponding incremental changes \( dQ \) and \( dW \) in heat and work are not, because the definite integrals of these quantities are path-dependent. These concepts can be used to great advantage in a precise mathematical formulation of thermodynamics.

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• The first law of thermodynamics is a generalization of the law of conservation of energy that encompasses changes in internal energy. It is a universally valid law that can be applied to many processes and provides a connection between the microscopic and macroscopic worlds.

• We have discussed two ways in which energy can be transferred between a system and its surroundings. One is work done by the system, which requires that there be a macroscopic displacement of the point of application of a force (or pressure). The other is heat, which occurs through random collisions between the molecules of the system. Both mechanisms result in a change in the internal energy of the system, and therefore usually result in measurable changes in the macroscopic variables of the system, such as the pressure, temperature, and volume of a gas.

• To better understand these ideas on a quantitative basis, suppose that a system undergoes a change from an initial state to a final state. During this change, energy transfer by heat $Q$ to the system occurs, and work $W$ is done by the system. As an example, suppose that the system is a gas in which the pressure and volume change from $P_i$ and $V_i$ to $P_f$ and $V_f$. If the quantity is measured for various paths connecting the initial and final equilibrium states, we find that it is the same for all paths connecting the two states.

• We conclude that the quantity is determined completely by the initial and final states of the system, and we call this quantity the change in the internal energy of the system. Although $Q$ and $W$ both depend on the path, the quantity $Q - W$ is independent of the path.

• When a system undergoes an infinitesimal change of state in which a small amount of energy $\partial Q$ is transferred by heat and a small amount of work $\partial W$ is done, the internal energy changes by a small amount $dU$. Thus, for infinitesimal processes we can express the first-law equation

$$dU = \partial Q - \partial W \quad (18)$$

where $\partial Q = nC\partial T$ and $\partial W = P\partial V$; $\partial T$ and $\partial V$ are infinitesimal changes of the temperature and volume, respectively. Here $C$ is the specific heat of the gas.

• The first-law equation is an energy conservation equation specifying that the only type of energy that changes in the system is the internal energy $U$. Let us consider some special cases in which this condition exists.

First, let us consider an isolated system—that is, one that does not interact with its surroundings. In this case, no energy transfer by heat takes place and the value of the work done by the system is zero; hence, the internal energy remains constant. We conclude that the internal energy $U$ of an isolated system remains constant or $\Delta U = 0$.

Next, we consider the case of a system (one not isolated from its surroundings) that is taken through a cyclic process—that is, a process that starts and ends at the same state. In this case, the change in the internal energy must again be zero, and therefore the energy $Q$ added to the system must equal the work $W$ done by the system during the cycle.

On a PV diagram, a cyclic process appears as a closed curve. It can be shown that in a cyclic process, the net work done by the system per cycle equals the area enclosed by the path representing the process on a PV diagram.

If the value of the work done by the system during some process is zero ($W = 0$), then the change in internal energy $\Delta U$ equals the energy transfer $Q$ into or out of the system: If energy enters the system, then $Q$ is positive and the internal energy increases. For a gas, we can associate this increase in internal energy with an increase in the kinetic energy of the molecules.
Conversely, if no energy transfer occurs during some process, but work is done by the system, then the change in internal energy equals the negative value of the work done by the system.

**SOME APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS**

It is useful to examine some common thermodynamic processes.

a) **Adiabatic process**

- An adiabatic process is one during which no energy is exchanged by heat between a system and its surroundings — that is Q = 0; an adiabatic process can be achieved either by thermally insulating the system from its surroundings (as shown in Fig. 20.6b, p 616, Halliday’s textbook) or by performing the process rapidly, so that there is little time for energy to transfer by heat. Applying the first law of thermodynamics to an adiabatic process, we see that

\[ \Delta U = -W \]  

(19)

- From this result, we see that if a gas expands adiabatically such that W is positive, then \( \Delta U \) is negative, and the temperature of the gas decreases. Conversely, the temperature of a gas increases when the gas is compressed adiabatically.

- If an ideal gas undergoes an adiabatic expansion or compression, using the first law of thermodynamics and the equation of state, one can show that (see pages 649 and 650, Halliday’s textbook)

\[ PV^\gamma = \text{const} \]  

(20)

where \( \gamma = C_p/C_V \) is assumed to be constant during the process.

\[ C_V = \frac{f}{2} R \]  

is the molar specific heat at constant volume.

\[ C_p = \left( \frac{f}{2} + 1 \right) R \]  

is the molar specific heat at constant pressure.

Using the equation of state, one can rewrite (20) as

\[ TV^{\gamma - 1} = \text{const} \]  

(21)

- Adiabatic processes are very important in engineering practice. Some common examples are the expansion of hot gases in an internal combustion engine, the liquefaction of gases in a cooling system, and the compression stroke in a diesel engine.

b) **Isobaric process**

- A process that occurs at constant pressure is called an isobaric process. In such a process, the values of the heat and the work are both usually nonzero. In an isobaric process, P remains constant.

- The work done by the gas is simply

\[ W = P(V_f - V_i) \]  

(22)
where P is the constant pressure; \( V_i \) and \( V_f \) are the initial and final volume of the gas, respectively.

c) Isovolumetric process

- A process that takes place at constant volume is called an isovolumetric process. In such a process, the value of the work done is clearly zero because the volume does not change. Hence, because \( W = 0 \), from the first law we see that in an isovolumetric process:

\[
\Delta U = Q \tag{23}
\]

- This expression specifies that if energy is added by heat to a system kept at constant volume, then all of the transferred energy remains in the system as an increase of the internal energy of the system.

d) Isothermal process

- A process that occurs at constant temperature is called an isothermal process. A plot of P versus V at constant temperature for an ideal gas yields a hyperbolic curve called an isotherm (see Figure 20.7, p 620, Halliday’s textbook). As mentioned earlier, the internal energy of an ideal gas is a function of temperature only. Hence, in an isothermal process involving an ideal gas, \( \Delta U = 0 \).

- For an isothermal process, then, we conclude from the first law that the energy transfer Q must be equal to the work done by the gas—that is, \( W = Q \). Any energy that enters the system by heat is transferred out of the system by work; as a result, no change of the internal energy of the system occurs (Figure 20.7: The PV diagram for an isothermal expansion of an ideal gas from an initial state to a final state. The curve is a hyperbola).

e) Isothermal expansion of an ideal gas

- Suppose that an ideal gas is allowed to expand quasi-statically at constant temperature, as described by the PV diagram shown in Figure 20.7 (Halliday’s textbook). The curve is a hyperbola and the equation of state of an ideal gas with T constant indicates that the equation of this curve is \( PV = \text{constant} \). The isothermal expansion of the gas can be achieved by placing the gas in thermal contact with an energy reservoir at the same temperature (as shown in Figure 20.6a, p 616, Halliday’s textbook).

- The work done by the gas in the expansion from state i (initial) to state f (final) is given by

\[
W = nRT \ln \left( \frac{V_f}{V_i} \right) \tag{24}
\]

Numerically, this work W equals the shaded area under the PV curve shown in Figure 20.7.

- Because the gas expands, the value for the work done by the gas is positive, as expected. If the gas is compressed, then the work done by the gas is negative.

**Example:** A 1.0-mol sample of an ideal gas is kept at 0.0 °C during an expansion from 3.0 L to 10.0 L.

(a) How much work is done by the gas during the expansion? (Ans. \( 2.7 \times 10^3 \) J)

(b) How much energy transfer by heat occurs with the surroundings in this process? (Ans. \( 2.7 \times 10^3 \) J)
(c) If the gas is returned to the original volume by means of a isobaric process, how much work is done on the gas? (Ans. \(-1.6 \times 10^3\) J)

3) THE SECOND LAW OF THERMODYNAMICS

- The second law of thermodynamics is a general principle which places constraints upon the direction of heat transfer and the attainable efficiencies of heat engines. In so doing, it goes beyond the limitations imposed by the first law of thermodynamics.

- The first law of thermodynamics, which we have previously studied, is a statement of conservation of energy, generalized to include internal energy. This law states that a change in internal energy in a system can occur as a result of energy transfer by heat or by work, or by both. As was stated in the previous section, the law makes no distinction between the results of heat and the results of work—either heat or work can cause a change in internal energy. However, an important distinction between the two is not evident from the first law. One manifestation of this distinction is that it is impossible to convert internal energy completely to mechanical energy by taking a substance through a thermodynamic cycle such as in a heat engine, a device we study in this section. Although the first law of thermodynamics is very important, it makes no distinction between processes that occur spontaneously and those that do not. However, we find that only certain types of energy-conversion and energy-transfer processes actually take place.

- The second law of thermodynamics, which we study in this section, establishes which processes do and which do not occur in nature. The followings are examples of processes that proceed in only one direction, governed by the second law:
  - When two objects at different temperatures are placed in thermal contact with each other, energy always flows by heat from the warmer to the cooler, never from the cooler to the warmer.
  - A rubber ball dropped to the ground bounces several times and eventually comes to rest, but a ball lying on the ground never begins bouncing on its own.
  - An oscillating pendulum eventually comes to rest because of collisions with air molecules and friction at the point of suspension. The mechanical energy of the system is converted to internal energy in the air, the pendulum, and the suspension; the reverse conversion of energy never occurs.
  - All these processes are irreversible—that is, they are processes that occur naturally in one direction only. No irreversible process has ever been observed to run backward—if it were to do so, it would violate the second law of thermodynamics.

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**Figure 19:** Schematic representation of a heat engine. The engine absorbs energy $Q_h$ from the hot reservoir, gives up $|Q_c|$ to the cold reservoir, and does work $W$.  

*Physic 1 Module 2: Thermodynamics*
From an engineering standpoint, perhaps the most important implication of the second law is the limited efficiency of heat engines. The second law states that a machine capable of continuously converting internal energy completely to other forms of energy in a cyclic process cannot be constructed.

HEAT ENGINES AND THE SECOND LAW OF THERMODYNAMICS

A heat engine is a device that converts internal energy to mechanical energy. For instance, in a typical process by which a power plant produces electricity: coal or some other fuel is burned, and the high-temperature gases produced are used to convert liquid water to steam. This steam is directed at the blades of a turbine, setting it into rotation. The mechanical energy associated with this rotation is used to drive an electric generator.

For example, the internal combustion engine in an automobile uses energy from a burning fuel to perform work that results in the motion of the automobile.

Although we have never observed a process occurring in the time-reversed sense, it is possible for it to occur. As we shall see later in the section, however, such a process is highly improbable. From this viewpoint, we say that processes occur with a vastly greater probability in one direction than in the opposite direction.

A heat engine carries some working substance through a cyclic process during which

1. the working substance absorbs energy from a high-temperature energy reservoir (the hot reservoir, at temperature $T_h$),
2. work is done by the engine, and
3. energy is expelled by the engine to a lower-temperature reservoir (the cold reservoir, at temperature $T_c$).

The process is illustrated by Figure 19.

It is useful to represent a heat engine schematically as in Figure 19. The engine absorbs a quantity of energy $Q_h$ ($Q_h > 0$) from the hot reservoir, does work $W$, and then gives up a quantity of energy $|Q_c|$ ($Q_c < 0$) to the cold reservoir. Because the working substance goes through a cycle, its initial and final internal energies are equal. Hence, from the first law of thermodynamics, $\Delta U = Q - W$, and with no change in internal energy, the net work $W$ done by a heat engine is equal to the net energy $Q_{\text{net}}$ flowing through it. As we can see from Figure 17, $Q_{\text{net}} = Q_h - |Q_c|$ therefore,

$$W = Q_h - |Q_c|$$

The thermal efficiency $e$ of a heat engine is defined as the ratio of the net work done by the engine during one cycle to the energy absorbed at the higher temperature during the cycle:

$$e = \frac{W}{Q_h} = \frac{Q_h - |Q_c|}{Q_h} = 1 - \frac{|Q_c|}{Q_h}$$

We can think of the efficiency as the ratio of what we get (mechanical work) to what we give (energy transfer at the higher temperature). In practice, we find that all heat engines uses only a fraction of the absorbed energy to do mechanical work, and consequently the efficiency is less than 100%. For example, a good automobile engine has an efficiency of about 20%, and diesel engines have efficiencies ranging from 35% to 40%.

Equation (26) shows that a heat engine has 100% efficiency ($e = 1$) only if $Q_c = 0$ - that is, if no energy is expelled to the cold reservoir. In other words, a heat engine with perfect efficiency would
have to use all of the absorbed energy to do mechanical work. On the basis of the fact that efficiencies of real engines are well below 100%, the Kelvin–Planck form of the second law of thermodynamics states the following:

*It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the absorption of energy from a reservoir and the performance of an equal amount of work.*

Or, *it is impossible to extract an amount of heat $Q_h$ from a hot reservoir and use it all to do work $W$. Some amount of heat $Q_c$ must be exhausted to a cold reservoir.*

- The statement of the second law means that, during the operation of a heat engine, $W$ can never be equal to $Q_h$, or, alternatively, that some energy $|Q_c|$ must be rejected to the surroundings. In other words, we must put more energy in, at the higher temperature, than the net amount of energy we get out by work.

**Example:** Find the efficiency of a heat engine that absorbs 2000 J of energy from a hot reservoir and exhausts 1500 J to a cold reservoir during a cycle. (Ans. 25%)

**HEAT PUMPS AND REFRIGERATORS**

- Refrigerators and heat pumps are heat engines running in reverse. Here, we introduce them briefly for the purpose of developing an alternate statement of the second law.

- In a refrigerator or heat pump, the engine absorbs energy $Q_c$ ($Q_c > 0$) from a cold reservoir (at temperature $T_c$) and expels energy $Q_h$ ($Q_h < 0$) to a hot reservoir (at temperature $T_h$), as shown in Figure 20. This can be accomplished only if work is done on the engine.

- From the first law, we know that the energy given up to the hot reservoir must equal the sum of the work done and the energy absorbed from the cold reservoir. Therefore, the refrigerator or heat pump transfers energy from a colder body (for example, the contents of a kitchen refrigerator or the winter air outside a building) to a hotter body (the air in the kitchen or a room in the building). In practice, it is desirable to carry out this process with a minimum of work. If it could be accomplished without doing any work, then the refrigerator or heat pump would be “perfect” (see Fig. 22.6, p 673, Halliday’s textbook).

- Again, the existence of such a perfect device would be in violation with the second law of thermodynamics, which in the form of the Clausius statement states:

*It is impossible to construct a cyclical machine whose sole effect is the continuous transfer of energy from one object to another object at a higher temperature without the input of energy by work.*

- In other words, it is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow. Energy will not flow spontaneously from a low temperature object to a higher temperature object.
In simpler terms, energy does not flow spontaneously from a cold object to a hot object. For example, we cool homes in summer using heat pumps called air conditioners. The air conditioner pumps energy from the cool room in the home to the warm air outside. This direction of energy transfer requires an input of energy to the air conditioner, which is supplied by the electric power company.

The Clausius and Kelvin–Planck statements of the second law of thermodynamics appear, at first sight, to be unrelated, but in fact they are equivalent in all respects. Although we do not prove so here, if either statement is false, then so is the other.

Heat pump and refrigerators are subject to the same limitations from the second law of thermodynamics as any other heat engine, and therefore a maximum efficiency can be calculated from the Carnot cycle (discussed later).

Heat pumps operating in heating mode are usually characterized by a coefficient of performance (COP) which is the ratio of the energy rejected from the hot reservoir ($|Q_h|$) to the work (W) done by the pump:

$$\text{COP (heating mode)} = \frac{|Q_h|}{W}$$  \hspace{1cm} (27)

Similarly, refrigerators are usually characterized by a coefficient of performance (COP) which is the ratio of the energy extracted from the cold reservoir ($|Q_c|$) to the work (W) done by the device:

$$\text{COP (cooling mode)} = \frac{|Q_c|}{W}$$  \hspace{1cm} (28)

### REVERSIBLE AND IRREVERSIBLE PROCESSES

- In the next section we discuss a theoretical heat engine that is the most efficient. To understand its nature, we must first examine the meaning of reversible and irreversible processes.

- In thermodynamics, a **reversible process**, or **reversible cycle** if the process is cyclic, is a process that can be "reversed" by means of infinitesimal changes in some property of the system without loss or dissipation of energy. Due to these infinitesimal changes, the system is at rest throughout the entire process.

- Since it would take an infinite amount of time for the process to finish, perfectly reversible processes are impossible. However, if the system undergoing the changes responds much faster than the applied change, the deviation from reversibility may be negligible.

- In a reversible cycle, the system and its surroundings will be exactly the same after each cycle.

- An alternative definition of a **reversible process** is a process that, after it has taken place, can be reversed and causes no change in either the system or its surroundings. In thermodynamic terms, a process "taking place" would refer to its transition from its initial state to its final state.

- In a reversible process, the system undergoing the process can be returned to its initial conditions along the same path shown on a PV diagram, and every point along this path is an equilibrium state.
• A process that is not reversible is termed **irreversible**. In an irreversible process, finite changes are made; therefore the system is not at equilibrium throughout the process. At the same point in an irreversible cycle, the system will be in the same state, but the surroundings are permanently changed after each cycle.

• All natural processes are known to be irreversible.

**CARNOT ENGINE AND CARNOT’S THEOREM**

• In 1824 a French engineer named Sadi Carnot described a theoretical engine, now called a Carnot engine, that is of great importance from both practical and theoretical viewpoints. He showed that a heat engine operating in an ideal, reversible cycle—called a Carnot cycle—between two energy reservoirs is the most efficient engine. Such an ideal engine establishes an upper limit on the efficiencies of all other engines. That is, the net work done by a working substance taken through the Carnot cycle is the greatest amount of work possible for a given amount of energy supplied to the substance at the higher temperature.

• Carnot’s theorem can be stated as follows:

  *No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.*

• The PV diagram for the Carnot’s cycle is shown in Figure 21.

As shown in Figure 21, the Carnot cycle consists of two adiabatic processes and two isothermal processes, all reversible:

1. Process $A \rightarrow B$ is an isothermal expansion at temperature $T_h$. The gas is placed in thermal contact with an energy reservoir at temperature $T_h$. During the expansion, the gas absorbs energy $Q_h$ from the hot reservoir and does work $W_{AB}$.

2. In process $B \rightarrow C$, the gas expands adiabatically—that is, no heat enters or leaves the system. During the expansion, the temperature of the gas decreases from $T_h$ to $T_c$, and the gas does work $W_{BC}$.

3. In process $C \rightarrow D$, the gas is placed in thermal contact with an energy reservoir at temperature $T_c$ and is compressed isothermally at temperature $T_c$. During this time, the gas expels energy $Q_c$ to the cold reservoir, and the work done on the gas is $W_{CD}$.

4. In the final process, $D \rightarrow A$, the gas is compressed adiabatically. The temperature of the gas increases to $T_h$, and the work done on the gas is $W_{DA}$.

• The net work done in this reversible, cyclic process is equal to the area enclosed by the path ABCDA in Figure 21. As mentioned earlier, because the change in internal energy is zero, the net work $W$ done in one cycle equals the net energy transferred into the system, $Q_h - |Q_c|$. The thermal efficiency of the engine is given by Equation (26):

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*Figure 21: PV diagram for the Carnot cycle. The net work done, $W$, equals the net energy received in one cycle, $Q_h - |Q_c|$. Note that $\Delta U = 0$ for the cycle.*
\[ e = \frac{W}{Q_h} = \frac{Q_h - |Q_c|}{Q_h} = 1 - \frac{|Q_c|}{Q_h} \]

- We can show that for a Carnot cycle (see page 678, Halliday’s textbook)

\[ \frac{|Q_c|}{Q_h} = \frac{T_c}{T_h} \quad (29) \]

- Hence, the thermal efficiency of a Carnot engine is

\[ e_c = 1 - \frac{T_c}{T_h} \quad (30) \]

The subscript c stands for the Carnot cycle.

- This result indicates that **all Carnot engines operating between the same two temperatures have the same efficiency**.

**ENTROPY**

- The zeroth law of thermodynamics involves the concept of temperature, and the first law involves the concept of internal energy. Temperature and internal energy are both state functions—that is, they can be used to describe the thermodynamic state of a system. Another state function—this one related to the second law of thermodynamics—is entropy \( S \). In this section we define entropy on a macroscopic scale as it was first expressed by Clausius in 1865.

- Consider any infinitesimal process in which a system changes from one equilibrium state to another. If \( \partial Q_r \) is the amount of energy transferred by heat when the system follows a reversible path between the states, then the change in entropy \( dS \) is equal to this amount of energy for the reversible process divided by the absolute temperature of the system:

\[ dS = \frac{\partial Q_r}{T} \quad (31) \]

- We have assumed that the temperature is constant because the process is infinitesimal. Since we have claimed that entropy is a state function, the change in entropy during a process depends only on the end points and, therefore, is independent of the actual path followed.

- The subscript \( r \) on the quantity \( \partial Q_r \) is a reminder that the transferred heat is to be measured along a reversible path, even though the system may actually have followed some irreversible path. When heat is absorbed by the system, \( \partial Q_r \) is positive and the entropy of the system increases. When heat is expelled from the system, \( \partial Q_r \) is negative and the entropy of the system decreases.

- Note that equation (31) defines not entropy but rather the change in entropy. Hence, the meaningful quantity in describing a process is the change in entropy. Entropy was originally formulated as a useful concept in thermodynamics; however, its importance grew tremendously as the field of statistical mechanics developed because the analytical techniques of statistical mechanics provide an alternative means of interpreting entropy.
• In statistical mechanics, the behavior of a substance is described in terms of the statistical behavior of its atoms and molecules. One of the main results of this treatment is that isolated systems tend toward disorder and that entropy is a measure of this disorder.

• If we consider a system and its surroundings to include the entire Universe, then the Universe is always moving toward a macrostate corresponding to greater disorder.

• Because entropy is a measure of disorder, an alternative way of stating this is the entropy of the Universe increases in all real processes. This is yet another statement of the second law of thermodynamics that can be shown to be equivalent to the Kelvin–Planck statement.

• To calculate the change in entropy for a finite process, we must recognize that $T$ is generally not constant. If $\delta Q_r$ is the energy transferred by heat when the system is at a temperature $T$, then the change in entropy in an arbitrary reversible process between an initial state and a final state is

$$\Delta S = \int_S^T dS = \int_S^T \frac{\delta Q_r}{T} \quad \text{(reversible path)}$$

Or

$$S_f = S_i + \int_S^T \frac{\delta Q_r}{T} \quad \text{(reversible path)}$$

• As with an infinitesimal process, the change in entropy $\Delta S$ of a system going from one state to another has the same value for all paths connecting the two states. That is, the finite change in entropy $\Delta S$ of a system depends only on the properties of the initial and final equilibrium states. Thus, we are free to choose a particular reversible path over which to evaluate the entropy in place of the actual path, as long as the initial and final states are the same for both paths.

• Let us consider the changes in entropy that occur in a Carnot heat engine operating between the temperatures $T_h$ and $T_c$. In one cycle, the engine absorbs energy $Q_h$ from the hot reservoir and expels energy $Q_c$ to the cold reservoir. These energy transfers occur only during the isothermal portions of the Carnot cycle; thus, the constant temperature can be brought out in front of the integral sign in equation (32). The integral then simply has the value of the total amount of energy transferred by heat. Thus, the total change in entropy for one cycle is

$$\Delta S = \frac{Q_h}{T_h} + \frac{Q_c}{T_c}$$

• We have shown that, for a Carnot engine,

$$\frac{|Q_c|}{Q_h} = \frac{T_c}{T_h}$$

• Combining equations (34) and (35) and noting that $Q_c < 0$, we find that the total change in entropy for a Carnot engine operating in a cycle is zero:

$$\Delta S = 0$$

• Now let us consider a system taken through an arbitrary (non-Carnot) reversible cycle. Because entropy is a state function—and hence depends only on the properties of a given equilibrium
state—we conclude that $\Delta S = 0$ for any reversible cycle. In general, we can write this condition in the mathematical form

$$\oint \frac{\partial Q}{T} = 0$$  \hspace{1cm} (36)$$

where the symbol $\oint$ indicates that the integration is over a closed path.

QUASI-STATIC, REVERSIBLE PROCESS FOR AN IDEAL GAS

Let us suppose that an ideal gas undergoes a quasi-static, reversible process from an initial state having temperature $T_i$ and volume $V_i$ to a final state described by $T_f$ and $V_f$. Let us calculate the change in entropy of the gas for this process.

Writing the first law of thermodynamics in differential form and rearranging the terms, we have

$$\partial Q = dU + \partial W$$

where $\partial W = PdV$. For an ideal gas, from (8) we have $dU = n \frac{f}{2} RdT$, and from the ideal gas law, we have $P = nRT/V$. Therefore, we can express the energy transferred by heat in the process as

$$\partial Q = n \frac{f}{2} RdT + nRT \frac{dV}{V}$$

Dividing all terms by $T$, we have

$$\frac{\partial Q}{T} = n \frac{f}{2} R \frac{dT}{T} + nR \frac{dV}{V}$$ \hspace{1cm} (37)$$

We see that each of the terms on the right-hand side of equation (37) depends on only one variable, integrating both sides of this equation from the initial state to the final state, we obtain

$$\Delta S = \int_i^f \frac{\partial Q}{T} = n \frac{f}{2} R \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

Or, using $C_V = \frac{f}{2} R$

$$\Delta S = \int_i^f \frac{\partial Q}{T} = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$ \hspace{1cm} (38)$$

This expression demonstrates mathematically what we argued earlier—that $\Delta S$ depends only on the initial and final states, and is independent of the path between the states. Also, note that in equation (38) that $\Delta S$ can be positive or negative, depending on the values of the initial and final volumes and temperatures.

Finally, for a cyclic process ($T_i = T_f$ and $V_i = V_f$), we see from equation (38) that $\Delta S = 0$. This is evidence that entropy is a state function.

ENTROPY CHANGES IN IRREVERSIBLE PROCESSES

By definition, calculation of the change in entropy requires information about a reversible path connecting the initial and final equilibrium states. To calculate changes in entropy for real (irreversible) processes, we must remember that entropy (like internal energy) depends only on the
state of the system. That is, entropy is a state function. Hence, the change in entropy when a system
moves between any two equilibrium states depends only on the initial and final states.

- We can show that if this were not the case, the second law of thermodynamics would be violated. We
now calculate the entropy change in some irreversible process between two equilibrium states
by devising a reversible process (or series of reversible processes) between the same two states and
computing \( \Delta S = \int_{\text{i}}^{\text{f}} \frac{\delta Q_{\text{r}}}{T} \) for that reversible process. In irreversible processes, it is critically
important that we distinguish between \( Q \), the actual heat transfer in the process, and \( Q_{\text{tr}} \), the energy
that would have been transferred by heat along a reversible path. Only \( Q_{\text{r}} \) is the correct value to be
used in calculating the entropy change.

- As we shall see in the following examples, the change in entropy for a system and its
surroundings is always positive (\( \Delta S > 0 \)) for an irreversible process. In general, the total entropy—
and therefore the disorder—always increase in an irreversible process. Keeping these
considerations in mind, we can state the second law of thermodynamics as follows:

\[ \text{The total entropy of an isolated system that undergoes a change can never decrease.} \]

The corresponding formula is

\[ \Delta S \geq 0 \quad (39) \]

where the ‘\( = \)’ sign applies to a reversible process and the ‘\( > \)’ sign to an irreversible process.

- Particularly, if the process is irreversible, then the total entropy of an isolated system always
increases. In a reversible process, the total entropy of an isolated system remains constant.

- When dealing with a system that is not isolated from its surroundings, remember that the increase
in entropy described in the second law (equation 39) is that of the system and its surroundings.
When a system and its surroundings interact in an irreversible process, the increase in entropy of
one is greater than the decrease in entropy of the other; consequently, the total entropy of the two
increases.

- Therefore, we conclude that the change in entropy of the Universe must be greater than zero for
an irreversible process and equal to zero for a reversible process. Ultimately, the entropy of the
Universe should reach a maximum value. At this value, the Universe will be in a state of uniform
temperature and density. All physical, chemical, and biological processes will cease because a state
of perfect disorder implies that no energy is available for doing work. This gloomy state of affairs
is sometimes referred to as the heat death of the Universe.

- In light of the statistical view of entropy, Boltzmann found an alternative method for calculating
entropy through use of the following relation:

\[ S = k_B \ln \Omega \quad (40) \]

where \( \Omega \) is the number of microstates (microscopic configurations) corresponding to the observed
thermodynamic macrostate of the system of interest. The symbol ‘\( \ln \)’ here is an abbreviation of the
natural logarithm.

- This definition is considered to be the fundamental definition of entropy (as all other definitions
can be mathematically derived from it, but not vice versa).
2.3. The third principle of thermodynamics (the third law of thermodynamics)

- The third law of thermodynamics states that **absolute zero is unattainable and there is no temperature lower than absolute zero.**

- It is possible to cool an object to temperatures arbitrarily close to absolute zero. Experiments have reached temperatures as low as $2.0 \times 10^{-8}$ K, but no object can ever be cooled to precisely 0 K.

- To cool an object, you can place it in thermal contact with a colder object. Heat transfer will occur, with your object ending up cooler and the other object ending up warmer. In particular, suppose you are given a collection of objects at 0 K for cooling other objects. You put your object in contact with one of the 0-K objects. Your object cools while the 0-K object warms slightly. You continue this process, each time throwing away the “warmed up” 0-K object and using a new one. Each time you cool your object, it gets closer to 0 K without ever actually getting there.

- Using equation (32) we can find the entropy difference between two arbitrary states. This still leaves us with one constant of integration, which could be system dependent. The third law of thermodynamics sets this constant to zero at zero temperature for all systems. The short form of the third law is

$$S(T = 0) = 0 \quad (41)$$

but this is not completely correct. First of all, we cannot reach zero temperature, and second, we need to take the thermodynamic limit. Therefore, the correct formulation of the third law is:

$$\lim_{N \to \infty} \lim_{T \to 0} \frac{S(T)}{N} = 0 \quad (42)$$

where $N$ is the number of molecules of the system of interest. Note that we cannot interchange the order of the limits, we have to take the limit for the temperature first. This is a general characteristic of the thermodynamic limit.

2.4. Examples of entropy calculation and application

1) Entropy change in thermal conduction

- Let us now consider a system consisting of a hot reservoir and a cold reservoir in thermal contact with each other and isolated from the rest of the Universe. A process occurs during which energy $Q$ is transferred by heat from the hot reservoir at temperature $T_h$ to the cold reservoir at temperature $T_c$. Because the cold reservoir absorbs energy $Q$ ($Q > 0$), its entropy increases by $Q/T_c$. At the same time, the hot reservoir loses energy $Q$, and so its entropy change is $-Q/T_h$.

- The change in entropy of the system (and of the Universe) is given by

$$\Delta S = \frac{Q}{T_c} + \left( -\frac{Q}{T_h} \right) = Q\left( \frac{1}{T_c} - \frac{1}{T_h} \right) \quad (43)$$

- Because $Q > 0$ and $T_h > T_c$, from equation (43) we see that the change in entropy of the system is greater than zero.

2) Entropy change in a free expansion
• Consider the irreversible free expansion of an ideal gas from an initial volume $V_i$ into a vacuum such that its final volume is $V_f$, as shown in Figure 22. Suppose that the gas is thermally insulated from the environment and at initial temperature of $T_i$.

![Figure 22: An Irreversible free expansion of a gas.](image)

• The process is clearly neither reversible nor quasi-static. The work done by the gas against the vacuum is zero, and because the walls are insulating, no energy is transferred by heat during the expansion. That is, $W = 0$ and $Q = 0$. Using the first law, we see that the change in internal energy is zero ($\Delta U = 0$). Because the gas is ideal, $U$ depends on temperature only (see equation 8), we conclude that $\Delta T = 0$. This implies that the initial and final temperatures are equal. Hence

$$T_i = T_f = T$$

(44)

• So the initial state of the gas is $T_i = T$, $V_i$ and the final state of the gas is $T_f = T$, $V_f$. We would like to replace the irreversible free expansion of the ideal gas with an equivalent reversible process. Since the initial and final temperatures are the same, we can replace the free expansion with an isothermal expansion of the gas at constant temperature, from volume $V_i$ to $V_f$.

• To see that an expansion at constant temperature is a reversible process, consider a gas in a piston and in contact with a heat bath at temperature $T$. If one pulls the piston very slowly, heat will flow in to keep the temperature at $T$; on the other hand, if one slowly compresses the piston, the gas will be compressed, and heat will flow back into the reservoir. So we can see that an isothermal expansion is reversible. All we need to do now is to compute the difference between the entropy of an ideal gas in the initial state $T_i$, $V_i$ and final state $T_f$, $V_f$.

• Because $T$ is constant in this process, equation (32) gives

$$\Delta S = \int_{V_i}^{V_f} \frac{\partial Q_r}{T} = \frac{1}{T} \int_{V_i}^{V_f} \partial Q_r$$

(45)

• For an isothermal process, the first law of thermodynamics specifies that $\int_{V}^{\partial} Q_r$ is equal to the work done by the gas during the expansion from $V_i$ to $V_f$, which is given by equation (24). Using this result, we find that the entropy change of the gas is
\[ \Delta S = nR \ln \frac{V_f}{V_i} \]  

(46)

- Because \( V_f > V_i \), from equation (46), we see that \( \Delta S \) is positive. This positive result indicates that both the entropy and the disorder of the gas increase as a result of the irreversible, adiabatic expansion, consistent with the second law.

3) **Entropy change in calorimetric processes** (see pages 691 and 692, Halliday’s textbook)

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