12. THE LAWS OF THERMODYNAMICS


Thermodynamics is the study of energy relationships that involve heat, mechanical work, and other aspects of energy and energy transfer. Thermodynamics is of central importance in the study of energy-conversion devices such as engines, batteries, and refrigerators and also in the functioning of living organisms.

We have studied energy transfer through mechanical work and through heat transfer. Now we are ready to combine and generalize those principles in the first law of thermodynamics.

12.1 The First Law of Thermodynamics

The first law of thermodynamics extends the principle of conservation of energy to include heat as well as mechanical energy and relates the change of an internal energy (total of all the energy of the molecules of a system) with transfer of energy by heat and mechanical work. The First Law of Thermodynamics states that the change in internal energy, \( \Delta U \), of a system is equal to the heat added to the system, \( Q \), minus the work done by the system, \( W \).

\[
\Delta U = Q - W \quad (12-1)
\]

The first law of thermodynamics is one of the great laws of physics and its validity rests on experiments to which no exceptions have been seen. Since \( Q \) and \( W \) represent energy transferred into or out of a system, the internal energy changes accordingly. Thus, the first law of thermodynamics is a great and broad statement of the law of conservation of energy.
We must be careful and consistent in sign conventions for \(Q\) and \(W\). If work is done by the system \(W > 0\). If work is done on the system \(W < 0\). If heat is added to the system \(Q > 0\). If heat leaves the system \(Q < 0\).

The internal energy of any thermodynamic system depends only on the initial and final states and not on the path taken. A system at any moment is in a particular state and can be said to have a certain amount of internal energy \(U\). But a system does not have a certain amount of heat \(Q\) or work \(W\). Rather, when work is done on a system (such as compressing a gas) or when heat is added to or removed from a system, the state of a system changes. Thus, work and heat are involved in thermodynamic processes that can change the system from one state to another by different paths but they are not characteristic of the state itself. In other words, \(Q\) and \(W\) are not state variables. State variables that we have studied are internal energy \(U\), pressure \(P\), volume \(V\), mass \(m\) or number of moles \(n\). The process depends only on the initial and final states, not on the path leading from one to the other. An equivalent statement is that the internal energy \(U\) of a system is a function of the State Coordinates \(P, V, T\) alone (actually, of any two of these, since the three variables are related by the Equation of State). These facts, that internal energy depends only on the state of a system and that it is path independent for any thermodynamic process, are an important additional part of the content of the 1st law in the analysis of the thermodynamic processes.

12.2 Thermodynamic Processes

We consider simple thermodynamic process in a very simple system: a fixed mass of an ideal gas enclosed in a container fitted with a movable piston. We choose this system because expression of the Internal Energy of an Ideal Gas is known (see section 11.2):

\[
U = (3/2)NkT = (3/2)nRT
\]

Another important reason is that the ideal gas model can be applied (to some extent) to real gases. Gases, as a rule, are used as working substances in heat engines. The importance of heat engines in life and technology is impossible to overestimate. Therefore, we will try to describe work and efficiency of heat engines by using an approach that combines simple thermodynamic processes.
There are four thermodynamic processes that occur often enough in practical problems to be worth some discussion: adiabatic, isochoric, isobaric, and isothermal.

An **Adiabatic Process** is a process in which there is not heat transfer into or out of the system \((Q=0)\). It can be achieved by using thermal insulating material or by performing the process in short time. In the case of adiabatic process, we can deduce from the first law:

\[
\Delta U = Q - W \rightarrow \Delta U = -W \quad (12-2)
\]

During adiabatic expansion of a gas, the piston is moving by expanding gas, so the system performs work on the environment. Therefore, \(W > 0\). Then, from (12-2) we can see that, in this case \(\Delta U = U_2 - U_1 < 0\) and \(\Delta U = (3/2)nk\Delta T\). When \(\Delta U < 0\) the temperature decreases: \(\Delta T < 0\). Example: the power stroke in an internal combustion engine. When the external force applied to the piston compresses the system adiabatically, the environment on the system does the work. So \(W < 0\), \(\Delta U > 0\), and \(\Delta T > 0\). The temperature of the gas increases. Example: The compression stroke of an internal combustion engine

**Isobaric Process** (from the Greek meaning “same pressure”). This is a constant pressure process. In an isobaric process, none of the three quantities \(\Delta U\), \(Q\) and \(W\) in the first law is zero. But, in this case, there is a simple formula to calculate the work \(W\).

\[
W = P\Delta V = P(V_2 - V_1) \quad (12-3)
\]

An **Isochoric Process** is a constant volume process. Work done always results in a change in the volume. See, for example, (12-3). If \(V=\text{constant}\) then \(\Delta V = 0\), so \(W = 0\). Thus, the first law of thermodynamics for an isochoric process is:

\[
U_2 - U_1 = \Delta U = Q \quad (12-4)
\]

In an isochoric process, all heat added to the system increases the internal energy of the system. Example: heating a gas in a constant volume container. In terms of our model, the position of the piston is fixed and heat is added to the gas in the cylinder.
An **Isothermal Process** is a constant temperature process. In an ideal gas, 
\[ \Delta U = \frac{3}{2} n k \Delta T, \]
therefore, if \( T = \) constant then \( \Delta T = 0 \) so \( \Delta U = 0 \). Then the first law of thermodynamics for an isothermal process can be written as follows:

\[ \Delta U = 0 \rightarrow Q = W \]  \( \text{(12-5)} \)

All heat added to the system must leave it as work done by the system. For most systems other than ideal gases, the internal energy depends on pressure as well as temperature so in these systems when \( T = \) constant, \( \Delta U \neq 0 \).

**EXAMPLE 12.1 Boiling water and the first law of thermodynamics**

One gram of water occupies a volume \( V_1 = 1.00 cm^3 \) at atmospheric pressure \( P_1 = 1 atm \). When this amount of water is boiled it becomes \( V_2 = 1671 cm^3 \) of steam. Calculate: (a) the work \( W \) done by the water when it vaporized; (b) the heat \( Q \) added to the system; (c) the change of the internal energy \( \Delta U \).

You may need the following:

The density of the water \( \rho = 1.00 \cdot 10^3 \ \frac{kg}{m^3} \)

The heat of vaporization of water \( L_v = 2.256 \cdot 10^6 \ \frac{J}{kg} \)

\( V_1 = 1.00 cm^3 = 1.00 \cdot 10^{-6} m^3 \)
\( V_2 = 1671 cm^3 = 1.671 \cdot 10^{-3} m^3 \)
\( \rho = 1.00 \cdot 10^3 \ \frac{kg}{m^3} \)
\( P_1 = P_2 = P = 1 atm = 1.013 \cdot 10^5 Pa \)

(a) \( W ? \)
(b) \( Q ? \)
(c) \( \Delta U ? \)

(a) The boiling occurs at constant pressure: \( P_1 = P_2 = P = \text{const} \). Thus, this is an isobaric process. The work done by the system is positive. It could be found by using equation (12-3).

\[ W = P \cdot \chi \cdot R \cdot V \]
\[ W = 169 J \]
(b) The heat $Q$ required to boil water could be found according to equation (11-5).

\[
Q = mL_v = \rho V_1 L_v
\]

\[
m = \rho V_1
\]

\[
Q = \left(1.00 \cdot 10^3 \frac{kg}{m^3}\right) \left(0.0 \cdot 10^{-6} m^3\right) \left(2.256 \cdot 10^6 \frac{J}{kg}\right)
\]

\[
Q = 2260 \cdot J
\]

(c) To find $\Delta U$ we will use the first law of thermodynamics, equation (12-1).

\[
\Delta U = Q - W = 2260 J - 169 J = 2090 J
\]

**EXAMPLE 12.2 First law of thermodynamics in isobaric and isochoric processes.**

An ideal gas is slowly compressed at a constant pressure $P = 2$ atm from $V_1 = 1.0 \cdot 10^{-2} m^3$ to $V_2 = 2.0 \cdot 10^{-3} m^3$. In this process, some heat flows out of the gas and the temperature drops from $T_1$ to $T_2$. Heat is then added to the gas, holding the volume constant $V_3 = V_2 = 2.0 \cdot 10^{-3} m^3$, and the pressure and temperature are allowed to rise until the temperature reaches its original value $T_3 = T_1$. Calculate: (a) the work done by the gas in the total process $1 \rightarrow 2 \rightarrow 3$; (b) the change in internal energy in the total process $\Delta U = U_3 - U_1$; (c) the total heat flow into the gas.

$P_1 = P_2 = 2 \text{ atm} = 2 \cdot 1.013 \cdot 10^5 Pa$

$V_1 = 1.0 \cdot 10^{-2} m^3$

$V_2 = 2.0 \cdot 10^{-3} m^3$

$V_3 = V_2$

$T_3 = T_1$

(a) $W_{123}$?

(b) $\Delta U = U_3 - U_1$?

(c) $Q_{123}$?

(a) The process $1 \rightarrow 2$ occurs at constant pressure. So this is an isobaric process. We can find work done

\[
W_{12} = P \left( V_2 - V_1 \right) = \left(1.03 \cdot 10^5 Pa\right) \left(0.0 \cdot 10^{-3} m^3 - 10 \cdot 10^{-3} m^3\right) = \left(0.026 \cdot 10^5 Pa\right) \left(8.0 \cdot 10^{-3} m^3\right)
\]
\[ W_{12} = -1.6 \cdot 10^3 J \]

The work done during the whole process \(1 \rightarrow 2 \rightarrow 3\): \( W_{123} = W_{12} + W_{23} \)

Process \(2 \rightarrow 3\) occurs at constant volume, so this is an isochoric process. For isochoric processes \(\Delta V = 0\) and \(W_{23} = 0\). Finally, for the total work done, \(W_{123} = -1.6 \cdot 10^3 J\).

(b) To answer this question, we should recall the definition of the internal energy of an ideal gas (11-3), \( U = \frac{3}{2} nkT \). From this expression we can figure out that \( \Delta U \propto \Delta T \). Therefore, when \( \Delta T = 0 \), \( \Delta U = 0 \). This is exactly the situation that we have in this problem. \( \Delta T = T_3 - T_1 = 0 \), so \( \Delta U_{123} = 0 \).

(c) Now we will use the first law of thermodynamics

\[ \Delta U_{123} = Q_{123} - W_{123} \]
\[ 0 = Q_{123} - W_{123} \]

so \( Q = W = -1.6 \cdot 10^3 J \)

Since \( Q < 0 \), 1600J of heat flows out of the gas for the whole process \(1 \rightarrow 2 \rightarrow 3\).

12.3 Heat Engines

A Heat Engine is a device for changing thermal energy by means of heat flow between two temperatures, into useful work. The heat engine takes heat \( Q_H \) from a source at temperature \( T_H \) converts part of it to work \( W \) and discards the remainder \( |Q_C| \), at a lower temperature \( T_C \).

The Thermal Efficiency of a heat engine is the useful work \( W \), done by the engine, divided by heat input \( Q_H \).

\[ e = \frac{W}{Q_H} \quad (12-5) \]

Since energy is conserved, the heat input \( Q_H \) must be equal the work done plus heat that flows out (is discarded) \( Q_C \) at the low temperature \( T_C \).

\[ Q_H = W + Q_C \quad (12-6) \]

Thus,

\[ W = Q_H - Q_C \quad (12-7) \]

and the efficiency of an engine is

\[ e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad (12-8) \]
To give the efficiency as a percent, we multiply equation (12-8) by 100. Note that \( e \) could be 1 (or 100%) only if \( Q_C = 0 \); that is, only if no heat was exhausted to the environment.

**EXAMPLE 12.3 Car Efficiency**

An automobile engine has an efficiency of 20% and produces an average \( 2.3 \times 10^4 \) J of work \( W \) per second during operation. Calculate: (a) heat input \( Q_H \) and (b) heat discarded \( Q_C \) per second.

\[
e = 20\% = 0.20 \\
W = 2.3 \times 10^4 \text{ J}
\]

(a) \( Q_H = ? \)

(b) \( Q_C = ? \)

(a) From equation (12-5)

\[
e = \frac{W}{Q_H} \rightarrow Q_H = \frac{W}{e} = \frac{2.3 \times 10^4 \text{ J}}{0.20} = 1.15 \times 10^5 \text{ J}
\]

(b) From equation (12-8)

\[
e = 1 - \frac{Q_C}{Q_H} \rightarrow Q_C = (1 - e)Q_H = (1 - 0.20) \times 1.15 \times 10^5 \text{ J} = 9.2 \times 10^4 \text{ J}
\]

12.4 **Carnot Engine**: The Most Efficient Heat Engine. **Real Heat Engine Efficiencies**

To see how to increase efficiency, the French scientist Carnot examined the characteristics of an ideal engine (now called a Carnot Engine). No Carnot engine actually exists, but as a theoretical idea it played an important role in the development of thermodynamics. There are four processes done by a Carnot engine in a cycle; two are adiabatic \((Q = 0)\) and two are isothermal \((\Delta T = 0)\). We learned that an adiabatic process is efficient in the transformation of work of an external force into an increase of internal energy that means an increase in temperature (adiabatic compression). The adiabatic process is efficient in the transformation of part of the internal energy, thus decreasing temperature, into work done by the system on the environment (adiabatic expansion). The isothermal process is efficient in the transformation of heat into mechanical work done by the system (isothermal expansion) or in the transformation of work done on the system into heat (isothermal compression). The **Carnot Cycle** operates between two sources (reservoirs) of heat with temperatures \( T_H \) and \( T_C \) \((T_H > T_C)\) and uses only **Reversible**
Processes: processes supposed to be performed so slowly that they can be treated as a series of equilibrium states. The processes can be reversed at any instant. Actually, this is impossible. Real processes are Irreversible Processes. Carnot showed that for an ideal reversible Carnot engine, heats $Q_H$ and $Q_C$ are proportional to the operating absolute temperatures correspondingly $T_H$ and $T_C$. Thus, the thermal efficiency of this ideal engine (Carnot engine) is:

$$e_{Carnot} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \quad (12-9)$$

From (12-9), we can clearly understand the basic idea behind any heat engine: mechanical work can be obtained from thermal energy only when heat is allowed to flow from a high temperature $T_H$ to a low temperature $T_C$. In this process, some of the heat can be transformed into mechanical work.

Equation (12-9) expresses the fundamental upper limit to the efficiency. No engine operating between the same two temperatures can be more efficient than a Carnot engine. Real engines always have efficiency lower than this because of losses due to friction and the like. It is important to know how to take heat from a source and convert as much of it as possible into work. This happens in steam engines (reciprocating type and turbines used in electric power production and in atomic plants), in internal combustion engines (used in most automobiles), in jet engines in airplanes, and many other systems. Thermodynamics is widely used in engineering sciences to improve heat engines. Nevertheless, real engines that are well designed reach 60% to 80% of the efficiency of the Carnot engine.

But, actually, why is a $\Delta T$ needed to drive a heat engine? The substance inside the heat engine that undergoes addition and subtraction of heat, expansion and compression and sometimes a phase change is called the Working Substance, for example, steam in the steam engine, a mixture of air and fuel in the automobile engine, and so on. If the temperatures of working substances are the same throughout an engine the pressure will also be the same from opposite sides of the turbine blades or pistons. As a result, there will be no force to push pistons or to rotate turbines. It will not be possible to have mechanical work output from the heat engines in this case.

12.5 The Second Law of Thermodynamics. Entropy

It is quite clear from equation (12-9) that at normal temperatures, a 100% efficient engine is not possible. Only if $T_C$ were at absolute zero could $e =$...
100%. But reaching absolute zero is impossible. Careful experimentation suggests that absolute zero is unattainable. This result is known as the Third Law of Thermodynamics. Because no engine can be 100% efficient, we can formulate the statement that is called the Kelvin-Planck statement of the Second Law of Thermodynamics: no device is possible whose whole effect is to transform a given amount of heat completely into work. Why? Since we cannot control the microscopic motion of individual molecules, we cannot convert this random motion (thermal energy) back to the organized macroscopic motion needed to perform mechanical work. Another equivalent statement of the second law is the Clausius statement of the Second Law of Thermodynamics: Heat can flow spontaneously from a hot object to a cold object; heat will not flow spontaneously from a cold object to a hot object.

These two formulations of the second law have a qualitative rather than a quantitative character. The Second Law of Thermodynamics was finally stated in a general way in terms of a physical quality called Entropy, a term which was introduced by Clausius. The change in entropy of a system, when an amount of heat \( Q \) is added to it by a reversible process at constant temperature \( T \) is given by:

\[
\Delta S = \frac{Q}{T} \quad (12-10)
\]

\( S \) is scalar. The unit of entropy in the SI system is \( \frac{J}{K} \). Entropy is a function of the state of a system. The Second Law of Thermodynamics can be stated in terms of entropy as follows: the entropy of an isolated system never decreases. It can only stay the same or increase. For an idealized reversible process:

\[
\Delta S = 0 \quad (12-11)
\]

For any real process in an isolate system:

\[
\Delta S > 0 \quad (12-12)
\]

If the system is not isolated, we have the second law for idealized reversible processes:

\[
\Delta S = \Delta S_s + \Delta S_{env} = 0 \quad (12-13)
\]
For any real process we have:

\[ \Delta S = \Delta S_s + \Delta S_{env} > 0 \quad \text{(12-14)} \]

where \( \Delta S_s \) is the change of the entropy of a system, \( \Delta S_{env} \) is the change of entropy of the environment.

So, a general statement of the Second Law of Thermodynamics is: the total entropy of any system plus that of its environment increases as a result of any natural process.

**EXAMPLE 12.4** Suppose you put an ice cube into a glass of warm water. Is it possible that heat flows from the ice to the water, cooling the ice cube to well below zero and heating the water to the boiling point? In consideration, use the second law of thermodynamics in terms of entropy.

The amount of heat that flows from the ice cube into the water we designate \( Q_w \). the temperature of the water \( T_w \) and the temperature of the ice cube \( T_c \), \( T_w > T_c \).

\[
\begin{align*}
Q_w &= \frac{Q_w}{T_w} \\
T_w &= T_c \\
T_w > T_c \\
\Delta S > 0? 
\end{align*}
\]

The change of entropy of the water, according to the second law of thermodynamics is

\[
\Delta S_w = \frac{Q_w}{T_w}
\]

the amount of heat received by the ice cube \( Q_c \) is \( Q_c = -Q_w \). Then

\[
\Delta S = \frac{Q_c}{T_c} = -\frac{Q_w}{T_c}
\]

Thus, the total change of entropy in the water-ice system could be according to (12-14)

\[
\Delta S = \Delta S_w + \Delta S_c = \frac{Q_w}{T_w} - \frac{Q_w}{T_c} = Q_w \left( \frac{1}{T_w} - \frac{1}{T_c} \right) = -Q_w \left( \frac{1}{T_c} - \frac{1}{T_w} \right)
\]
Since \( T_w > T_c \) it follows that \( \frac{1}{T_w} < \frac{1}{T_c} \) so that \( \left( \frac{1}{T_w} - \frac{1}{T_c} \right) < 0 \) and \( \Delta S < 0 \).

Thus, the flow of heat from the ice cube into the water would correspond to a decrease of entropy, which contradicts the second law of thermodynamics. If, however, heat flows from the warm water into the ice, the signs are reversed, the change of entropy becomes positive, and the process is in accord with the second law of thermodynamics.

The concept of entropy looks rather abstract, so far. To get a feel for the concept of entropy we can relate it to the more ordinary concepts of order and disorder. The entropy of a system can be considered a measure for the disorder of the system. Now we can formulate the **second law of thermodynamics** as **natural processes tend to move toward a state of greater disorder** (because they have greater probability). The separate hot and cold objects could serve as the high- and low-temperature regions for a heat engine and thus could be used to obtain useful work. But after the two objects are put in contact and eventually reach the same uniform temperature, no work can be obtained from them. Thus, in any natural process, some energy becomes unavailable to do useful work. As time goes on, energy is degraded: it goes from more orderly forms (mechanical energy) to the least orderly form (internal or thermal energy).

The laws of thermodynamics place very general limitations on the conversion of energy from one form to another. In these times of increasing energy demand and diminishing resources, such matters are of the utmost practical importance. Therefore, physics plays an important role in the development of new sources of energy and energy-saving technologies.