

Module 3 First Law of Thermodynamics

This module is designed to help you to:

- explain the first law of thermodynamics;
- justify that the first law of thermodynamics is basically a re-statement of the principle of conservation of energy;
- obtain the relation between the two specific heat capacities (C_p and C_v) of a gas, using the first law of thermodynamics;
- illustrate some applications of the first law of thermodynamics;
- relate the meaning of the term state variables for a given (thermodynamic) system;
- list the significances of the first law of thermodynamics
- assess the limitations of the first law of thermodynamics and thereby the need for a second law
- explain the term equation of state and its form for an ideal gas and for a real gas

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12.3.1 Introduction

We know from the principle of conservation of energy that –'Energy can not be created, nor can it be destroyed; but it can be transformed from one form to another, the total amount of energy in this universe remaining constant.' When this principle is extended to the case of transformation of energy between heat and any other form, we arrive at the first law of thermodynamics, that is whenever heat energy is converted into any other form of energy or vice versa, each is equivalent to the other. We shall see that the first law defines heat as an energy in transit.

In this module, we shall study several applications of the first law of thermodynamics and we shall also see its relevance in connection with the equations of state.

12.3.2 First law of thermodynamics

We have seen that the internal energy, U , of a system can change through two modes of energy transfer. Let

ΔQ = Heat supplied to the system by the surroundings
 ΔW = Work done by the system on the surroundings
 ΔU = Change in internal energy of the system

The general principle of conservation of energy then implies that

$$\Delta Q = \Delta U + \Delta W \quad (12.3.1)$$

i.e. the energy (ΔQ) supplied to the system goes in part to increase the internal energy (ΔU) of the system and the rest in doing work (ΔW) on the surroundings. It is known as the mathematical statement of the First Law of Thermodynamics.

It is important to note that in some texts, one may find the first law of thermodynamics written in the form

$$\Delta U = \Delta Q - \Delta W \quad (12.3.2)$$

This form of the equation is also correct. The difference results from a different sign convention followed in these texts. Here, ΔW represents the work done on the system by the surroundings instead of work done by the system on the surroundings (that we have taken).

It is important to remember that ΔU depends only on the initial and final states and not on the path taken by the gas to go from one state to the other state. It is a state variable. However, ΔQ and ΔW will, in general, depend on the path taken to go from the initial to final states.

First law of thermodynamics is based on the principle of conservation of energy. Here it needs to be stressed that the first law of thermodynamics is simply a restatement of the principle of conservation of energy applied to any system in which the energy transfer from or to the surroundings is taken into account. It needs to be further stressed that (while applying the first law of thermodynamics), it is important to note that the sign of the quantities of heat supplied or work done depends on the direction in which change is taking place. For example, if the work done by system A on system B is ΔW , then the work done by system B on system A , is $-\Delta W$. Similarly, if the heat supplied to a system A , by system B , is ΔQ then the heat supplied to system B by system A is $-\Delta Q$.



Let Us Reflect

Q.12.3.1 Air pressure in a car tyre increases during driving. Why?

Q.12.3.2 An electric heater supplies heat to a system at a rate of 100 joules per second. If the system performs work at a rate of 75 joules per second, find the rate at which the internal energy, of the system, increases.



Answers

A.12.3.1 While the car is in motion, the temperature of air inside the tube increases primarily due to friction of the tyre with the road, and also due to violent motion of air inside the tube. With increase of temperature, pressure increases following the Law of Pressure.

A.12.3.2

$$\Delta U = \Delta Q - \Delta W = 100 - 75 = 25 \text{ Js}^{-1}$$

12.3.3 Thermodynamic state variables

Every equilibrium state of a thermodynamic system is completely described by specific values of some macroscopic variables, that are known as its state variables. The value of a state variable depends only on the given state of the system and not on the path taken to arrive at that state. For example, an equilibrium state of a gas is completely specified by the values of pressure, volume, temperature, and mass (and composition, if there is a mixture of gasses).

The various state variables are, in general, not independent of one-another. The relation between the state variables is called ‘the equation of state’. For example, for an ideal gas, the equation of state is the ideal gas equation:

$$P V = \mu R T \quad (12.3.3)$$



Let Us Reflect

Q.12.3.3 A cylinder with a movable piston contains 3 moles of hydrogen at standard temperature and pressure. The walls of the cylinder are made of a heat insulator and the piston is insulated by having a pile of sand on it. By what factor does the pressure of the gas increase if the gas is compressed to half its original volume?



Answers

A.12.3.3 With the symbol having their usual meaning.

$$PV^\gamma = \text{a constant}$$

$$\therefore P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\therefore P_2 = P_1 \left(\frac{V_1}{V_2} \right)^\gamma$$

$$\text{Given } V_2 = \frac{V_1}{2},$$

$$\text{So, } \frac{V_1}{V_2} = 2$$

$$\text{For Hydrogen, } \gamma = 1 + \frac{2}{5} = 1.4$$

$$\therefore \frac{P_2}{P_1} = 2^\gamma = 2^{1.4}$$

So pressure increases by factor of $2^{1.4}$.

12.3.4 A simple application of the first law of thermodynamics

We can use the first law of thermodynamics to obtain a relation between the two specific heat capacities, C_p (specific heat capacity at constant pressure) and C_v (specific heat capacity at constant volume), for a gas.

Consider n moles of a gas put in a cylinder with a movable piston. Let the gas be first heated, through a temperature ΔT , say, by keeping the piston fixed in its position, i.e., by keeping the volume of the gas constant. The work done by the gas in this case, is zero. The change in its internal energy is

$$\Delta U = n C_v \Delta T \quad (12.3.4)$$

Let the gas be next heated, through the same temperature ΔT , by allowing the piston to move and keeping the pressure of the gas constant. If the specific heat capacity of the gas, at constant pressure, is denoted by C_p , the heat added to the system, in the case, would be given by

$$\Delta Q = n C_p \Delta T \quad (12.3.5)$$

As per the first law of thermodynamics,

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

In this case also, $\Delta U = n C_v \Delta T$

Also $\Delta W = P \Delta V$

As per the gas equation $PV = nRT$

When pressure is kept constant, we have $P \Delta V = nR \Delta T$

$$\Delta W = P \Delta V = nR \Delta T$$

$$\therefore \Delta Q = n C_p \Delta T = n C_v \Delta T + nR \Delta T, \quad \text{So, } C_p = C_v + R$$

$$\text{This gives: } C_p - C_v = R \quad (12.3.6)$$

This is the relation between the two molar specific heat capacities of a gas.

12.3.5 Additional applications of the first law of thermodynamics

The first law of thermodynamics, as we have seen, is essentially the law of conservation of energy. It can, therefore, be used to analyze the relevant changes in a system when its 'state' changes via different types of thermodynamic processes.

An interesting application of the first law is related with the concept of 'latent heat' for a system undergoing a change of state –from solid to liquid phase or from liquid to gaseous (vapor) phase and vice-versa. We know that, during such a change of state, there is no change in the temperature of the system. It may, therefore, appear that there is no change in the internal energy. There is however, a change in the volume of the 'system'. If the change in volume, during a given change of state of a unit mass of the system, equals ΔV and if this change is taking place at a constant pressure, say P , the external work done would be

$$\Delta W = P\Delta V$$

By the first law of thermodynamics,

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

We may think that $\Delta U = 0$ so that $\Delta Q = \Delta W$

Further, during changes of state (at constant temperature) of a unit mass of the system,

$$\Delta Q = 1 \times L \quad \text{where } L \text{ is the corresponding latent heat.}$$

Hence $1 \times L = P\Delta V$ or $L = P\Delta V$

Here ΔV is the change in volume, for a unit mass, during the (relevant) change of state.

A close look at the relation, and the known values of ΔV and L for water, say, during change from (ice to water) and water to steam] reveal that the above relation is not consistent with the observed values. The reason for this is that $\Delta U \neq 0$, during change of state even though this change takes place at a constant temperature. The 'constant temperature' strictly implies that there is no change in kinetic energy. The internal energy, for practical systems, also has a 'potential energy' part and this potential energy part (associated with the 'bonds' between molecules) changes during changes of state. We should, therefore, write

$$L = \Delta U + p \Delta V \quad (12.3.7)$$

We, therefore, need the value of ΔU (the change in PE for a unit mass) to get the correct value of L through the (additional) known values of P and ΔV . Alternatively, we can calculate the value of ΔU , if the values of L , P and ΔV are known. ΔU in the instant case is known as ‘Internal Latent Heat’.

Example 12.3.1

It is given that the latent heat of steam = $2268 \times 10^3 \text{ J kg}^{-1}$; specific volumes of steam and water are 1671 and 1 (in $10^{-3} \text{ m}^3 \text{ kg}^{-1}$) respectively. Use Eq (12.3.7) to obtain the value of internal latent heat of steam in J kg^{-1} . Assume that the atmospheric pressure = 10^5 Nm^{-2} .

Solution:

With symbols having their usual meanings,

$$p \Delta V = (10^5 \text{ Nm}^{-2})(1671 - 1)(10^{-3} \text{ m}^3 \text{ kg}^{-1}) = 167 \times 10^3 \text{ J kg}^{-1}.$$

So, from Eq (12.3.7), we get,

$$\text{The Internal Latent Heat} = \Delta U = L - p \Delta V = (2268 - 167) \times 10^3 = 2101 \times 10^3 \text{ J kg}^{-1}$$

You have learnt that ‘latent’ means ‘hidden’, and it is said that since this heat input does not get manifested in the form of rise in temperature, it remains hidden, and hence the name, ‘latent’. But, now we know what is actually hidden. A part of it goes to perform isobaric external work due to expansion of volume under constant atmospheric pressure, which is only $(\frac{167}{2268} \times 100) = 7.4\%$ of the input energy, and the remaining 92.6% goes for breaking the internal potential barrier for transition from liquid to vapor state, which is the manifestation of what we call the internal latent heat.

12.3.6 Significances and limitations of the first law of thermodynamics

Now that we have studied various examples based on the first law of thermodynamics, let us collate the different significances of the first law of thermodynamics -

- 1) If a machine exists that can work without expenditure of any input energy, then it would just be required to start the machine, and it would keep on working. Such a machine is called the ‘perpetual motion machine of the first kind’, and the first law rules out such a machine.
- 2) It defines ‘internal energy’ as a function of the state of the system
- 3) It defines heat as an energy in transit. As it is wrong to say ‘Work in a body’ it is also wrong to say ‘Heat in a body’.

But the law has its limitations too, which are as under -

- 1) It is unable to explain unidirectional processes in nature. Whenever a hot body comes in contact with a cold body, heat always flows from the former to the latter, but never from the latter to the former. If in case of a hot body coming in contact with a cold body, the cold body loses 10 J of heat and the hot body gains 10 J of heat; then the first law will say that the hotter body loses 10 J of internal energy and the cooler body gains 10 J of internal energy at its cost. So, the first law is not able to see anything wrong with the process.
- 2) If a machine had duly obeyed the dictum of the first law and had expended heat energy by taking it from the ocean, by way of cooling it, and converted the same into work, then the first law would not have stood violated. Such a machine can be made to work perpetually. This kind of machine is called a perpetual motion machine of the second kind; and it cannot be ruled out by the first law.

Based on the above significance and limitations, we can assess the need for a second law, about which we shall study in the next module.

Before going over to the next module let us briefly talk about ‘Equation of state’.

12.3.7 Equation of state

As we have noted above, the three thermodynamic variables (P , V , T), usually used for describing the thermodynamics state of a system, are not independent of one another. There is a relation between them and we call this relation the equation of state for the given system.

We know that for an ideal gas, this relation is Eq (12.3.3),i.e.,

$$PV = \mu R T$$

where P = Pressure, V = Volume, T = Temperature and μ = number of moles of the gas; R is a constant known as the universal gas constant.

For real gasses, the above relation is not strictly valid. The equation of state, for real gasses, most often used, is the one obtained by Van-der-Waal. This Van-der-Waal equation of state, for real gases, has the form

$$\left(P + \frac{a}{V^2}\right)(V - b) = \mu RT \quad (12.3.8)$$

where a and b are constants. This equation also does not work too well for real gases. There are other equations which fulfill the conditions of real gases more adequately. But Eq (12.3.8) is quite popular, as just by looking at it one can visualize the departure from the ideal gas equation (12.3.3).

Among the description of the ideal gas model, two assumptions are very crucial -

- (i) Absence of intermolecular forces
- (ii) Molecules being point masses, occupying no volume

Since, there are departures from the ideal situations getting reflected through the above assumptions, correction terms appear, It is a for (i), and b for (ii).

Example 12.3.2

What are the units of a and b in SI units ?

Solution

a is equivalent to $(Pr)(Vol)^2 = (Nm^{-2})(m)^6 = Nm^4$

b is equivalent to volume, and hence the unit is m^3 .

12.3.7 Summary

- The general principle of conservation of energy then implies that

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

i.e. the energy (ΔQ) supplied to the system goes in part to increase the internal energy (ΔU) of the system and the rest in doing work (ΔW) on the surroundings. This statement is known as the first Law of Thermodynamics.

- The first law rules out the perpetual motion machine of the first kind. It defines internal energy as a function of the state of the system and it defines heat as an energy in transit.
- The first law cannot rule out the perpetual motion machine of the second kind, nor can it explain the reason behind unidirectional processes in nature, and thus it becomes necessary to have a second law.
- The various state variables are, in general, dependent on each other. The relation between the state variables is called the equation of state. For example, for an ideal gas, the equation of state is the ideal gas equation:

$$P V = \mu R T$$

- For an ideal gas, molar specific heat at constant pressure and the one at constant volume are related by equation $C_p - C_v = R$ known as Mayer's relation.
- For real gasses, the above relation is not strictly valid. The equation of state, for real gasses, most often used, is the one obtained by Van-der-Waal. This Van-der-Waal equation of state, for real gasses, has the form

$$\left(P + \frac{a}{V^2}\right)(V - b) = \mu RT$$

where a and b are constants.

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