

Module 1 Scope of Thermodynamics

This module is designed to help you to:

- describe the scope of thermodynamics;
- justify the macroscopic nature of the science of thermodynamics;
- explain the concept of thermal equilibrium;
- state the significance of the zeroth law of thermodynamics;
- discuss the thermodynamic definition and meaning of temperature;
- explain the meaning of the terms heat, internal energy and work and the differences between them;
- describe the correlation between internal energy of a system and its temperature.

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12.1.1 Introduction

Thermodynamics is the branch of physics that deals with the concepts of heat and temperature and the interconversion between heat and other forms of energy. It is concerned with macroscopic objects characterized by macroscopic properties such as pressure, volume and temperature. The values of such properties are referred to as thermodynamic coordinates that describe a thermodynamic state. The laws that govern thermal energy and the relative processes where work is converted into heat and vice versa are the mainstay of thermodynamics. Application of these laws leads to far reaching consequences as regards understanding nature.

12.1.2 Thermodynamics is a macroscopic science

Thermodynamics deals with bulk systems and not with the (tiny) individual microsystems they are made of. Its concepts and laws were formulated in the nineteenth century before the molecular picture of matter was firmly established. Thermodynamic description involves macroscopic variables of the system, which can be (usually) measured directly. For example, the state of a gas, in thermodynamics, is specified by measurable macroscopic variables such as pressure, volume, temperature, mass and composition. Thermodynamics may also involve other macroscopic variables such as magnetic and electric fields.

Kinetic theory of gasses on the other hand, is a study of a microscopic description of gas. It gives a molecular interpretation of pressure and temperature of a gas, and is consistent with the Gas Laws and Avogadro's hypothesis.



Q.12.1.1 Which among the following is/are thermodynamic variables and why?

- (A) Pressure
- (B) Volume
- (C) Temperature

(D) Root mean square speed of the gas molecules

A Answers

A.12.1.1 (A), (B) and (C) are macroscopic parameters as they can be felt by our senses so they are thermodynamic variables; whereas (D) cannot be perceived by our senses. Its concept can be considered as an outcome of the postulates of the kinetic theory of gases, and it is hence a microscopic description. So, it is not a thermodynamic variable.

[Note: *Macroscopic description such as pressure and temperature can be arrived at by easing microscopic description.*]

12.1.3 Thermal equilibrium

The state of a system is an equilibrium state if the macroscopic variables that characterize the system do not change in time. Suppose two systems, A and B, are put in proximity but are separated by an adiabatic wall (Fig.12.1.1). (An adiabatic wall is a thermally insulating wall that does not allow flow of energy (Heat) across it). The systems are isolated from the rest of the surroundings also by similar adiabatic walls. In this case, if the characteristic variables of one system are changed, it will have no effect on the properties of the other system.

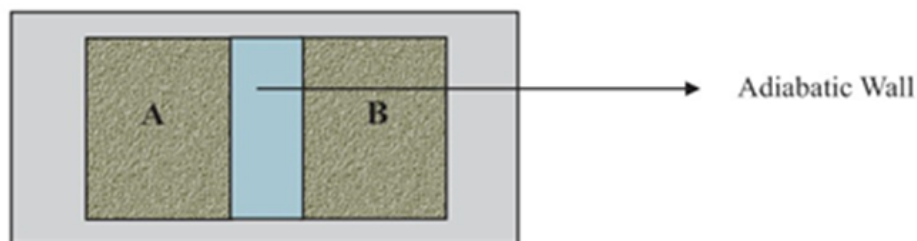


Fig.12.1.1 systems A and B (two gases) separated by an adiabatic wall- insulating wall that does not allow flow of heat.

Next, suppose that the adiabatic wall is replaced by a diathermic wall (Fig.12.1.2). [A diathermic wall is a thermally conducting wall that permits flow of energy (heat) across it]. It is then found that the macroscopic variables (e.g. pressure, temperature) of the systems A and B change. These changes are rapid in the beginning and become slower as time passes. Finally all measured characteristic variables of each system approach constant values. After that there is no further change. There is no more energy (heat) flow from one to another. We then say that system A is in ‘thermal equilibrium’ with system B .

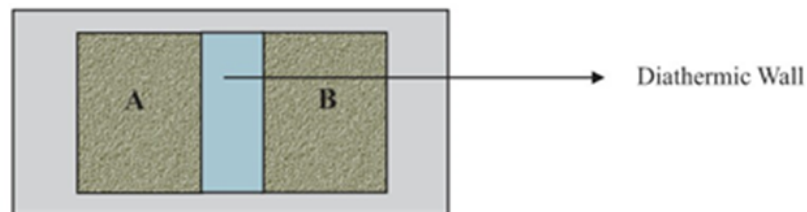


Fig. 12.1.2 the same system A and B separated by a diathermic wall- a conducting wall that allows heat flow from one to another.

Suppose the two systems of gases which have different pressures, volumes and temperatures, initially. After these gases reach thermal equilibrium with each other, their pressures and volumes might be different but their temperatures are always found to be equal.

The two systems are said to be in thermal equilibrium if the temperatures of the two systems are equal.

12.1.4 Zeroth law of thermodynamics

Suppose two systems A and B each is in thermal equilibrium with a third system C (Fig.12.1.3).

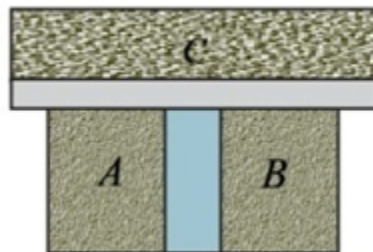


Fig. 12.1.3 Two systems A and B in thermal equilibrium with a third system C via conducting wall

Zeroth law of thermodynamics states that ‘two systems, in thermal equilibrium with a third system separately, are also in thermal equilibrium with each other’. This law was formulated by R.H. Fowler in 1931 long after the first and second laws of thermodynamics were stated. But it turned out to be more fundamental. So, it is referred to as the zeroth law.

The zeroth law clearly suggests that when two systems A and B, are in thermal equilibrium, there must be a physical quantity that has the same value for both. This scalar quantity, whose value is equal for two systems in thermal equilibrium, is called temperature (T). Though we all are familiar with the everyday use of temperature, we define the concept of temperature formally via the zeroth law.

If a thermometer comes in thermal equilibrium with both systems A and B separately, and indicates the same temperature reading for both the systems then we can not say that systems A and B are in thermal equilibrium unless they are in thermal contact. Isolated systems showing the same value for their temperatures are not to be considered in thermal equilibrium.

The zeroth law of thermodynamics helps us to understand the thermodynamic definition and meaning of temperature.

We realize that any two systems, that are in thermal equilibrium with each other, have a characteristic property that has the same value for both of them. It is this characteristic property that has been given the name temperature of the system.

We may, therefore, say that, as per thermodynamics, the temperature of a given system is a characteristic property of that system that decides whether, or not, that system would be in thermal equilibrium with another given system.

It needs to be remembered here that thermal equilibrium of two systems does not imply that there is no exchange of heat between them when they are put in thermal contact with each other, rather there is no net flow of thermal energy from one system to another.



Let Us Reflect

Q.12.1.2 (a) What is meant by thermodynamic equilibrium?

(b) Identify precisely the thermodynamic systems which come into thermal equilibrium with each other when we insert a thermometer under the tongue of a patient to measure the body temperature.



Answers

A.12.1.2 (a) When the thermodynamic coordinates attached with the thermodynamic system do not change with time then the system is in thermodynamic equilibrium.

(b) The portion of the patient's body under his tongue and the bulb of the thermometer.

12.1.5 Heat, internal energy and work

Heat, internal energy and work can all be conceived as forms of energy. They are intimately related and the interplay between them is the subject of the first law of thermodynamics. First we shall examine the role of heat as a form of energy.

12.1.5.1 Heat as a form of energy

Historically, it took a long time to arrive at the proper concept of heat. During early studies, heat was regarded as a fine invisible fluid filling in the pores of a substance. It was suggested that on contact between a hot body and a cold body, this fluid (called caloric) flowed to the colder bodies from the hotter body until the caloric levels (i.e., the temperatures) equalize. In time, the picture of heat as a fluid was discarded in favor of the present day concept of heat as a form of energy.

Heat is a form of energy that flows from the body at a higher temperature to the one at lower temperature. The net flow of heat stops when the temperatures equalize; the two bodies are then said to be in thermal equilibrium with each other.

The old unit of heat was calorie. Since heat is just a form of energy, it is now preferable to use the unit joule, J for it also. The so-called mechanical equivalent of heat, defined as the amount of work needed to produce 1 calorie of heat, is in fact, just a conversion factor between two different units of energy: calorie and joule. In SI units, we now use the unit joule for heat, work or any other form of energy. Hence the term mechanical equivalent of heat is now superfluous and need not be used.

12.1.5.2 Internal energy

Every bulk system consists of a large number of molecules. Kinetic energy is associated with the random motion of these molecules and potential energy is associated with the forces between these molecules which may tend to disturb their equilibrium configuration. The sum, of the kinetic energies and potential energies of all these molecules, is called the internal energy of the system.

It has to be noted here that the internal energy (of a system) is to be thought of as, only the sum of its molecular kinetic and potential energies. The internal energy of a system is generally denoted by U .

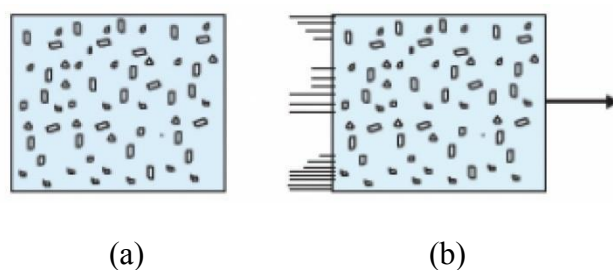


Fig. 12.1.4 (a) Internal energy U of a gas is the sum of the kinetic and potential energies of its molecules when the box is at rest. Kinetic energy due to various types of motion (translational, rotational,

vibrational) is to be included in U . (b) if the same box is moving as a whole with the same velocity the kinetic energy of the box is not to be included in U .

If we neglect the small intermolecular forces in a gas, the internal energy of a gas is just the sum of the kinetic energies associated with the various random motions of its molecules. In a gas, this motion is not only translational (i.e. motion from one point to another in the volume of the container); it also includes rotational and vibrational motions of the molecules (Fig. 12.1.4(a,b)).

The internal energy of a system can be increased in two ways. One way is to put the system in contact with a body at a higher temperature. The temperature difference will cause a flow of energy (heat) from the hotter body to the system, thus increasing the internal energy of the system. The other way is to do work on the system, which again results in increasing the internal energy of the system (Fig. 12.1.5).

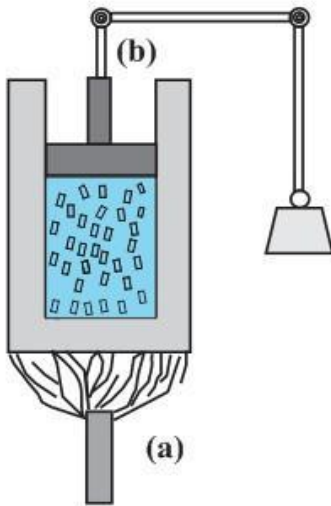


Fig. 12.1.5 (a) Heat is energy transfer due to temperature difference between the system and the surroundings. (b) Work is energy transfer brought about by other means (e.g. moving the piston by raising or lowering some weight connected to it) that do not involve such a temperature difference.

Internal energy (U) is simply a macroscopic variable of the system. The important thing about internal energy is that it is a thermodynamic state variable, that is, its value depends only on the given state of the system; not on the 'path' taken to arrive at that state.

12.1.5.3 Internal energy and temperature

Temperature is a measure of internal energy of a body. If the internal energy of a body is increased, the molecules of this body might acquire this energy in several different forms: increase in translational kinetic energy, rotational kinetic energy, vibrational kinetic energy or potential energy. However, only the increase in translational kinetic energy will produce an increase in temperature.

When a body is at higher temperature, its molecules have on average higher translational kinetic energy as compared to the molecules of a body at lower temperature. When the body at higher temperature is placed in contact with a body with lower temperature, the collisions between molecules of two bodies, (at the contact surface) will transfer energy from the body at higher temperature to the body at lower temperature. This energy, which flows from the body at higher temperature, to the body at lower temperature, is heat.

12.1.5.4 Heat and temperature

Students, many times, use the terms 'heat' and 'temperature' interchangeably. Hence it is very important to distinguish between the concepts of heat and temperature.

Heat is a form of energy, however, it is an energy in transit. Temperature, on the other hand, is a measure of internal energy of the body.

A statement like a gas in a given state that has a certain amount of heat is as meaningless as the statement that a gas in a given state has a certain amount of work. In contrast, the statements that a certain amount of heat is supplied to the system or a certain amount of work was done by the system are perfectly meaningful. Heat and work are not intrinsic properties of a system. However, temperature is an intrinsic property of a given system.

Both heat transfer and work done are associated with the processes through which a system is taken from one equilibrium state to another. The amount of work done, or amount of heat transfer will depend on the path that the process takes to reach from one state to another. However, temperature and internal energy are thermodynamic state variables; their value depends only on the given state of the system, not on the path taken to arrive at that state.

The internal energy of the body, and thus its temperature, can be increased either by supplying heat to it, or by doing work on it, or both. However a supply of heat may not necessarily lead to an increase in temperature of the system. For example, when heat is supplied for melting ice at 0°C ; there is no increase in temperature during the melting process. The heat supplied here just leads to an increase in the internal energy of the system through an increase in its potential energy only.



Let Us Reflect

Q.12.1.3 The temperature of the highly viscous liquid taken in a container is raised from 30°C to 40°C by (a) heating it using a burner, (b) stirring it vigorously, (c) combination of heating and stirring.

Since the temperature of the liquid increases by 10°C in each case, what is your observation (state or non-state) about the nature of the functions work, heat and internal energy?



Answers

A.12.1.3 In each case the change in internal energy is the same. Equal changes in internal energy have been brought about in Case (a), by application of heat only; Case (b), by application of work only and in Case (c), by partial application of work and partial application of heat. So, the amounts of heat and work required for

the same change in internal energy are not the same. So, internal energy is a state function, but work and heat are non-state functions.

12.1.6 Summary

- Two bodies or systems are said to be in thermal equilibrium if they are at the same temperature.
- Zeroth law of thermodynamics states that two systems, in thermal equilibrium with a third system separately, are also in thermal equilibrium with each other.
- The sum, of the kinetic energies and potential energies of all these molecules, is called the internal energy of the system.
- Temperature is a measure of internal energy of the system.

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