1.2 TEMPERATURE AND THERMAL EQUILIBRIA

When an object is placed in a new environment the energy of the object may change through interaction of the molecules of the object with the external world. The macroscopic changes in the system as a result of the interactions among the molecules of the body themselves and the interactions the body with the external world would eventually stop if the system is left in the new environment for a considerable period of time. This is the idea behind equilibrium of a system. We now discuss three types of processes and the corresponding equilibria that are considered important for thermodynamic equilibrium.

1.2.1 Mechanical Equilibrium

Recall that we have already defined mechanical equilibrium of a multiparticle system as the condition in which the net force on each particle is equal to zero.

For instance, in the case of a movable piston in a gas cylinder, the force on the piston must be same on both sides. Therefore, the pressure inside the gas container must be equal to the pressure outside.

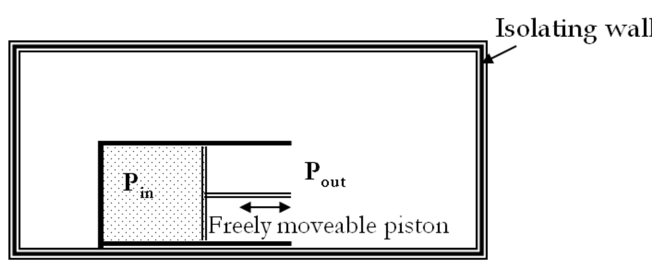

Figure 1.3: Mechanical equilibrium, pressure inside equals the pressure outside, $p_{\text{in}} = p_{\text{out}}$, if the boundary is free to move.

1.2.2 Thermal Equilibrium

Now, consider a system that is in a thermal contact with its environment. Then, after a long time has elapsed, no more heat would be transferred to the system or taken away from the system. At this point we say that the system has reached a thermal equilibrium with the environment (Fig. 1.4). We will use the small letter t for the temperature in an arbitrary temperature scale and reserve the capital letter T for the temperature in a particular scale called the Absolute or Kelvin scale.

Two systems in thermal equilibrium with each other are said to have the same value of a property called **temperature**. Just as systems in mechanical equilibrium have the same pressure, systems in thermal equilibrium have the same temperature.

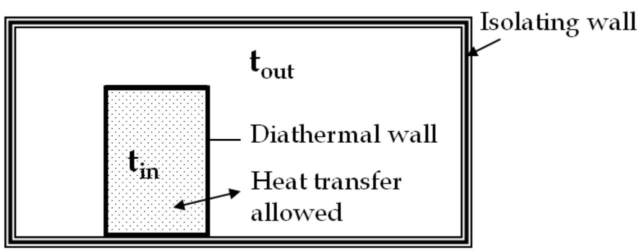

Figure 1.4: Thermal equilibrium between two systems that are in thermal contact implies temperature of the two systems are equal, $t_{in} = t_{out}$.

One important consequence of the definition of temperature in terms of the thermal equilibrium is that if a system is in thermal equilibrium internally, the temperature at all points inside the system will be the same. When this happens we say that the system is at a particular temperature. If a system is not in thermal equilibrium internally, then the system would have different temperatures at different points inside the system. For instance, when you heat water on a hot plate, the water near the plate is usually at a higher temperature than the water at points further away.

1.2.3 Chemical Equilibrium

When the chemical composition of a system changes with time, either because chemical reactions are taking place in the system or chemicals are being added or removed from the system, then we say that the system is not in a chemical equilibrium. A chemical equilibrium occurs when the chemical composition and the amount of each chemical species is constant.

The concept of the chemical equilibrium helps define a macroscopic property for each chemical in the system called the **chemical potential**. Suppose two systems are isolated from the rest of the universe, but they exchange chemicals freely. For instance, you might think of a closed container containing that has both the liquid water and the water vapor. Suppose the vapor part is one system and the liquid part another system. Then, at the chemical equilibrium, the number of molecules that goes from the liquid will equal the number going from the vapor to the liquid. At this point, we say that the two systems are in a chemical equilibrium, and the chemical potential of water in the vapor and liquid phases are equal.

1.2.4 Thermodynamic Equilibrium

A system in chemical, mechanical and thermal equilibriums is said to be in a thermodynamic equilibrium. Such systems have well-defined values of pressure, temperature, and chemical potentials.

Simplification in this book
To keep our discussions simple, we will study systems in this book that have materials of homogeneous unchanging chemical composition. Therefore, they will always be in chemical equilibrium with some fixed chemical potential for each chemical species. Since we will not study situations of varying chemical potential, we will not discuss chemical potential any further.

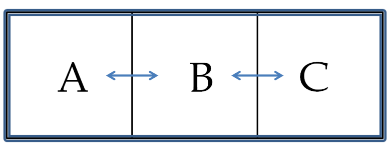

Figure 1.5: Zeroth Law: If system A is in equilibrium with system B which is in equilibrium with another system C also, then A is also in equilibrium with C. All three systems in equilibrium will have the same temperature.

1.2.5 Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states that if a system A is in thermal equilibrium with a system B, which, in turn, is in thermal equilibrium with another system C, then systems A and C are also in thermal equilibrium with each other regardless of whether or not A and C are in direct contact. Thus all systems at the same temperature can be thought to be in thermal equilibrium with each other, or equivalently, all systems in thermal equilibrium must have the same temperature. If two systems, which are not in thermal contact but have the same temperature, are brought in thermal contact, then there will be no heat transfer between them.

1.2.6 Thermodynamic Systems

You have already encountered the use of the word "system" in the course of your studies in this book. Simply put, a system is any body or group of bodies whose physics we wish to study. When you studied mechanics, a physical object was separated from the rest of the universe in order to study the motion of the object alone. The rest of the universe was considered to be external to the system.

In thermodynamics also we practice the same general idea and select a body or bodies to focus our attention to. However, unlike mechanics, where we studied the motions of the individual particles and the macroscopic bodies, to study the thermodynamic properties **we require the thermodynamic systems to be macroscopic**. This requirement is necessary to implement the notions of thermodynamic equilibrium we have given above. The thermodynamic equilibrium allows us to define the macroscopic properties such as pressure, temperature, chemical potential, etc. When a system is internally in an equilibrium, the system will have definite values of the macroscopic variables. If a system consists of only one particle or only a few particles, then we find that the macroscopic properties such as the temperature lose their meanings.

Every system in thermodynamics can be classified as one of the following three types: isolated, closed, or open.

1. Isolated System When a system is completely separated from the rest of the universe such that it does not interact with the outside world in any way, then from mechanics we know that the energy, momentum and angular momentum of the system will not change with time. Such systems do not exchange energy, momentum or angular momentum with any other object in the universe. The entire universe is, of course, an isolated system.

2. Closed System A closed system is not completely isolated from the rest of the universe. A closed system is restricted to have a constant mass. But, a closed system can interact with the external world. Suppose you place some water in a closed container and heat the container. The energy of the water in the container will go up even though the amount of water remains the same. The water in the closed container is an example of a closed system. Most of the examples in this book will be presented for closed systems.

3. Open System An open system can exchange even matter with the environment. This is most general type of system. Your body, for instance, is an open thermodynamic system since the chemical content of your body is constantly changing.

You can start from an isolated system and divide up the space into smaller parts and obtain open or closed systems which would be the sub-systems of the larger isolated system. The conservation laws of physics, such as the conservation of energy, the conservation of momentum, and the conservation of angular momentum, apply to the isolated systems. Suppose you look at the conservation of energy of the universe as whole. Now, if you divide up the universe into two parts, say a nitrogen gas tank and the rest of the universe. The two subsystems will exchange energy and the energies of the individual subsystems will change with time but the energy of the combined system will be unchanging. We will be using arguments of this type throughout this book.