Fundamentals of Thermodynamics
Lecture 2. Concepts and Definitions

2.1 What is Thermodynamics?

The word thermodynamics comes from the Greek words (therme, meaning “heat”) and (dynamis, meaning “power”). As a definition: Thermodynamics is the branch of science that deals with the relationship of various forms of energy and matter and study the various processes that change energy from one form into another (such as converting heat into work) and uses variables such as temperature, volume, and pressure. The objects studied in thermodynamics are called systems.

2.2 Branches of Thermodynamics

A. *Classical Thermodynamics:* is the branch of thermodynamics that concerns with the states and properties of energy and with the laws of thermodynamics without the atomic interpretation.

B. *Statistical thermodynamics:* is the branch of thermodynamics that every molecule is under the spotlight, i.e. the properties of every molecule and how they interact are taken into consideration to characterize the behavior of a group of molecules.

C. *Chemical thermodynamics:* is the branch of thermodynamics that studies how work and heat relate to each other in chemical reactions and in changes of states.

D. *Equilibrium Thermodynamics*: is the branch of thermodynamics that studies the transformations of energy and matter as they approach the state of equilibrium.

2.3 Distinction Between Mechanics and Thermodynamics

The distinction between mechanics and thermodynamics is worth noting. In mechanics, we solely concentrate on the motion of particles or bodies under the action of forces and torques. On the other hand, thermodynamics is not concerned with the motion of the system as a whole. It is only concerned with the internal macroscopic state of the body.

2.4 The Basic Principles of Thermodynamics

Thermodynamics is based on a number of laws which are taken as axioms. The zeroth law deals with the concept of thermodynamic equilibrium; the first law is an extension of the concept of conservation of energy, and the second law tells us about the natural direction of heat flow.

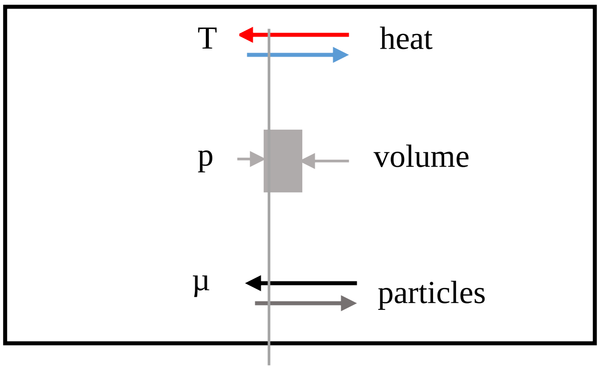
2.4.1 Equilibrium

Thermodynamic equilibrium is a state in which three types of equilibrium all have to be present. To illustrate them, imagine a container that is fully isolated from the outside world, and subdivided into two compartments (See the figure below). The two compartments are in thermodynamic equilibrium with each other if they are in mechanical, thermal and chemical equilibrium.

A mechanical object is in equilibrium when both the sum of the forces and the torques acting on it are zero. Suppose the dividing wall between the two compartments can move, but the outside walls are rigidly fixed. Then, if the air pressure in one (say the left) compartment is larger than in the other, there will be a net force on the wall, which will move it towards the right, reducing the right compartment's volume, and expanding that of the left compartment. This goes on until the pressure in both compartments is the same - i.e., they both exert the same force (per unit area) on the wall, at which point there is mechanical equilibrium.

Now suppose that the wall separating the two compartments cannot move, but heat exchange is possible. Then, if the left compartment is warmer than the right one, heat will flow from the left to the right. Consequently, the temperature of the colder compartment will rise, whereas that of the hotter one will drop, until they are equal and have reached thermal equilibrium.

Finally, suppose that particles can be freely exchanged between the two compartments. Clearly if all particles are in one compartment, there is an imbalance that will not be stable, as some particles will move over to the other compartment over time, resulting in a net particle flow. Again, this goes on until the flow of particles from left to right balances that from right to left. The equivalent quantity to pressure and temperature for this type of exchange is called the chemical potential, and when there is no more net particle flow between the two compartments, they are said to be in chemical equilibrium.



2.4.2 Heat and Energy

In the example of the previous section, when there is no mechanical equilibrium, it can be reached by doing *work,* in this case moving the wall. This work originates from the pressure (force/ area) acting on the wall, resulting in a change of volume:

$$W = \int F\,dr = \int \frac{F}{A} A\,dr = \int \Delta p\,dV \qquad (1)$$

Where dr is the distance over which the wall moves, A the area of the wall, and $dV = A\,dr$ is the amount of volume added to the compartment with the larger pressure. Equation (1) tells us that a pressure difference can be used to move objects, and thus that work can be extracted. However, if we are interested in the properties of the gas (that is, after all, the system which we are studying here), we should instead calculate the work done on the gas, which is minus the work done by the gas on the wall:

$$W = -\int p\,dV \qquad (2)$$

Equation (2) tells us that when the two compartments move towards mechanical equilibrium, mechanical energy is exchanged between them, until their pressures are equal. Similarly, we have defined thermal equilibrium as the state in which the temperatures of the two compartments are equal, and noted that an imbalance in temperature leads to a flow of heat which is also a form of energy. Microscopically, we can identify temperature as the kinetic energy of the constituent particles of a material, so an exchange in temperature between two systems, i.e. a heat flow, is simply an exchange in kinetic energy.

2.4.3 Heat Capacity

Unsurprisingly, the larger the difference in temperature between two bodies in thermal contact, the larger the heat flow between them. The relation turns out to be linear. The proportionality factor is known as the heat capacity of the body (denoted C), and we can write:

$$Q = C\,\Delta T \qquad (3)$$

We can then define a (mass) specific heat of the substance (denoted c), which is simply its heat capacity per unit mass.

$$c = \frac{C}{m} = \frac{Q}{m\,\Delta T} \qquad (4)$$

Water has a high specific heat ($c_w = 4.184\ J/kg.K$), much higher than typical solids, which is why the sea warms up and cools down much more slowly than land, causing the difference in climate between coastal and inland regions. We have two different heat capacity C_v and $C_{p.}$

$$C_v = \left(\frac{dQ}{dT}\right)_v \qquad (5)$$

$$C_p = \left(\frac{dQ}{dT}\right)_p \qquad (6)$$

2.4.4 Heat Transfer

Heat can commonly be transferred in three different ways, conduction, radiation, and convection. Conduction of heat happens when two objects, or two parts of the same object, are in direct physical contact. If one part has higher temperature than the other, heat will flow from the hotter to the colder part. This process is described by the *heat equation*:

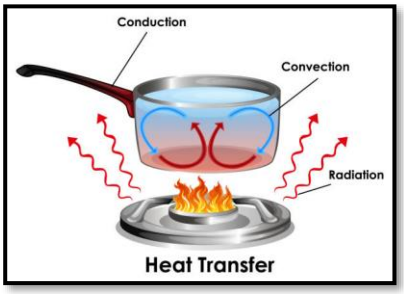
$$\frac{\partial u}{\partial t} = \alpha\, \nabla^2 u \qquad (7)$$

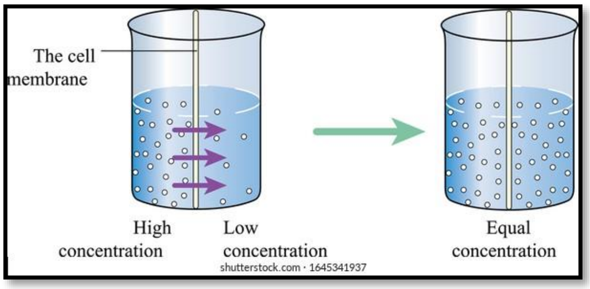
$u = u(x, y, z, t)$ is the solution of heat equation, and $[\frac{\partial u}{\partial t} = \alpha\, (\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2})]$

Where α is the thermal diffusivity of the medium. Equation (7) describes the flow of heat in a homogeneous and isotropic medium, with $u(x, y, z, t)$ being temperature at the point x, y, z and t, governed by the thermal diffusivity. If the medium is not homogeneous and isotropic, then α would not be a fixed coefficient.

By the second law of thermodynamics, heat will flow from hotter bodies to adjacent colder bodies in proportion to the difference of temperature and of the thermal conductivity of the material between them.

Heat equation is mathematically equivalent to the diffusion equation which describes the spread over time of a chemical concentration.

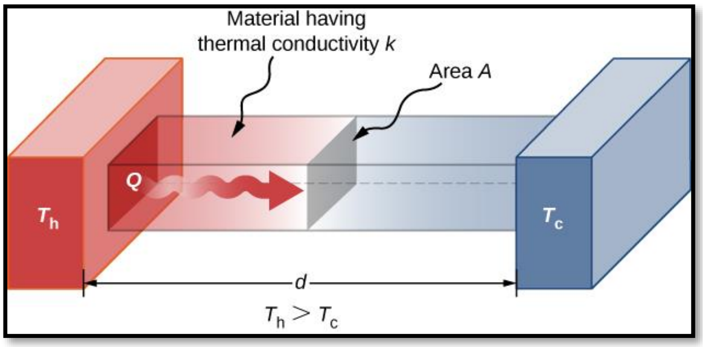




For the heat flow through a uniform rod with cross-sectional area A, the rate of the flow of heat per unit area, q, equals minus the temperature gradient across the rod:

$$q = -k\, \nabla u \qquad (8)$$

where the material constant k is the thermal conductivity of the material.



Equation (8) is known as Fourier's law. The heat equation can be derived from Fourier's law and conservation of energy. The latter gives that the rate of change of the internal heat in a small volume element in the material, $\frac{\partial Q}{\partial t}$, must be equal to the flow of heat out of that volume element:

$$\frac{\partial Q}{\partial t} = -\nabla . q \qquad (9)$$

On the other hand, by definition of the temperature, the rate of change of heat is proportional to the rate of change of the temperature, $\frac{\partial u}{\partial t}$:

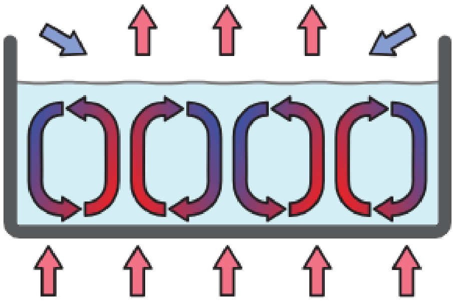
$$\frac{\partial Q}{\partial t} = c\,\rho\,\frac{\partial u}{\partial t} \qquad (10)$$

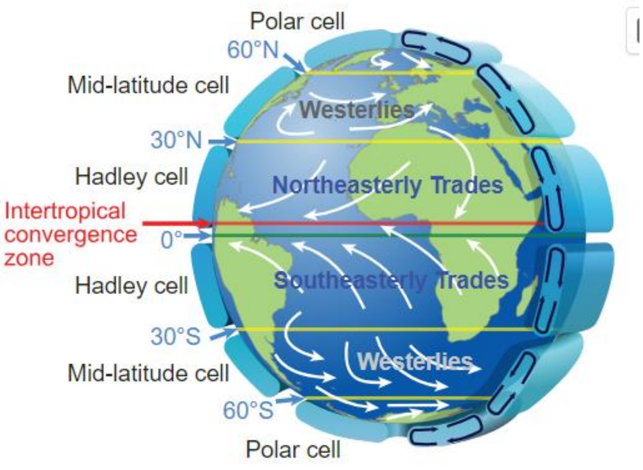
where c is the specific heat and ρ the density of the material. Combining equations (8)-(10), we retrieve the heat equation (7), with a relation between the thermal diffusivity and the thermal conductivity, $\alpha = k/c\,\rho$.

For the specific case of steady-state heat flow through an object of thickness Δx and cross-sectional area A, due to a temperature difference ΔT, we can write:

$$H = \frac{\partial Q}{\partial t} = -k\,A\,\frac{\Delta T}{\Delta x} \qquad (11)$$

Convection of heat happens due to the fact that fluids density decrease with temperature. The hotter fluid will rise, and the colder fluid above will fall down, creating an instability which results in the formation of convective cells. This setup is known as the Rayleigh-Bernard cell, and convective cells are seen at many scales, from tabletop setups to planetary and solar atmospheric motion, see the figure below.





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