Basic quantities in Thermodynamics

Temperature:

- It is a statistical property . i.e., a collective property of a large number of particles (atoms, molecules etc.).

-Zeroth law of Thermodynamics enables us to develop the scientific concept of temperature as well as measurement of temperature

Temperature

We can ‘feel’ the temperature, i.e., the degree of hotness or coldness of a given object

Can we define and measure the temperature ?

Answer is Yes !

For that, we first need to understand the concept of <u>thermal equilibrium</u>

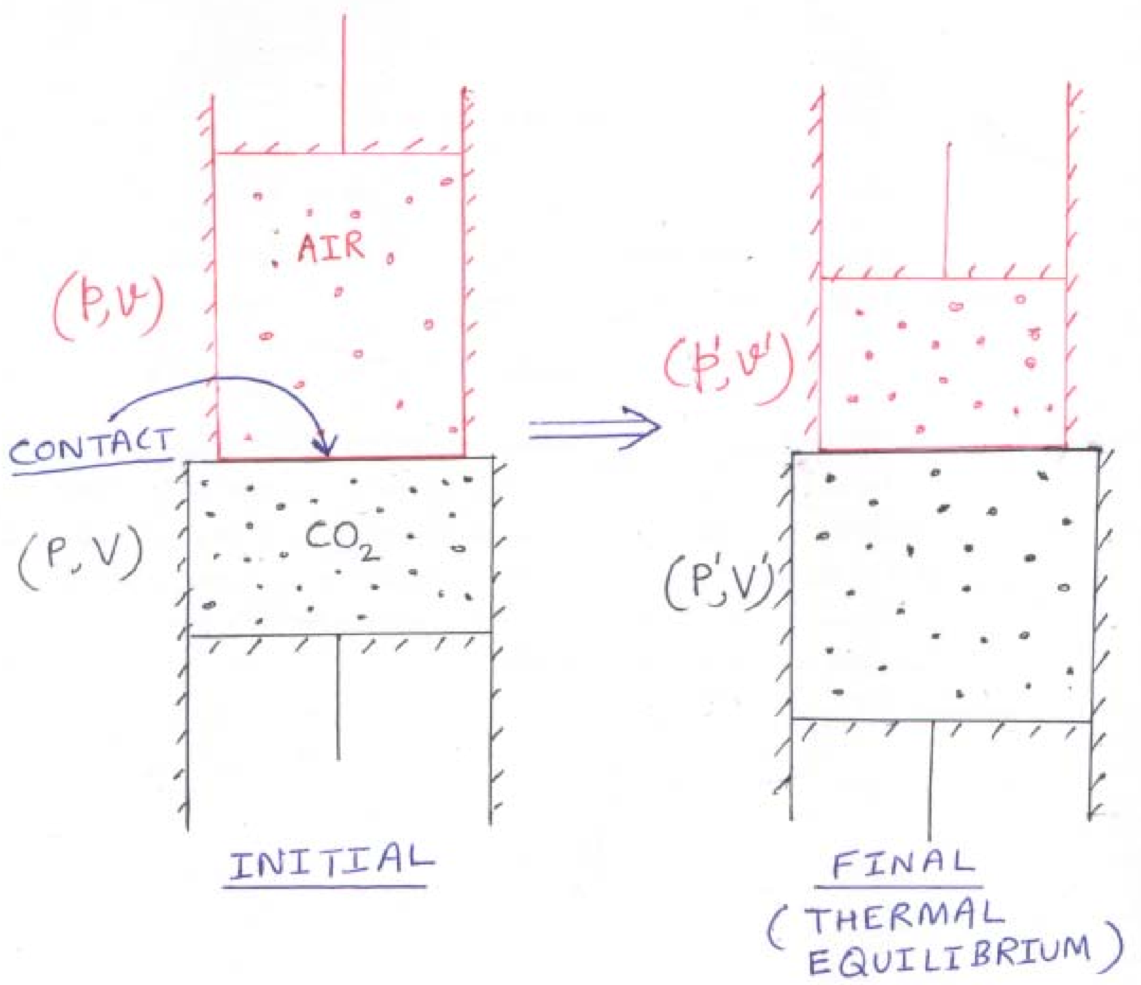
Thermal equilibrium

Systems can be in thermal contact either directly
(e.g. Copper blocks) or through a non-permeable
wall (e.g. two gases)

Systems in thermal contact are influenced by each other.

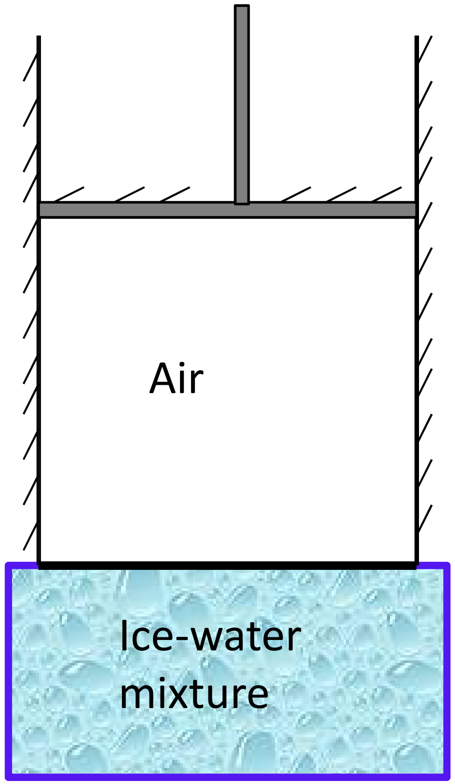
After a sufficient time, all observable changes come to an end
Then two systems are said to be in thermal equilibrium
with each other

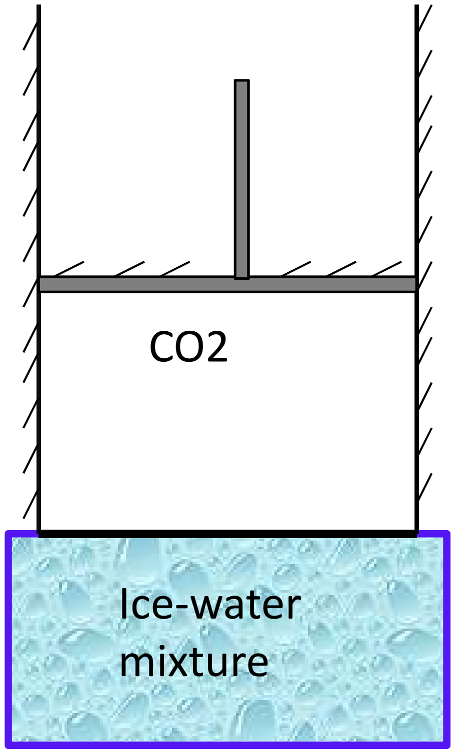
Thermal equilibrium



We expect that systems in thermal equilibrium have some property in common

Thermal equilibrium and Zeroth law :

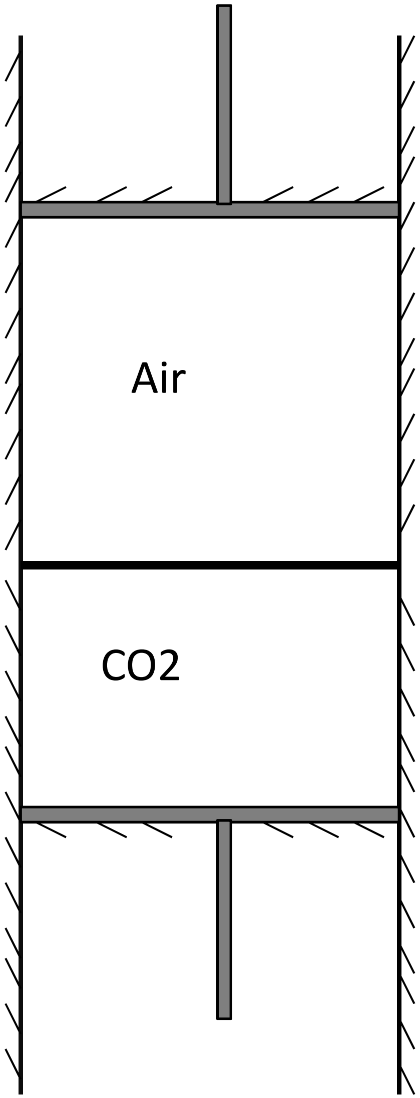




Air is in thermal equilibrium with ice-water mixture,

CO_2 is in thermal equilibrium with ice-water mixture,

Thermal equilibrium and Zeroth law :

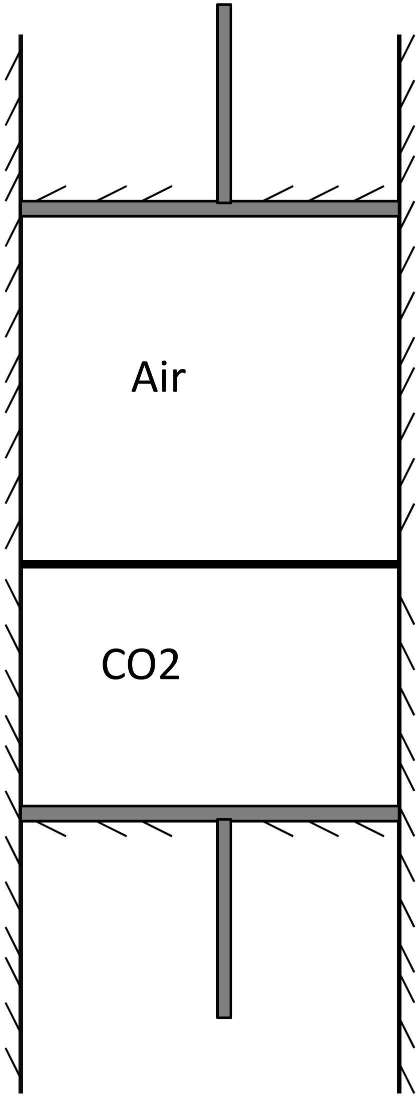


If Air and CO_2 which are separately in thermal equilibrium with ice-water mixture are brought in thermal contact.

Question : Will these remain in equilibrium ? Or will their state (pressure or volume) change ?

Answer : Due to complex nature of the interactions between Air and CO_2 molecules (across the wall), it is not obvious !!

Zeroth law of Thermodynamics



"If two bodies are in thermal equilibrium with a third body, these are also in thermal equilibrium with each other"

As with other laws, this law is based on practical experience.

<u>Significance :</u>

Any body which is in thermal equilibrium with a reference phase (say) ice-water mixture will have a property in common. That property is **<u>Temperature</u>**

Temperature scales

These are based on easily reproducible states.

1. Ice point : A state in which ice and water are in equilibrium with air which is saturated with water vapor at a total pressure of 1 atmosphere

   On Celcius scale, ice point corresponds to 0 ^{0}C
   On Fahrenheit scale, ice point corresponds to 32 ^{0}F

2. Steam point : A state in which water is in equilibrium with steam (with no air) at a total pressure of 1 atmosphere.

   On Celcius scale, ice point corresponds to 100 ^{0}C
   On Fahrenheit scale, ice point corresponds to 212 ^{0}F

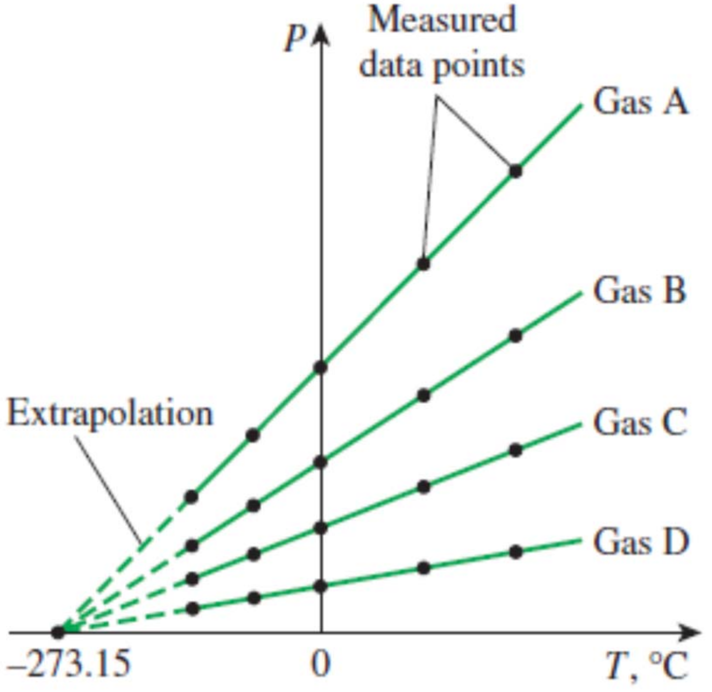
Constant volume gas thermometer

Provided that pressures are sufficiently low (ideal gas limit), change in temperature is found to be linearly proportional to change in pressure at constant volume.

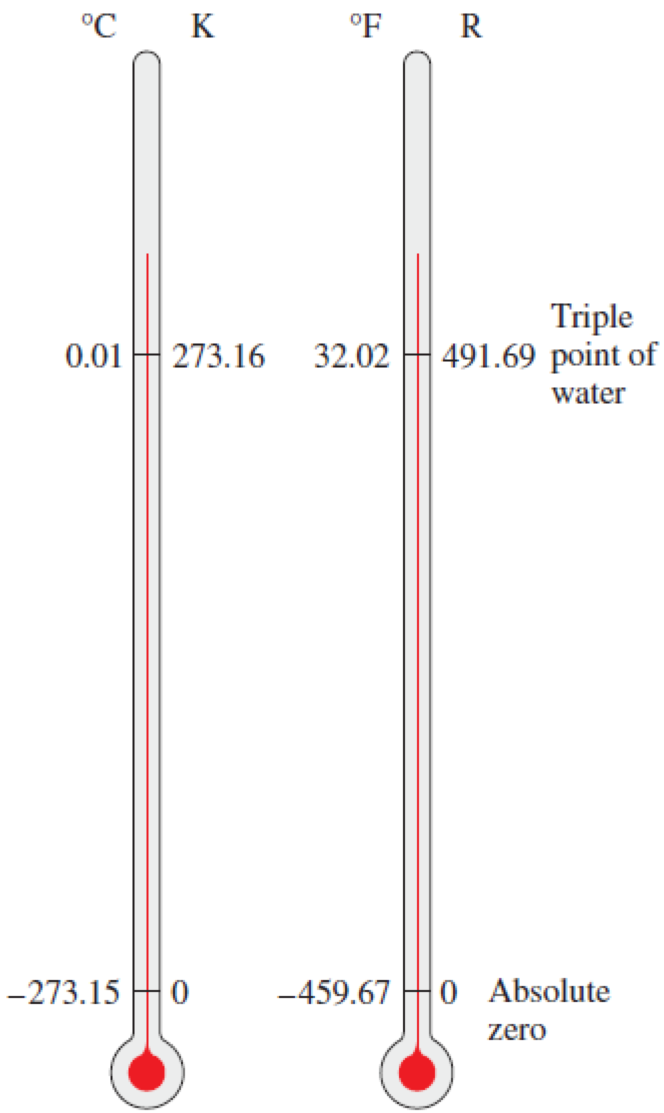
$$dT = b dP$$

Upon Integrating,

$$T = a + b\,P$$



Temperature scales



$$T(\mathrm{K}) = T(^\circ\mathrm{C}) + 273.15$$

$$T(\mathrm{R}) = T(^\circ\mathrm{F}) + 459.67$$

$$T(\mathrm{R}) = 1.8T(\mathrm{K})$$

$$T(^\circ\mathrm{F}) = 1.8T(^\circ\mathrm{C}) + 32$$

Kelvin scale and Rankine scale are known as <u>Thermodynamic temperature scales</u> in SI and English Units, respectively.

Basic quantities in Thermodynamics:

Density and specific volume :

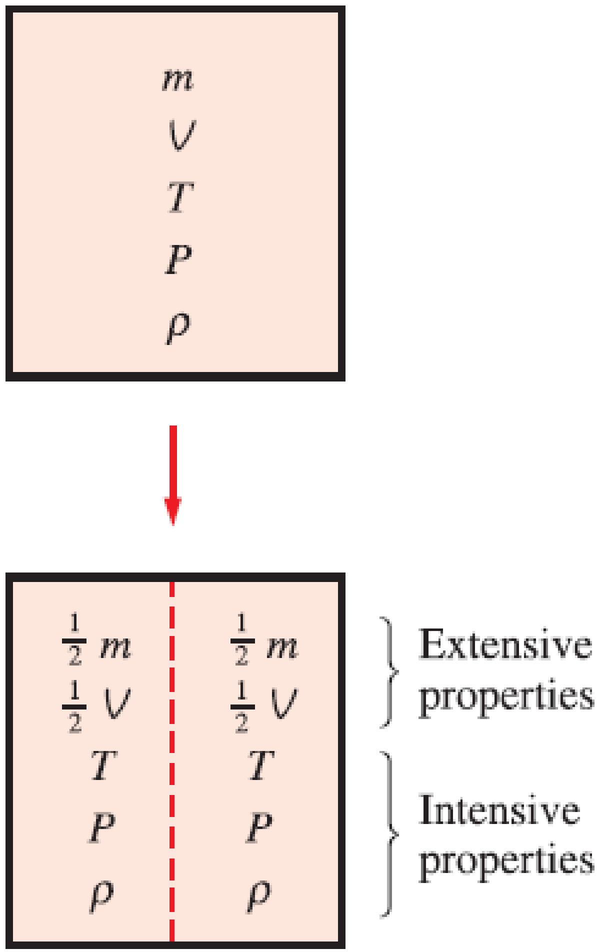
Density is defined as : $$\rho = \frac{m}{V} \quad (kg/m^3)$$

Here, m is mass and V is volume

Specific volume is defined as : $$v = \frac{V}{m} \quad (m^3/kg)$$

Besides these there are other important quantities like mole fractions, internal energy U etc. We will describe these in detail later.

Intensive and extensive properties:



T, P, ρ are <u>intensive properties</u>

m, V are <u>extensive properties</u>

Equilibrium state :

Equilibrium state or state of equilibrium is where **all** (macroscopic) driving forces are balanced and hence there is no observable change in the system.

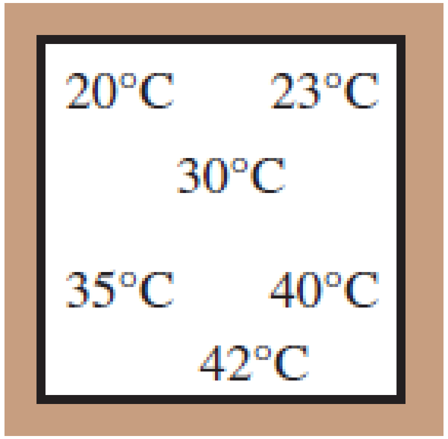
There are different types of equilibria depending upon the driving force:

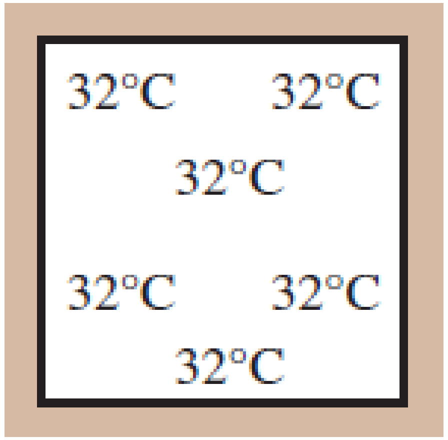
Besides mechanical and thermal equilibrium, we also deal with chemical equilibrium in engineering applications.

When a system has achieved chemical equilibrium, there is no further change in composition of the system.

Equilibrium state :

All systems reach an equilibrium state after sufficient time



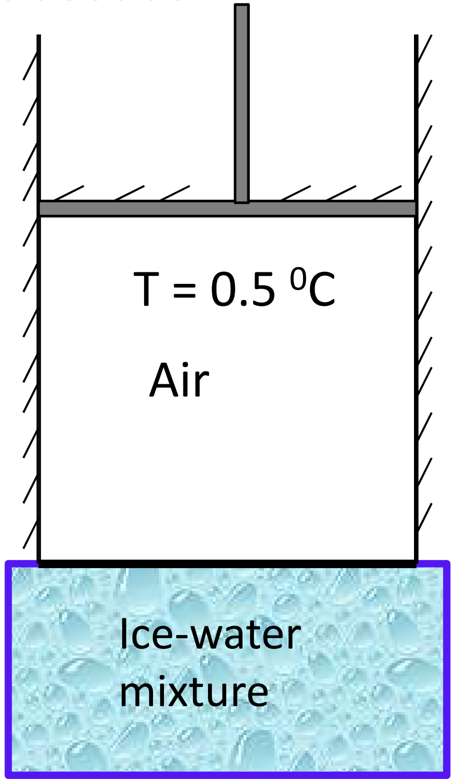


Initial (non-equilibrium) state

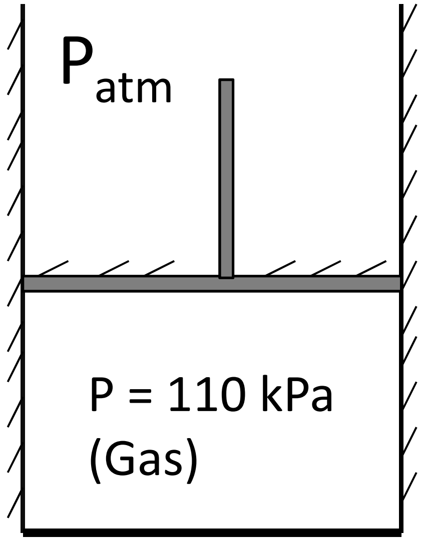
Final (equilibrium) state

‘Internal’ Equilibrium state :

This is based on separation of time scales of different processes



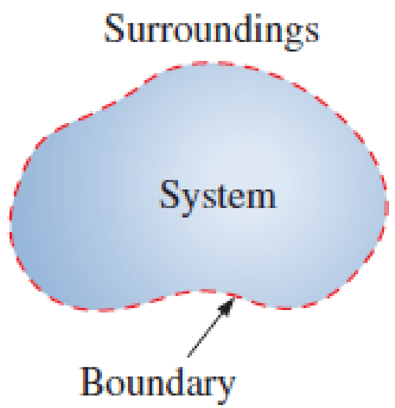
Gas is in thermal equilibrium <u>internally</u>



$P > P_{atm}$

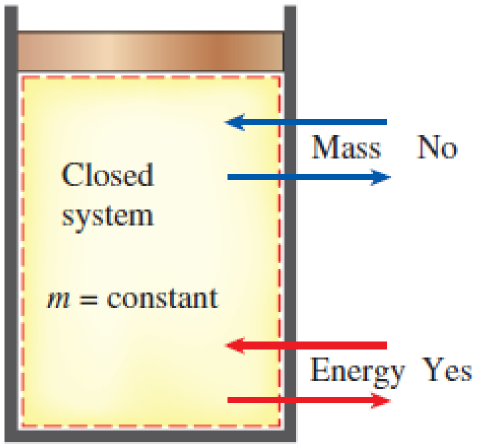
Gas is in mechanical equilibrium <u>internally</u>

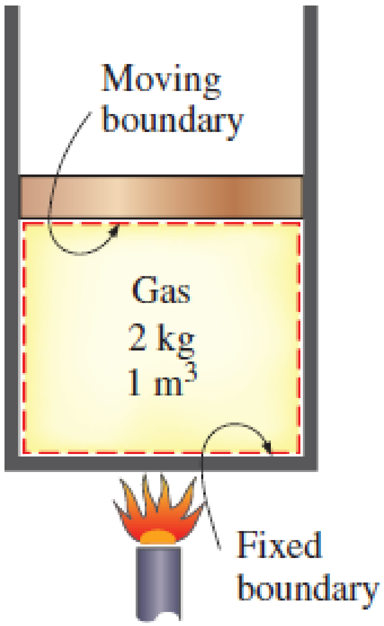
Systems :



Thermodynamic analysis : we define a system and its surroundings by means of a boundary

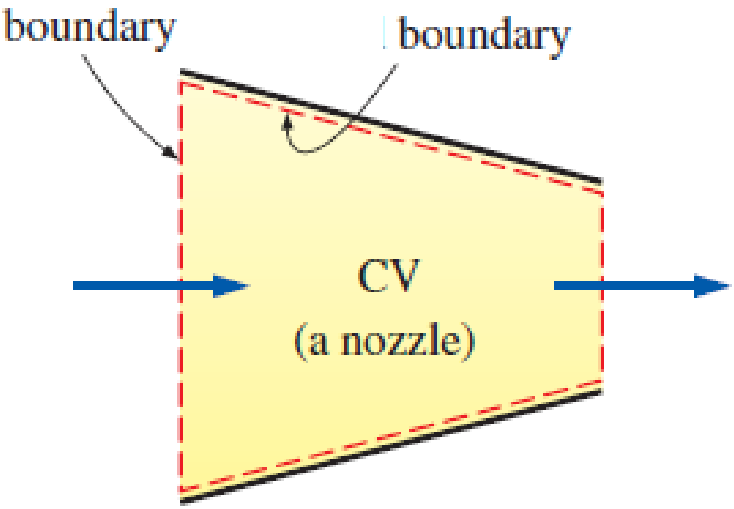
<u>Closed system or Control mass</u>

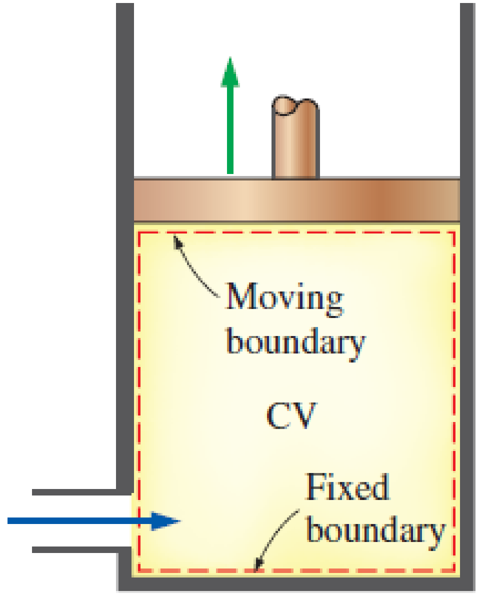




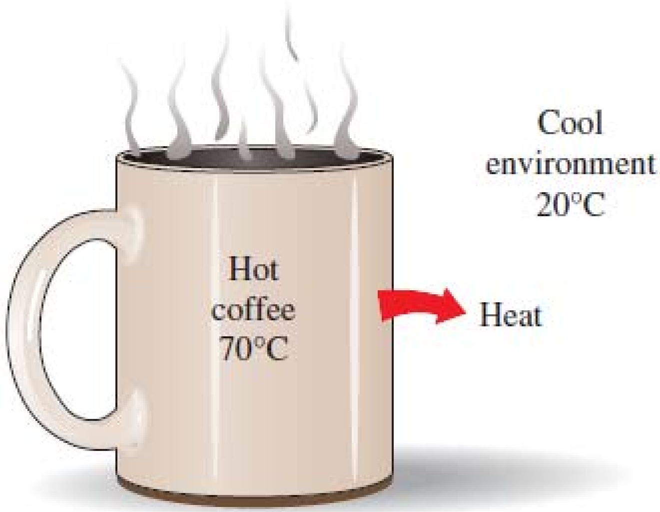
Systems :

<u>Open system or a control volume</u>:





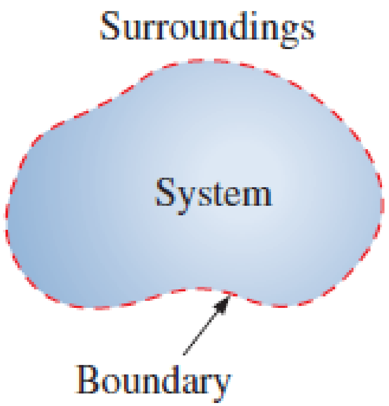
Examples :



Systems :

Isolated system : No mass or energy can can cross the boundary

For example, System + Surroundings = Isolated system



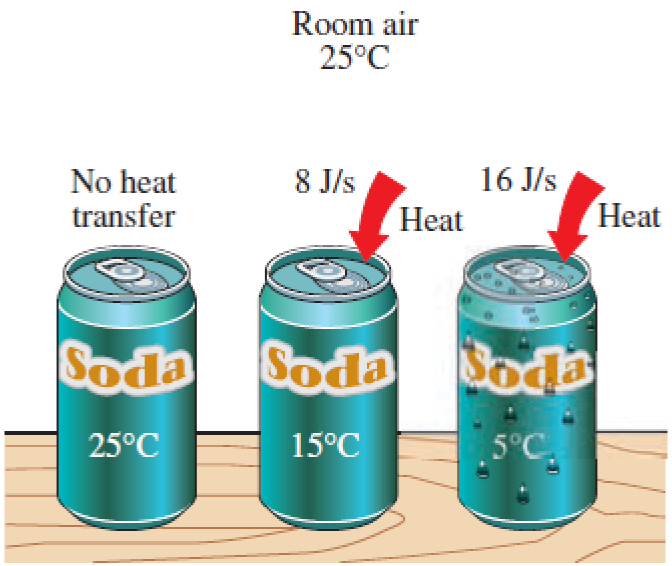
Sometimes useful for analysis based on 2nd law of thermodynamics

Energy transfer by Heat :

Heat is that part of the energy transfer which occurs due to temperature difference

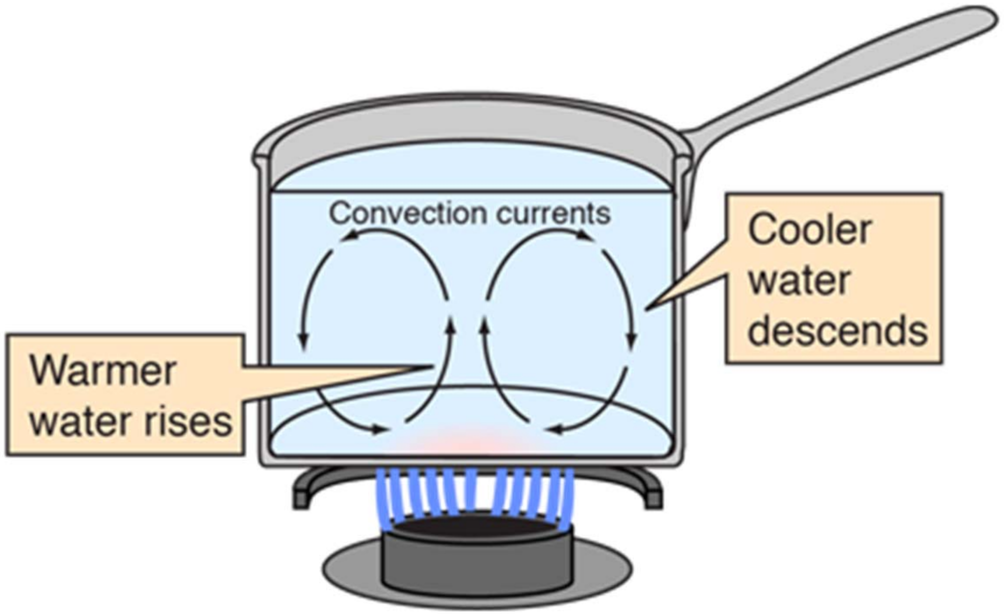
Systems at different temperatures exchange heat by three modes : (i) conduction (ii) convection and (iii) radiation

Conduction :



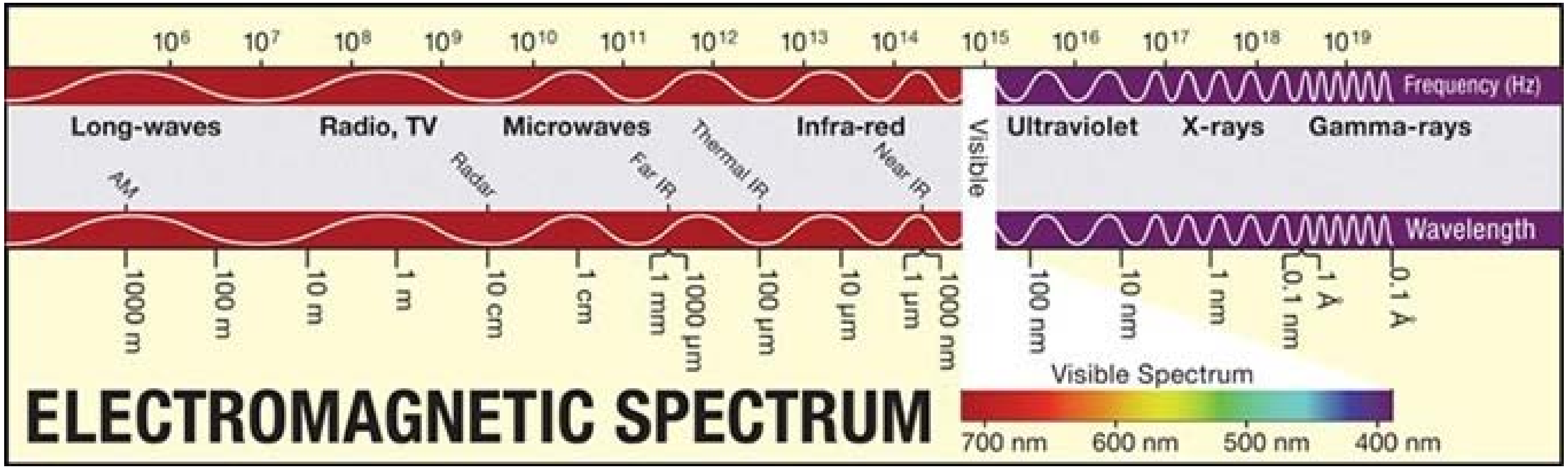
Energy transfer by Heat :

Convection : is the heat transfer due to bulk movement of fluid between regions with different temperatures



Energy transfer by Heat :

Radiation : is the heat transfer due to electromagnetic waves generated by thermal motion of particles in matter . Thermal radiation has a wavelength in the range of 0.1 to 100 µm (Infrared, visible and UV)

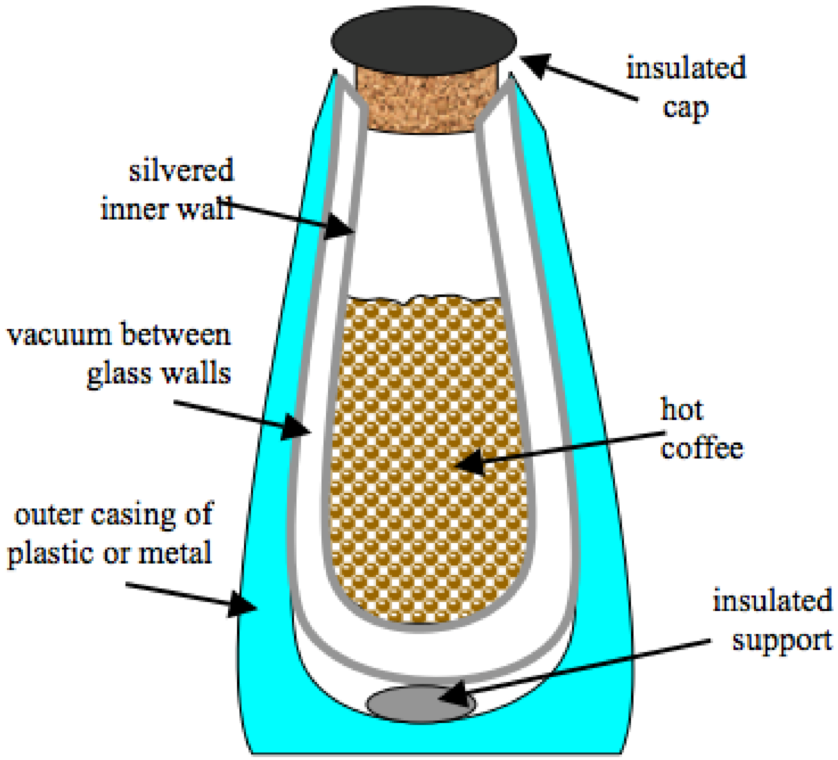


Infrared thermometer

Adiabatic process :

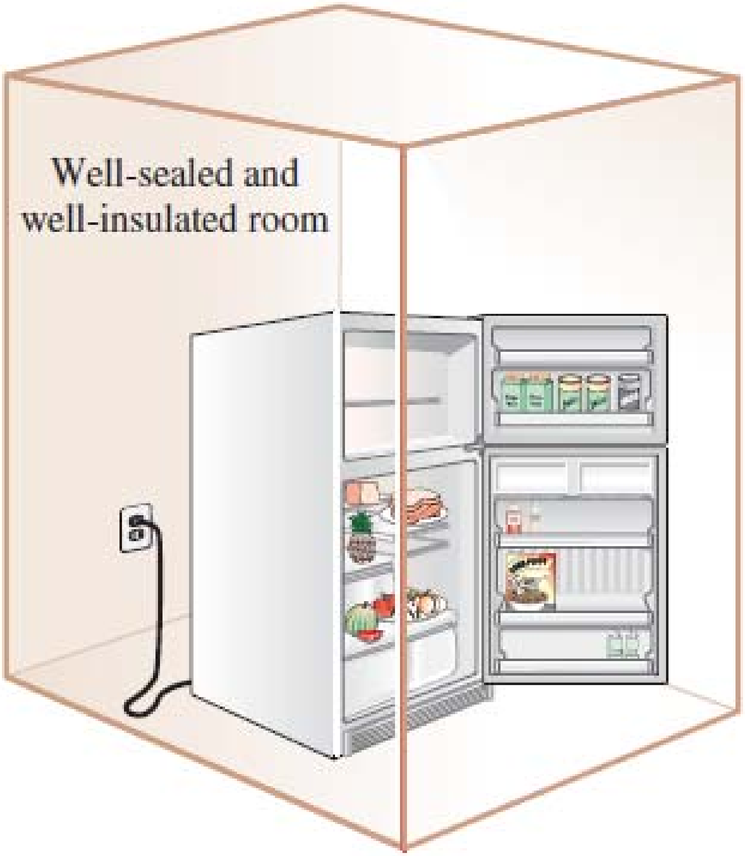
In this process, energy transfer is only due to work.

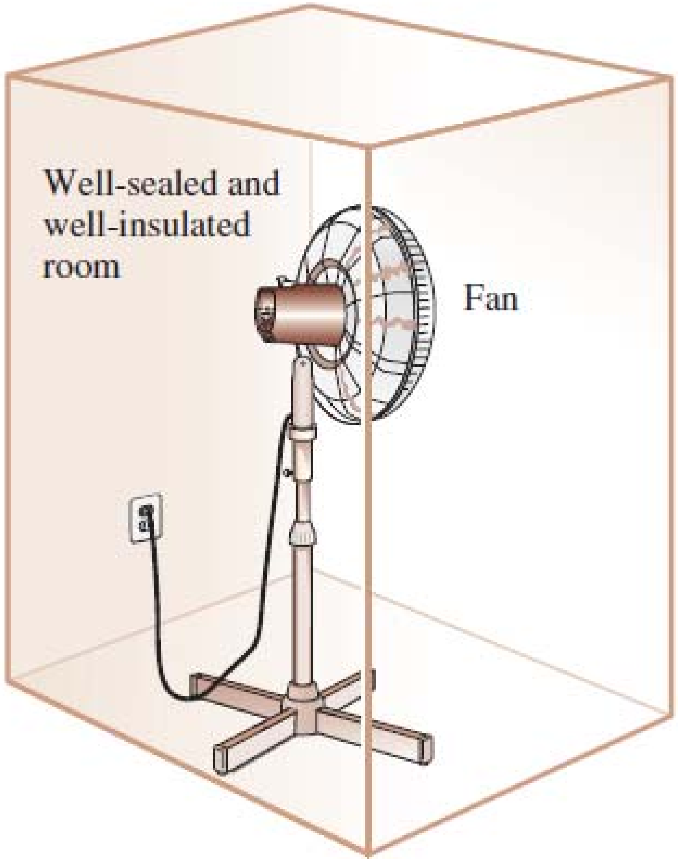
System is enclosed in a container with ‘adiabatic’ walls



Adiabatic process :

If surface tension effects and force field effects are not important, then the energy of the system can only be changed by Compression, expansion or by causing internal motion.





Adiabatic process :

Careful work measurements (in adiabatic processes) were performed by Joule in years 1843-1848

These experiments led to the concept of internal energy (U) and the formulation of first law of thermodynamics.