THERMODYNAMICS AND STATISTICAL MECHANICS

CHAPTER 1 –INTRODUCTION

Poopalasingam Sivakumar

Outline Of Course

The course is organized into three parts:

i. Classical Thermodynamics: Macroscopic laws of thermodynamics, thermodynamic potentials, and applications.

ii. Classical and Quantal Statistical Mechanics: Microscopic foundations of thermodynamics, statistical ensembles, and ideal classical and quantum gases.

iii. Phase Transitions: Phase coexistence, critical behavior, and an introduction to interacting many-particle systems.

Classical Thermodynamics

- A macroscopic theory that describes the behavior of physical systems using directly measurable quantities such as pressure, volume, temperature, and entropy. Relationships between these quantities are expressed through equations of state and thermodynamic potentials.
- Classical thermodynamics makes no explicit assumptions about the microscopic structure of matter or radiation. Instead, it is based on experimentally established laws and principles.

Classical Thermodynamics

- The theory focuses on energy transfer and transformation, as governed by the laws of thermodynamics, including:
  - Energy exchange between systems and their surroundings (e.g., heat and work).
  - Redistribution of energy among different macroscopic forms (mechanical, thermal, chemical), without requiring detailed knowledge of microscopic degrees of freedom.

Classical thermodynamics provides a framework that is valid across many physical systems, regardless of their underlying microscopic composition.

Temperature

Most familiar concept in thermodynamics is temperature, generally measured with thermometers.

Typically, it is reported in degrees Celsius or degrees Fahrenheit.

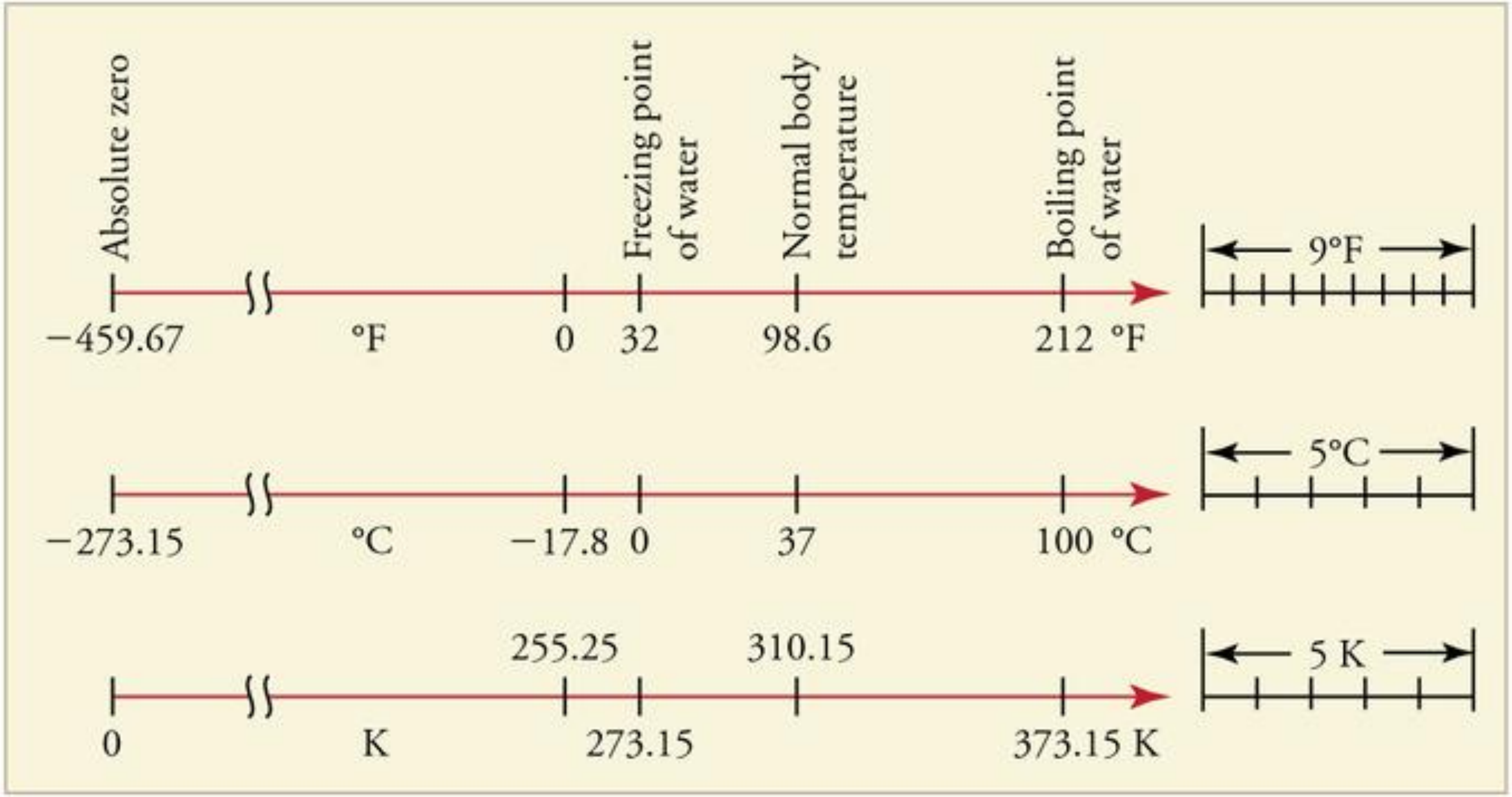
$$\frac{T_c - 0}{100 - 0} = \frac{T_F - 32}{212 - 32}$$

$$T_c = \frac{5}{9}\,(T_F - 32)$$

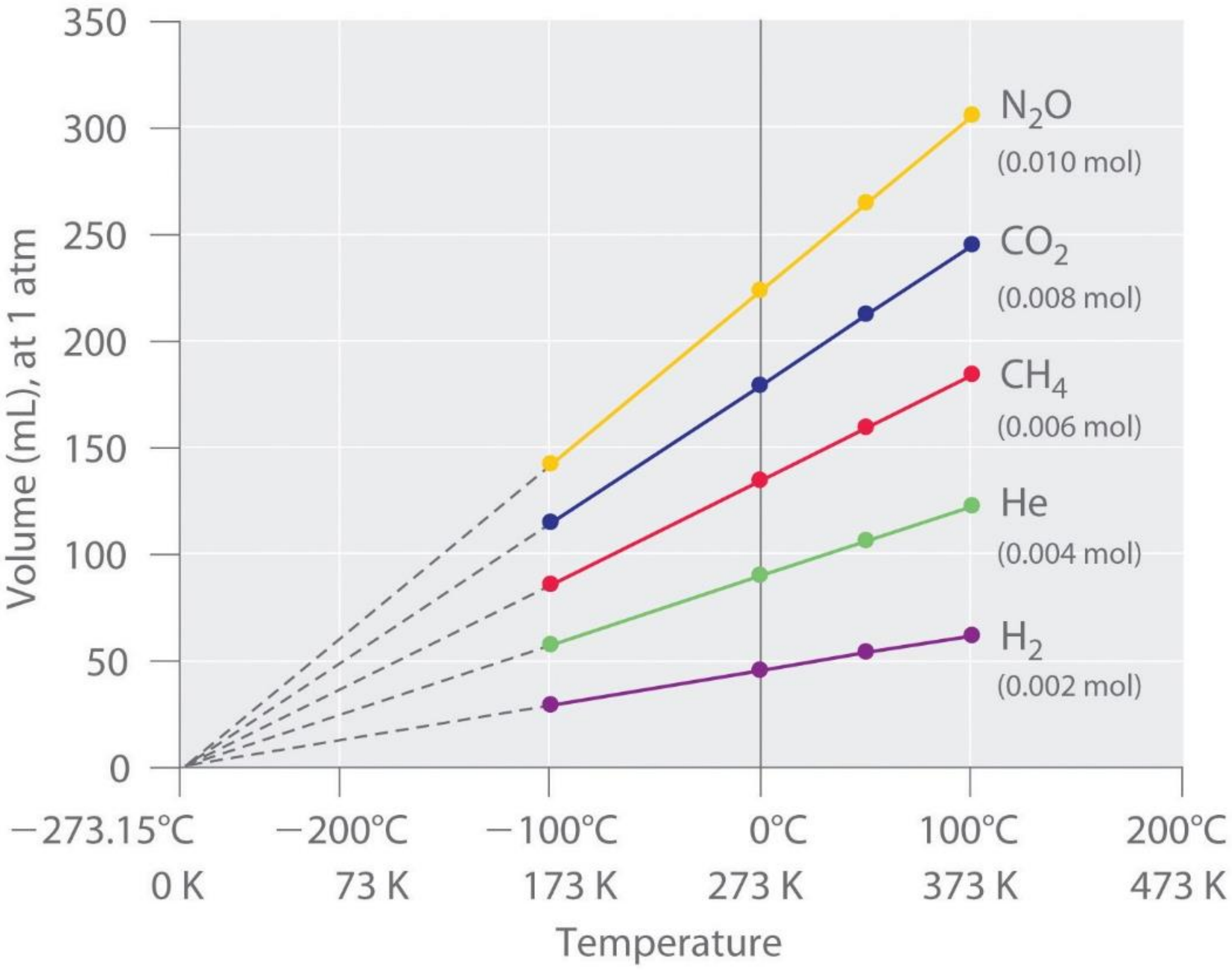
$$\Delta C = \frac{5}{9}\Delta \mathrm{F}$$

Temperature

Relationship between the Fahrenheit, Celsius, and Kelvin temperature.



Temperature



At absolute zero temperature (0 K), the pressure of an ideal gas at fixed volume extrapolates to zero. This concept was first proposed in 1848 by William Thomson, later known as Lord Kelvin, an Irish-Scottish physicist, engineer, and mathematician, after whom the Kelvin temperature scale is named.

Example-01

(a) If the person temperature is $98.6^o F$, what would be the reading in Celsius?

(b) The outdoor temperature in December is $-20.0^o C$. Find the corresponding temperature in the Fahrenheit scale.

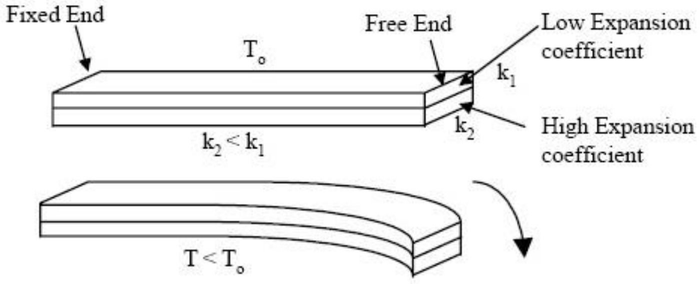
Quiz-C1-1

At what temperature do the Celsius and Fahrenheit temperature scales give the same numerical value?

Thermometric Property

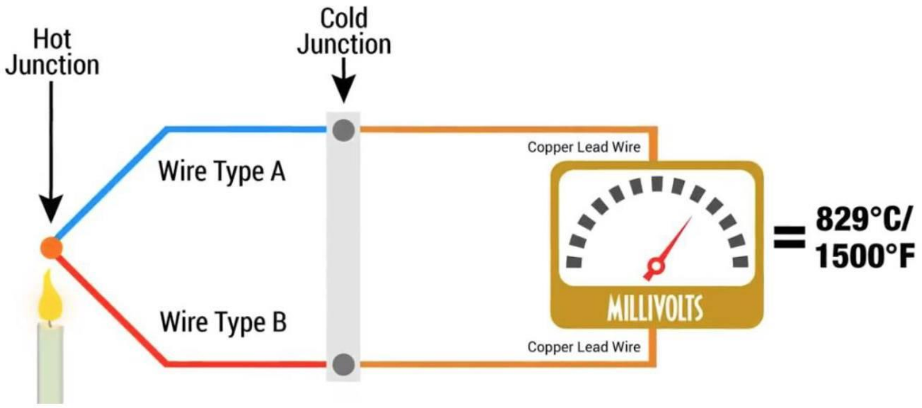
A property that changes with temperature. Thermal expansivity: $\boldsymbol{\Delta L = \alpha\, L\, \Delta T}$

Where α coefficient of linear expansion. Similarly for the thermal expansion coefficient of volume is $\boldsymbol{\beta = \frac{\Delta V}{V\, \Delta T}}$



Good example of thermometric property is thermocouple: two dissimilar metals are put into contact with each other, which create a small voltage in the range of mV is degenerated, called the **thermoelectric EMF,** arises from the difference in Fermi Levels of the two metals and depends on temperature. Thermocouple has three thermoelectric effects:

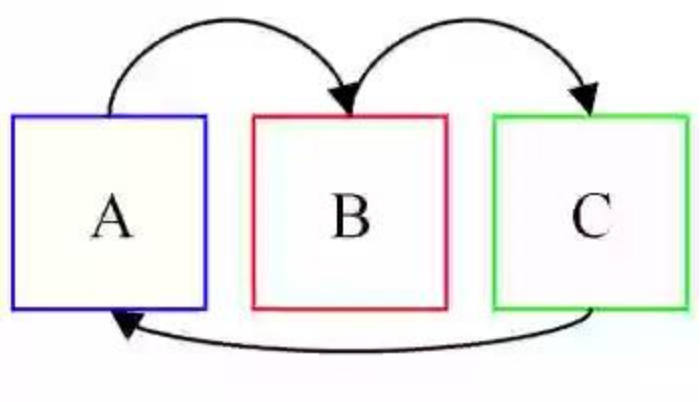
- Seebeck effect – generation of voltage due to a temperature difference.
- Peltier effect – absorption or release of heat when current flows through a junction.
- Thomson effect – heating or cooling along a single conductor with a temperature gradient when current flows.



Thermal Equilibrium

Two objects are said to be in **thermal equilibrium** when, after being in contact, they reach the same temperature and no net heat flows between them.

The time required for a system to reach thermal equilibrium is called the **Relaxation time**.



A is equilibrium with B and B is in equilibrium with C. So, A and C are in thermal equilibrium.

Other types of Equilibrium

- Diffusive Equilibrium: Molecules or particles move and mix freely until there is no net movement of matter in any direction.
- Mechanical Equilibrium: when net force become zero, the system is said at mechanical equilibrium.
- Chemical Equilibrium: there is no net change in concentration of reactants and products, meaning no net chemical change occurs.
- Thermodynamic Equilibrium: A system is in thermodynamic equilibrium when it is simultaneously in thermal, mechanical, and chemical equilibrium.

Example: Hot-Air Ballon

A hot-air balloon interacts with its environment in multiple ways:

- **Thermal interaction**: exchanges heat with the surrounding air.
- **Mechanical interaction**: exchanges volume and pressure with the atmosphere.
- **Diffusive interaction**: air molecules can mix in and out of the balloon

Not all interactions are necessarily at equilibrium at the same time, illustrating how different types of equilibrium can vary within a single system.

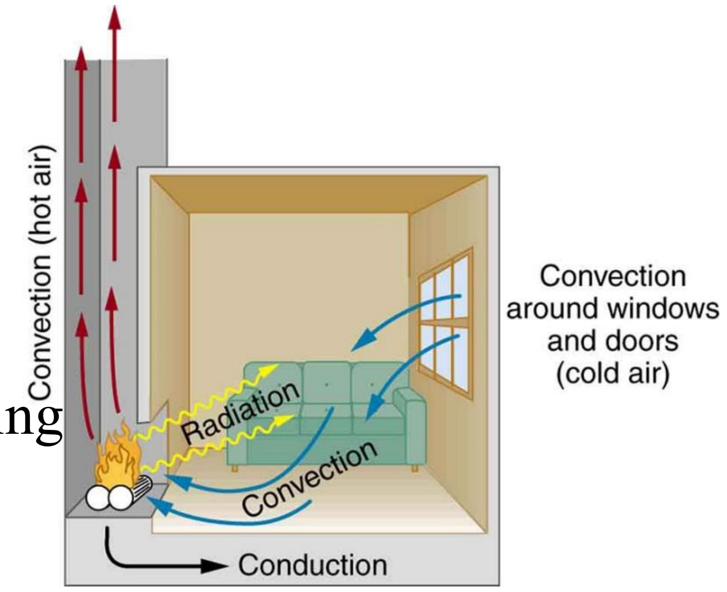
Modes of Heat Transfer

Heat transfer occurs through three fundamental mechanisms:

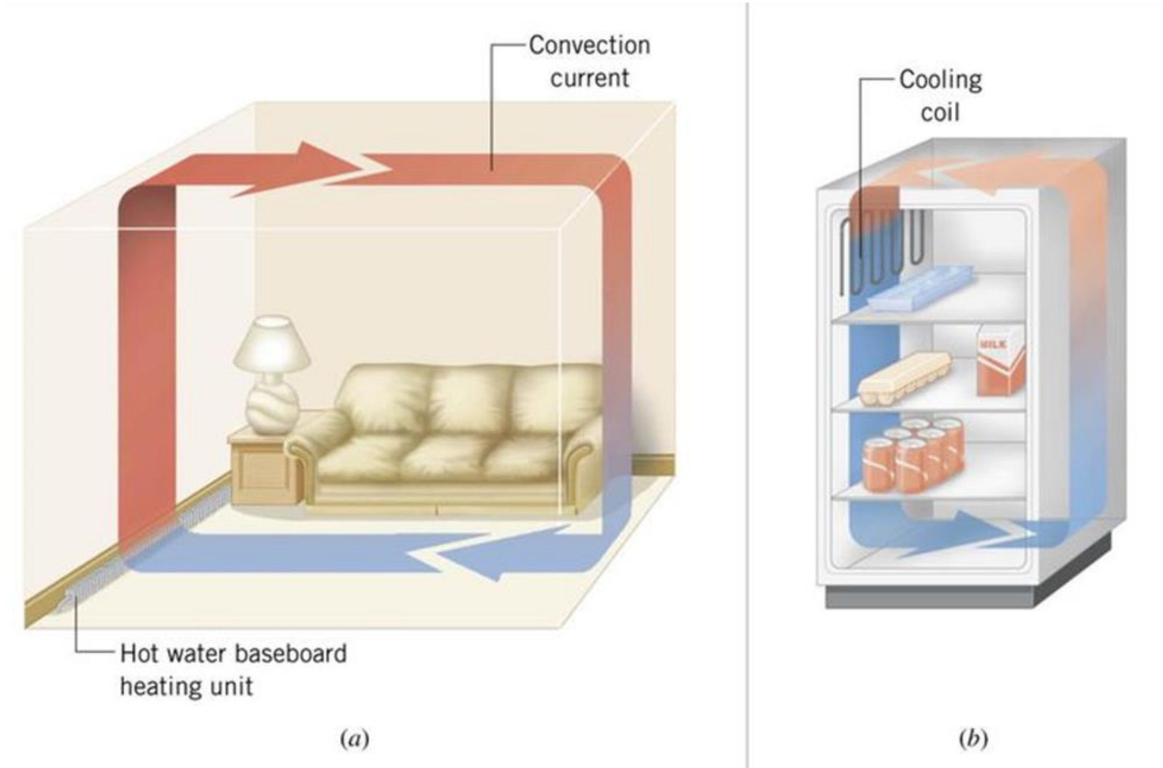
- Conduction: Transfer of thermal energy through direct microscopic interactions (molecular collisions and electron interactions),typically in solids or between objects in contact.

- Radiation: Transfer of energy via electromagnetic waves (thermal radiation),requiring no material medium and occurring even in a vacuum.

- Convection: Transfer of energy through the bulk motion of a fluid (liquid or gas).Warmer, less dense fluid rises, while cooler, denser fluid sinks under the influence of gravity, producing convection currents.



Application of Heat Transfer by Convection



(a) Hot-water baseboard heating units are mounted near the floor, allowing warm air to rise and circulate naturally through the room by convection.

(b) The cooling coil in a refrigerator is mounted near the top, so the cooled, denser air sinks and spreads downward, producing efficient natural convection throughout the interior.

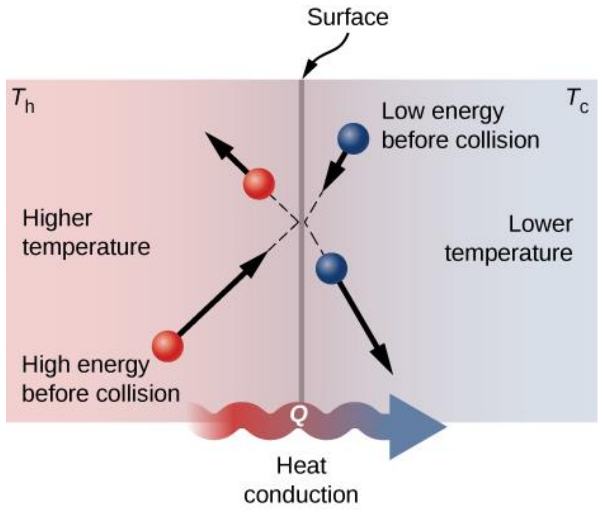
Heat Transfer by Conduction

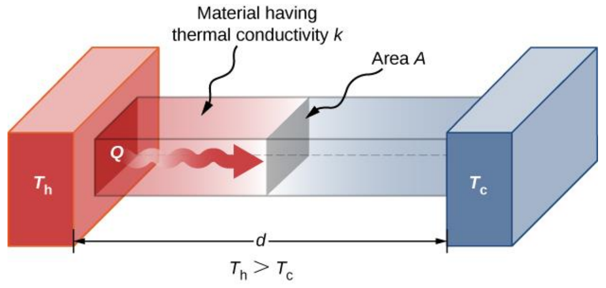
Conduction is the transfer of thermal energy through a material without any bulk motion of the material.

The microscopic mechanism of conduction is the transfer of energy through atomic or molecular interactions:

- Particles in the hotter region have greater kinetic energy and vibrate or move more vigorously.
- Energy is transferred to neighboring, lower-energy particles through collisions and lattice vibrations.

In metals, conduction is enhanced by the motion of free electrons, which efficiently transport energy.





Rate of heat transfer (power) $P = \frac{dQ}{dt} = \frac{kA(T_H - T_C)}{d} = -kA\frac{dT}{dx}$

Where k is thermal conductivity ($Wm^{-1}{}^oC^{-1}$)

Thermal Conductivity of Selected Materials

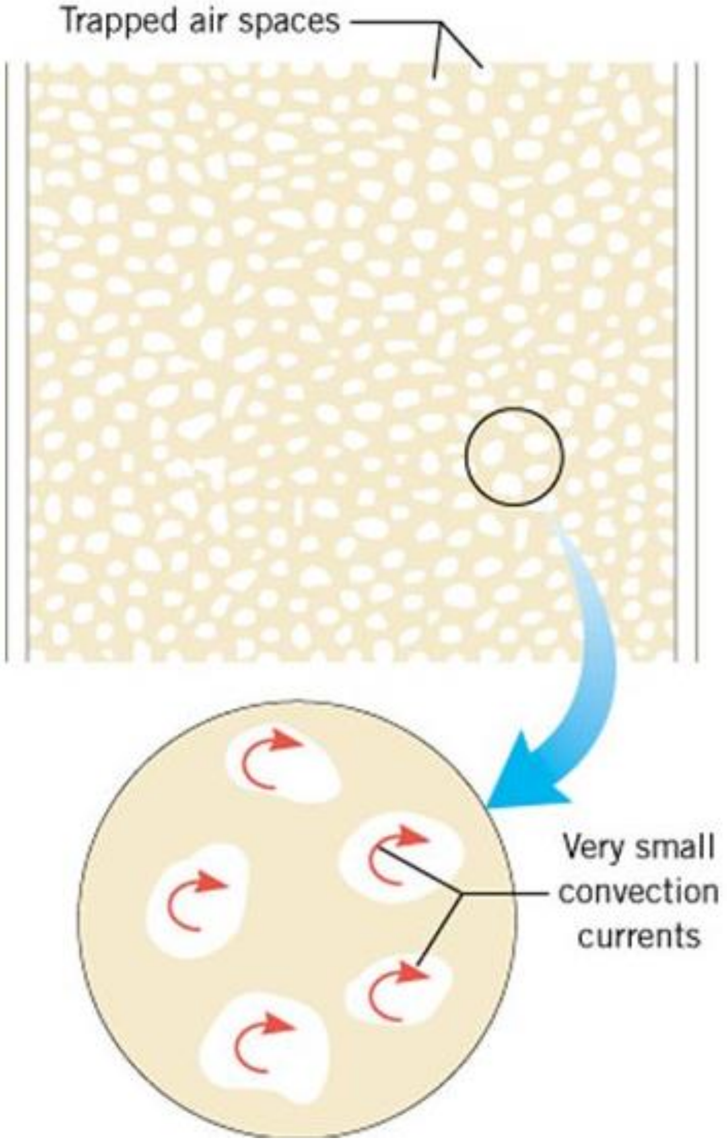
Thermal Conductivities

Substance	Thermal Conductivity, k $\frac{J}{(s \cdot m \cdot C^\circ)}$	Thermal Conductivity, k $\frac{kcal}{(s \cdot m \cdot C^\circ)}$
Silver	420	10×10^{-2}
Copper	380	9.2×10^{-2}
Aluminum	200	5.0×10^{-2}
Steel	40	1.1×10^{-2}
Ice	2	5×10^{-4}
Glass	0.84	2.0×10^{-4}
Brick	0.84	2.0×10^{-4}
Concrete	0.84	2.0×10^{-4}
Water	0.56	1.4×10^{-4}
Human tissue	0.2	0.5×10^{-4}
Wood	0.1	0.3×10^{-4}
Fiberglass	0.048	0.12×10^{-4}
Cork	0.042	0.10×10^{-4}
Wool	0.040	0.10×10^{-4}
Goose down	0.025	0.060×10^{-4}
Polyurethane	0.024	0.057×10^{-4}
Air	0.023	0.055×10^{-4}

Prevention of Convention Heat Transfer

Materials containing dead-air spaces are usually excellent thermal insulators.

For example, Styrofoam consists of many small, trapped pockets of air that suppress convection currents, preventing heat transfer by bulk fluid motion. In addition, air itself has a very low thermal conductivity, which further reduces heat transfer by conduction.

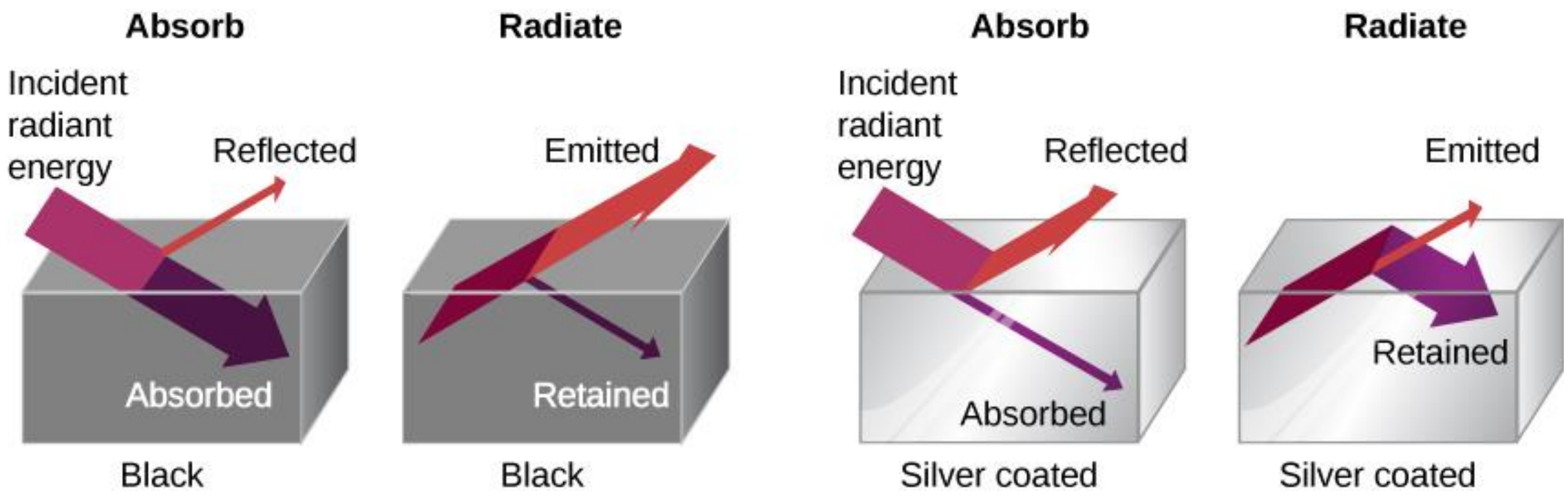


Radiation

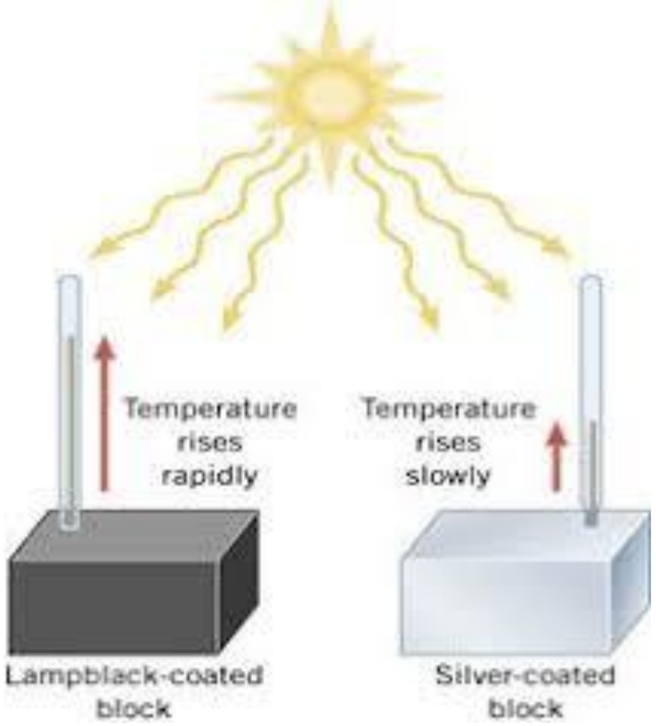
Radiation is the transfer of energy by means of electromagnetic waves and does not require a material medium.

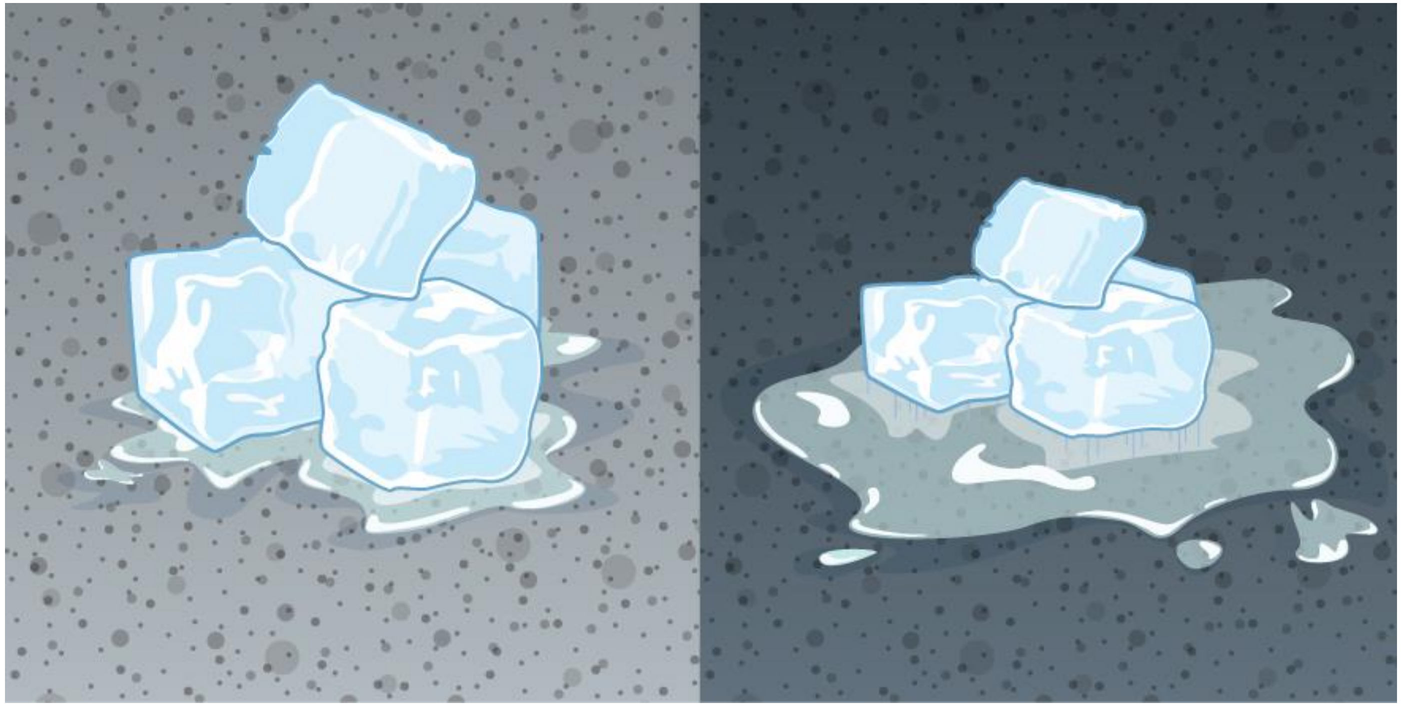
A material that is a good absorber of radiation is also a good emitter at the same wavelength and temperature (Kirchhoff's law of thermal radiation).

A material that absorbs all incident radiation is called a perfect blackbody. A blackbody is also the ideal emitter, radiating the maximum possible energy at a given temperature.



Radiation



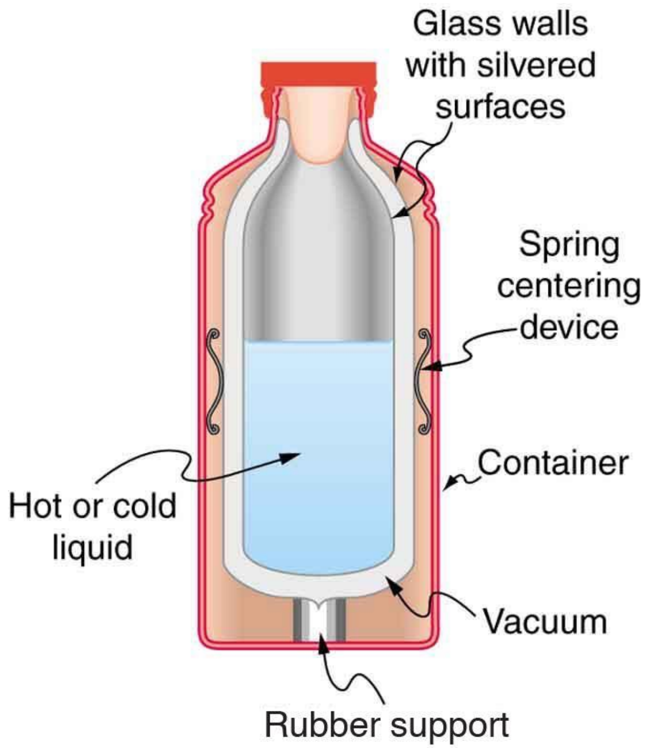


A darker object becomes hotter than a lighter-colored object when both are exposed to sunlight for the same amount of time and have the same thermal conductivity. This occurs because darker surfaces absorb more incident radiation, whereas lighter surfaces reflect a larger fraction of the incoming radiation.

Prevention of Heat Transfer

Heat transfer in a thermos bottle is minimized by reducing conduction, convection, and radiation.

- **Conduction** is minimized by the vacuum between the walls and narrow support structures.
- **Convection** is eliminated because the vacuum prevents fluid motion.
- **Radiation** is reduced by highly reflective (silvered) surfaces that reflect thermal radiation back toward the contents.



Example of Transfer of Heat: The Greenhouse Effect

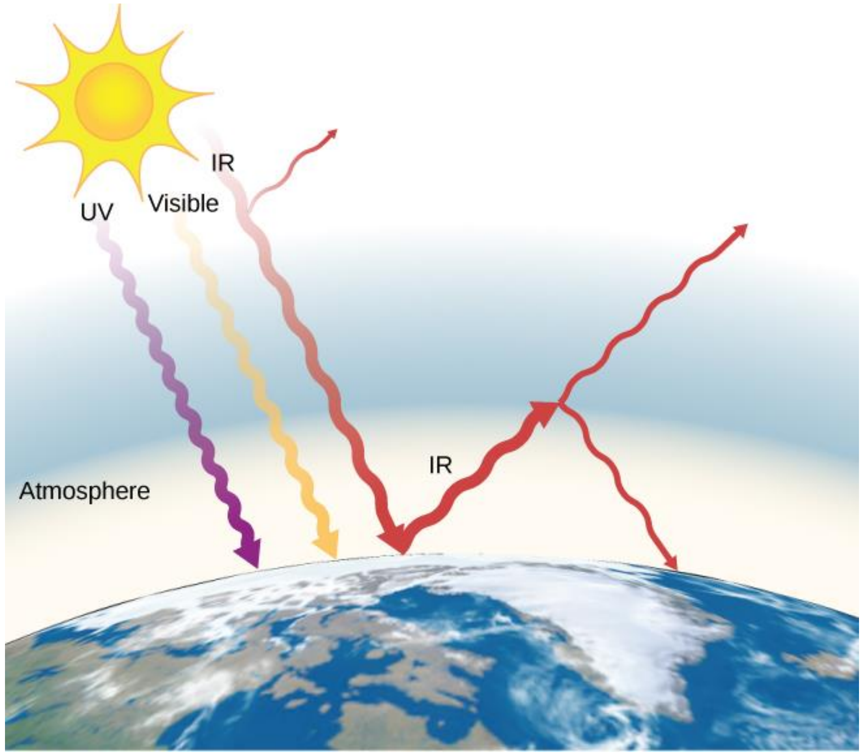
An important example of heat transfer by radiation is the greenhouse effect.

Visible (Vis) and near-infrared (IR) radiation from the Sun pass through Earth's atmosphere with relatively little absorption.

Earth's surface absorbs this radiation and, because Earth's temperature is much lower than the Sun's, re-emits energy as lower-energy infrared radiation (longer wavelengths).

The atmosphere absorbs a significant portion of this outgoing infrared radiation and re-radiates it in all directions, including back toward Earth's surface.

This process reduces heat loss to space, thereby keeping Earth warmer than it would be otherwise.



Stefan-Boltzmann Law of Radiation

The total radiation at all wavelength from unit area at unit time of a hot surface is:

$$p_{tot} = e\,\sigma\,T^4$$

where e is emissivity which is a dimensionless number between zero and one and $\sigma = 5.67\times 10^{-8}\,J/(s.m^2.K^4)$ is Stefan-Boltzmann constant.

Example-03

The super-giant star Betelgeuse has a surface temperature of about 2900 K and emits a power of approximately $4 \times 10^{30}\ W$. Assuming that Betelgeuse is a perfect emitter and spherical, find its radius.

Where $\sigma = 5.67 \times 10^{-8}\ J/(s.m^2.K^4)$ & $e = 1$

Heat and Phase Changes

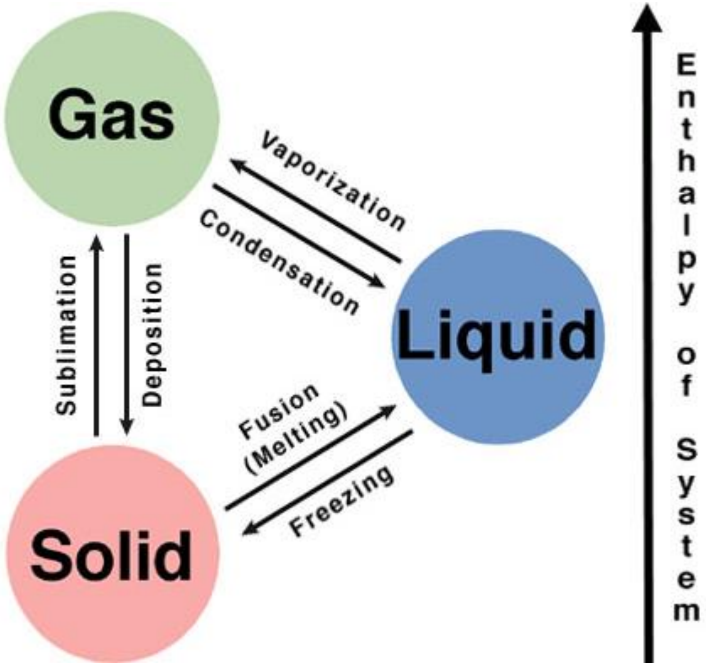
There are four common states of matter: solid, liquid, gas, and plasma. In this course, we focus on solids, liquids, and gases.

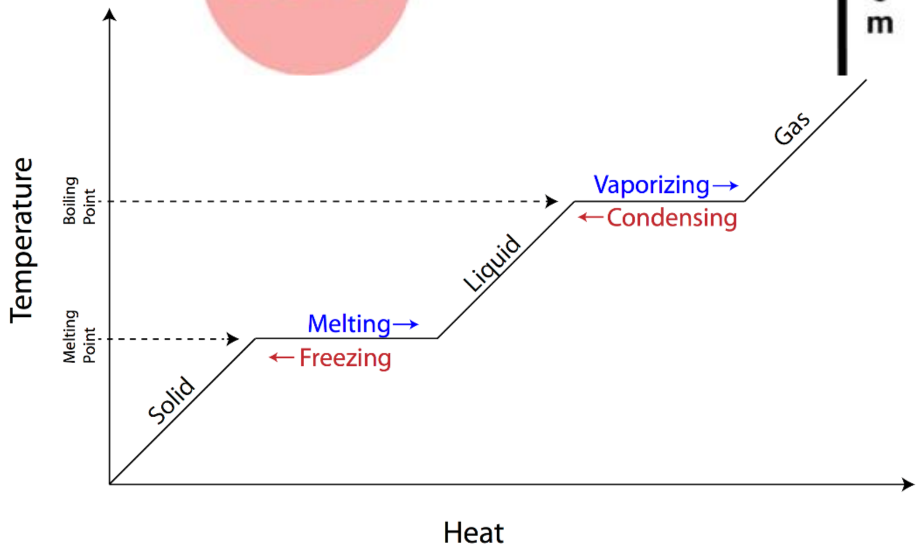
During a phase change (such as melting, freezing, boiling, or condensation), the temperature of the system remains constant, provided the system is in thermal equilibrium.

Latent Heat: The heat energy absorbed or released during a phase change is given by,

$$Q = m L$$

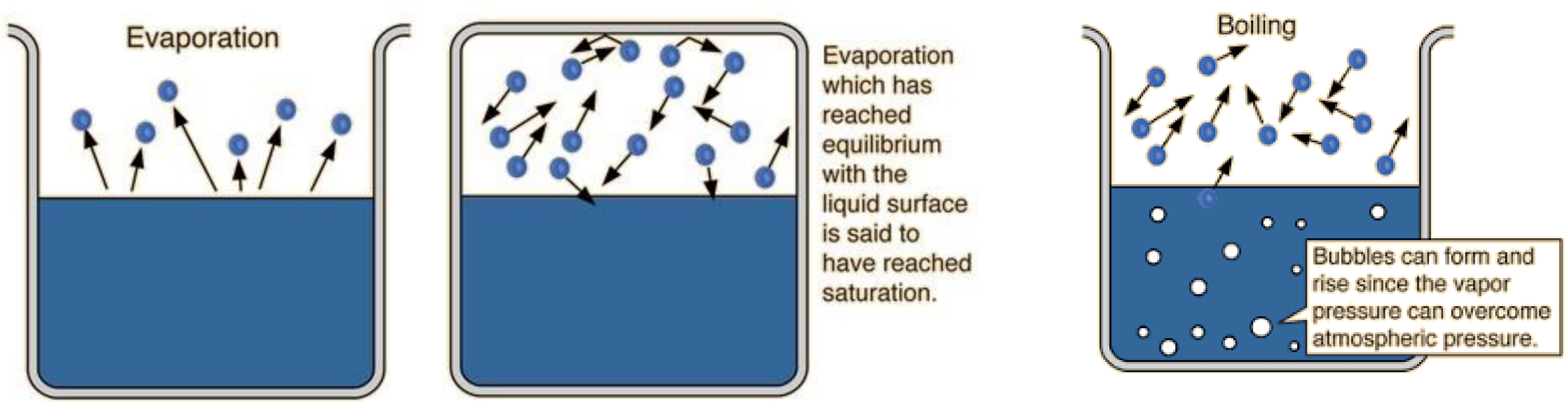
where L is latent heat (J/kg) and m is mass.



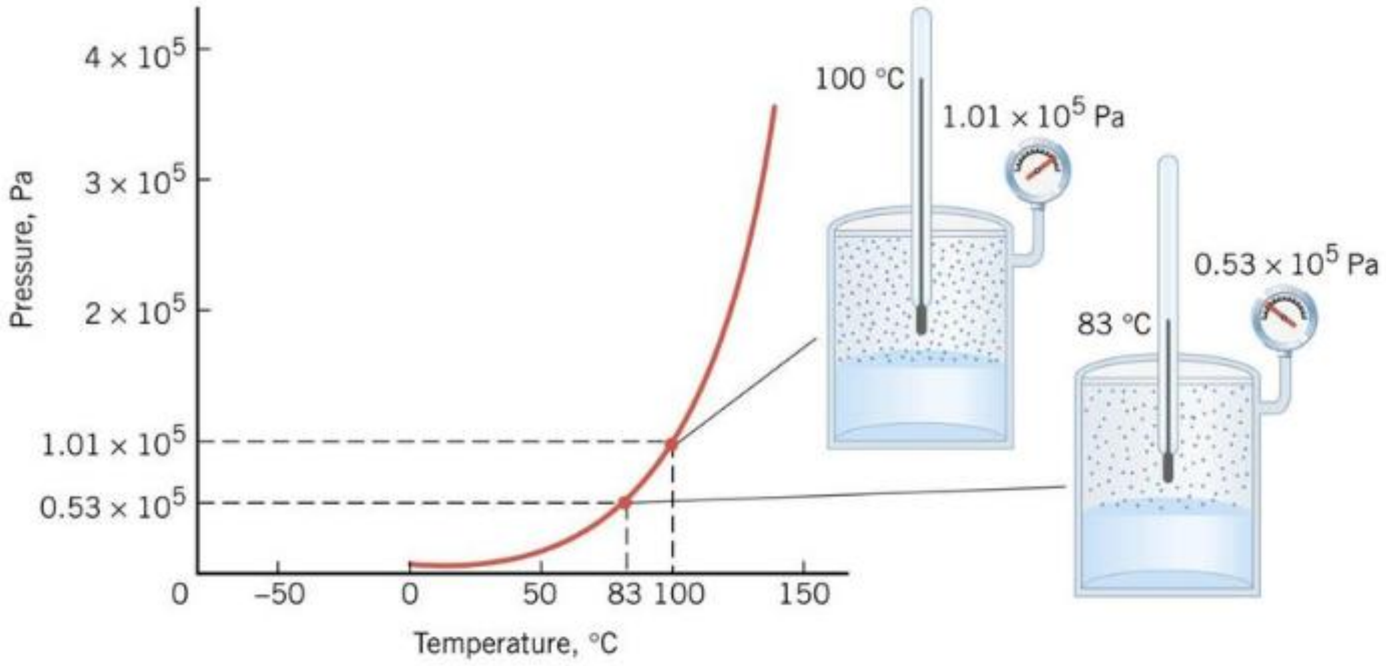


Equilibrium of Vapor Pressure

The equilibrium vapor pressure of a liquid is the pressure exerted by its vapor when the vapor and liquid coexist in dynamic equilibrium at a given temperature.



Equilibrium Between Phase of Matter



A point on the phase curve represents a condition where the liquid and vapor phases coexist in equilibrium.

The position of this point depends on the temperature and the corresponding equilibrium vapor pressure of the liquid.

Thank you very much for your attention