STATISTICAL MECHANICS
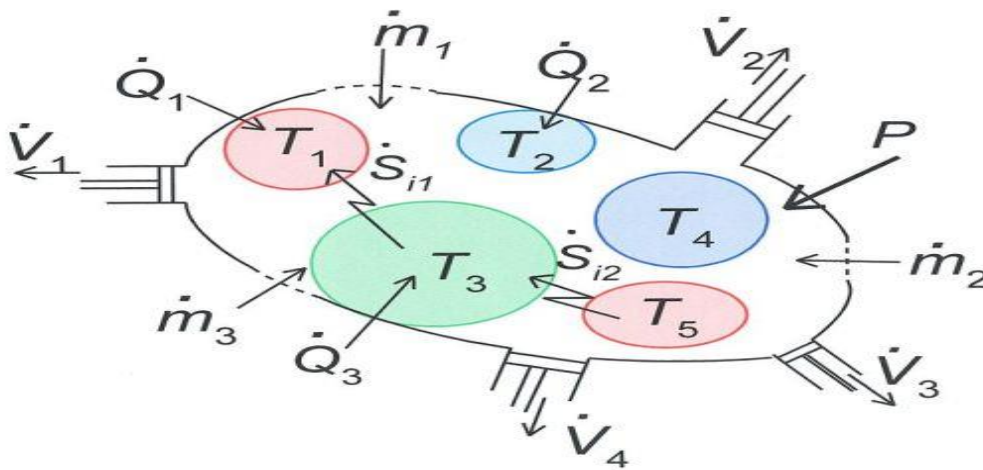
Third Year Physics

Lecture One

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A Thermodynamic System

Thermodynamics

Basic Concept and Definition of Thermodynamics

STATISTICAL MECHANICS

Course Description

Statistical mechanics or statistical thermodynamics is a branch of Physics that applies probability theory, which contains mathematical tools for dealing which large populations, to the study of the thermodynamic behavior of systems composed of a large number of particles . In physics, statistical mechanics is a mathematical framework that applies statistical methods and probability theory to large assemblies of microscopic entities. It does not assume or postulate any natural laws, but explains the macroscopic behavior of nature from the behavior of such ensembles.

Thermodynamics

The study of effect of work, heat flow and energy on a system movement of thermal energy.

Or thermodynamics can defined as the study of energy, energy transformations and its relation to matter.

Thermodynamics in physics is a branch that deals with heat, work and temperature, and their relation to energy, radiation and physical properties of matter.

Thermodynamic contains from two terms (thermos it means heat and dynamic it means power).

Thermodynamics is the science of Macroscopic systems, i.e. of systems composed of N particles (atoms, molecules, ions,….ect.), N beings very large (N>>1).

* Under normal conditions, the typical distance between particles is approximately:

* $3A^0$= 0.3nm= 3×10^{-10}m for solids or liquids

3 nm in gases. In $1cm^3$ of matter.

* Recall that amole is defined as the amount substances in 12g of Carbon12 and the Avogadro constant N_A gives the number of particles per mole.

N_A= 6.022×10^{23} mol^{-1}

Thermodynamic Systems

*A system is defined as quantity of matter or a region in space chosen for study.

Surrounding: The mass or region outside the system .

Boundary: The real imaginary surface that separates the system from its surrounding. The Boundaries of a system can be fixed or movable. Mathematically, the boundary has Zero thickness, no mass, and no volume.

Open System: refers to the fact that both matter and energy can be exchanged between the system and its surroundings. i.e. control volume.

Closed System: refers to the fact that matter cannot flow either in or out of the system (a closed system is therefore characterized by a fixed mass. (Note the number of moles and the composition are not necessarily constant during a process in a closed system. i.e. control mass.

System = Part of the Universe one is trying to understand and model

Surroundings (of a system): Part of the Universe that is "interacting" (i.e. exchanging energy or matter) with the System

Universe = System + Surroundings
System models

Thermal energy versus temperature

Thermal energy is Kinetic energy in transit from one object to another due to temperature deference. (Joules)

Temperature is average Kinetic energy of particles in an object-not the total amount of kinetic energy particles.

Temperature is the measure of hotness or coldness expressed in terms of any of several scales, including Fahrenheit and Celsius

When two systems A and B with deferent temperatures T_A and T_B are brought in to contact, the energy(in the form of heat) flows spontaneously from the body having the highest temperature to the body having the lowest one.

Temperature scales

*Scale	Freezing point of water	Boiling point of water
*Celsius	$0C^o$	$100 \ C^o$
*Fahrenheit	32F	212F
*Kelvin	273K	373K

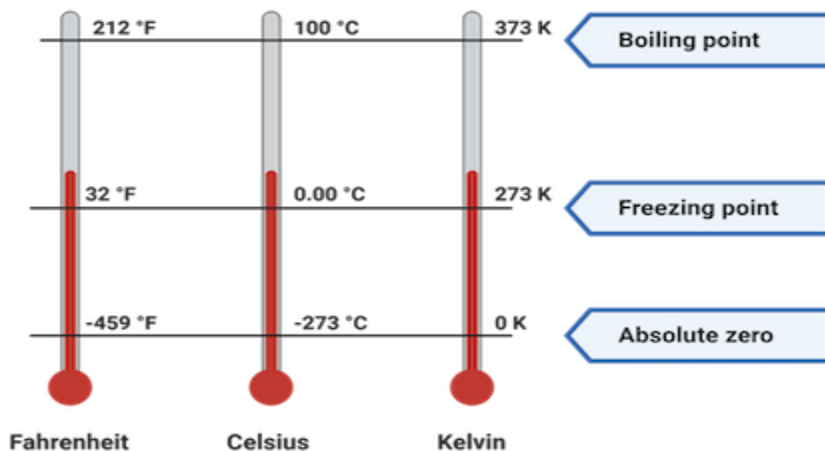Mater is made of molecules in motion(Kinetic motion).

An increase in temperature increase motion

A decrease in temperature decrease motion

Absolute Zero occurs when all kinetic energy is removed from object.

Temperature Scale Conversion

To convert	Use this equation:	Example
Celsius to Fahrenheit °C ⟶ °F	$°F = \left(\frac{9}{5} \times °C\right) + 32$	Convert 45°C to °F. $°F = \left(\frac{9}{5} \times 45°C\right) + 32 = 113°F$
Fahrenheit to Celsius °F ⟶ °C	$°C = \frac{5}{9} \times (°F - 32)$	Convert 68°F to °C. $°C = \frac{5}{9} \times (68°F - 32) = 20°C$
Celsius to Kelvin °C ⟶ K	$K = °C + 273$	Convert 45°C to K. $K = 45°C + 273 = 318\ K$
Kelvin to Celsius K ⟶ °C	$°C = K - 273$	Convert 32 K to °C. $°C = 32\ K - 273 = -241°C$

212 °F	100 °C	373 K	Boiling point
32 °F	0.00 °C	273 K	Freezing point
-459 °F	-273 °C	0 K	Absolute zero
Fahrenheit	Celsius	Kelvin	

H.W/ Is thermodynamic related to energy and health?

State and Equilibrium

Or Thermodynamic Equilibrium

*State and equilibrium, At a given state, all the properties of system have fixed values. Thus, if the value of even one property changes, the state will change to different one.

*In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system. A system in equilibrium experiences no changes when its isolated from its surroundings. thermal equilibrium: when the temperature is the same throughout the entire system.

*Thermal equilibrium is obtained when touching objects within a system reach the same temperature.

*This occurs through thermal energy transfer.

*The movement or transfer of thermal energy commonly occurs via:

* Convection:

The transfer of thermal energy by movement of fluid (liquid or gas), when fluid is heated, it expand, become less dence.

* Conduction

The transfer of thermal energy with in an object or between objects from molecule to molecule.

* Radiation

The process by which energy is transmitted through a medium, including empty space, as electromagnetic waves.

*When thermal equilibrium is reach, the system loses its ability to do work. Why is this? To answer, an advanced concept needs to be introduced: The gradient have many form: *Mathematical

Height   Energy
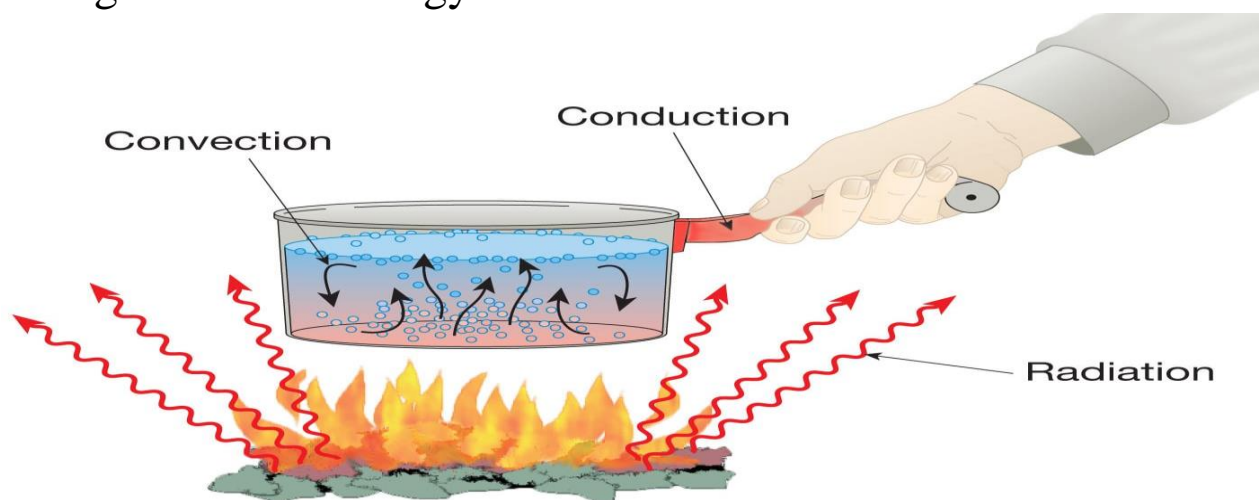
Thermodynamics deals with energy gradients. So what is it?

In general, a gradient is the imbalance created by difference in something.

A gradient can have many forms:

Mathematical   (1,2,3,4,5,………)

Height   (Cliff, water fall, Hil..)

Energy   (Battery, Fire, Falling…..)

Thermos deals with energy gradients.

In thermodynamics, a thermodynamic system is in thermodynamic equilibrium when it is in thermal equilibrium, mechanical equilibrium, , and chemical equilibrium. Equilibrium means a state of balance. In a state of thermodynamic equilibrium, there are no net flows of matter or of energy, no phase changes, and no unbalanced potentials (or driving forces), within the system. A system that is in thermodynamic equilibrium experiences no changes when it is isolated from its surroundings.

Thermal equilibrium: When the temperature is the same throughout the entire system.

Mechanical equilibrium: When there is no change in pressure at any point of the system.

Chemical equilibrium: When the chemical composition of a system does not change with time, i.e., no chemical reactions occur.

Phase equilibrium: In a two phase system, when the mass of each phase reaches an equilibrium level.

Properties of a system

Systems can be characterized by a number of properties (Temperature, Pressure, Volume, Composition, Density, Heat Capacity, Energy, Mass, Number of Moles, Expansion Coefficient, etc...)...

extensive property: Value that are dependent on size of the system such as mass, volume, No. of mole n, and total energy U. They are additive.

intensive property: Are those that are independent of the size (mass)of a system, such as temperature, pressure, and density. They are not additive.

Extensive Property	Intensive Property
Mass (m)	Temperature (T)
Number of Moles (n)	Pressure (P)
Volume	density
Total energy	

Specific properties: extensive property per unit mass are called Specific properties, e.g. specific volume (v=V/m)

Any change a system under goes from one equilibrium state to another is called a process, and the series of states through which a system passes during a process is called a **path**. To specify a process, initial and final states and path must be specified.

Transformations

__A reversible transformation :__ when the path of the process can be followed, in the same external environment, by reversing the direction of time (in other words, the transformations obtained by reversing the procedure is credible).

__Irreversible transformation:__ that is only feasible in the normal direction of time is described as irreversible.

The following terms are used for thermodynamic transformations:

*Isobaric ↔ **the pressure p of the system is constant**

*Isochoric ↔ **the volume V of the system is constant**

*Isotherm ↔ **the temperature T of the system is constant**

*Adiabatic ↔ **the system evolves with out heat exchange with its surroundings**

*Isolated system: Is a thermodynamic system that cannot exchange either energy or matter outside the boundaries of the system.

Internal energy U

*The energy of a system E_{tot} can be divided into, the macroscopic energy and the microscopic energy or internal energy U.

*The Macroscopic energy includes the overall motion of a system (solid in rotating, flow in a fluid, ect.), and so on.

*The Microscopic energy are those related to the molecular structure of the system and the degree of the molecular activity, and they are independent of outside reference frames.
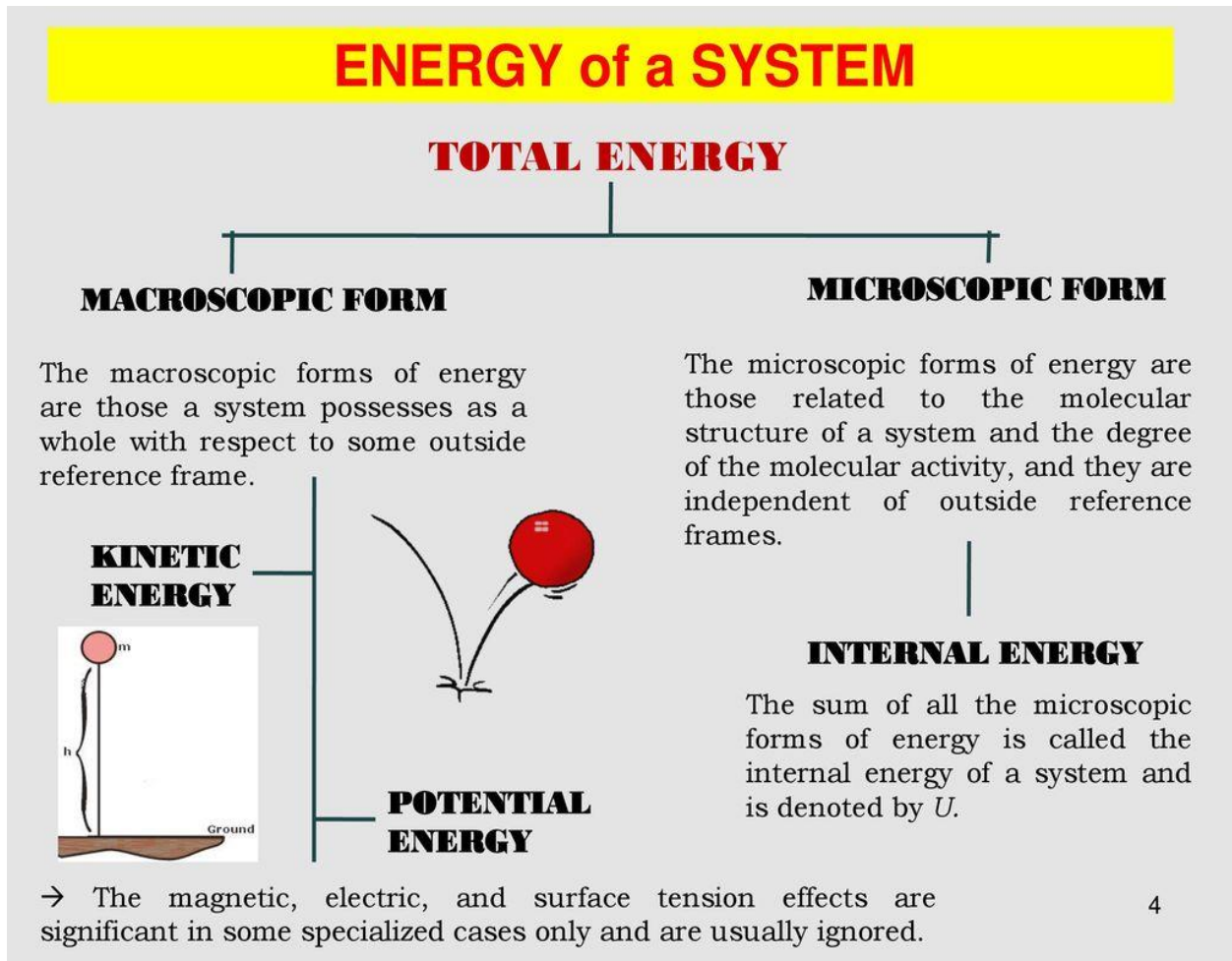
*The internal energy represents the rest of the energy of the system: molecular motion, energy of interaction between particles, ect.

*In thermodynamics, one almost considers situations where the macroscopic energy is constant: the system is immobile(macroscopically), does not change altitude, ect.

*The energy variations of the system are then equal to the variations of the internal energy:

*$\Delta E_{tot} = \Delta U$ (in most cases).

The internal energy is defined as the sum of several terms:

ENERGY of a SYSTEM

TOTAL ENERGY

MACROSCOPIC FORM

The macroscopic forms of energy are those a system possesses as a whole with respect to some outside reference frame.

KINETIC ENERGY

Ground

POTENTIAL ENERGY

MICROSCOPIC FORM

The microscopic forms of energy are those related to the molecular structure of a system and the degree of the molecular activity, and they are independent of outside reference frames.

INTERNAL ENERGY

The sum of all the microscopic forms of energy is called the internal energy of a system and is denoted by U.

→ The magnetic, electric, and surface tension effects are significant in some specialized cases only and are usually ignored.

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Different types of internal energies

*Translational kinetic energy E_{trans} is the kinetic energy accounting for the motion of the particles.
*For classical system at rest, it is written as

$$E_{trans} = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2$$

*The sum is over the N particles of the system
*m_i mass of the particle i
*v_i velocity (vector)of the center of mass of particle i (it is mor complicated for a quantum system…)

* Interaction energy between particles E_{int} which can be written as:

$$E_{int} = \sum_{i,j} U(i,j)$$

*The sum is over all pairs of particles; hence there are N(N-1)/2 terms $r_{i,j}$: distance between particles i et j
U: interaction potential.

*Rotational kinetic energy E_{rot} which represents the kinetic energy due to the rotation of the particles on them selves.

*Vibrational kinetic energy E_{vib} which represents the kinetic and elastic energy due to the internal vibrations of the particles.

*Other energy terms may contribute depending on the application, e.g. the energy in the excitations of the electronic cloud (at high temperature), the interaction energy with the magnetic field, ect.

*the internal energy is the sum of all these terms:

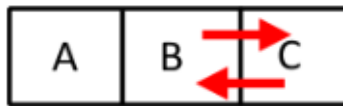$U = E_{trans} + E_{int} + E_{rot} + E_{vib}$

Thermodynamics laws

* <u>Zeroth law of thermodynamics</u>: If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.
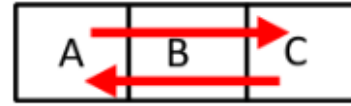
Temperature, *T.*   *(Zeroth law)*

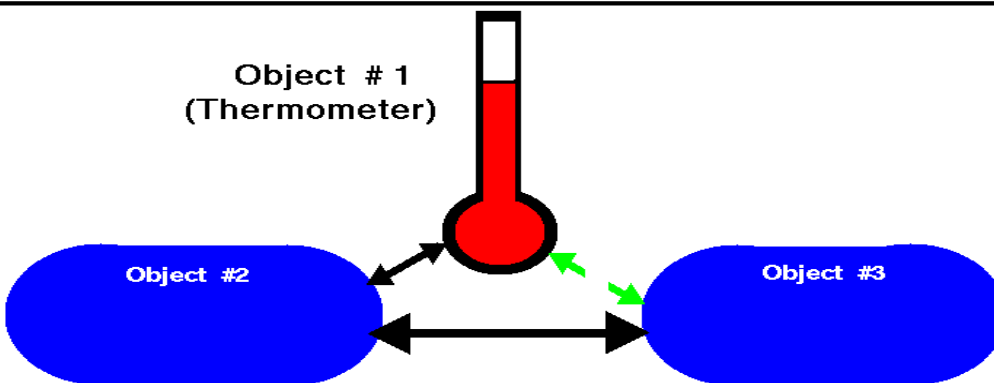| No heat flows from A to B as they are in thermal equilibrium. | No heat flows from B to C as they are in equilibrium | Then we will find that no heat flows in between A and C. |

When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

*__First law of thermodynamics:__ The increase in internal energy of a closed system is equal to difference of the heat supplied to the system and the work done by it:

$$\Delta U = Q - W$$
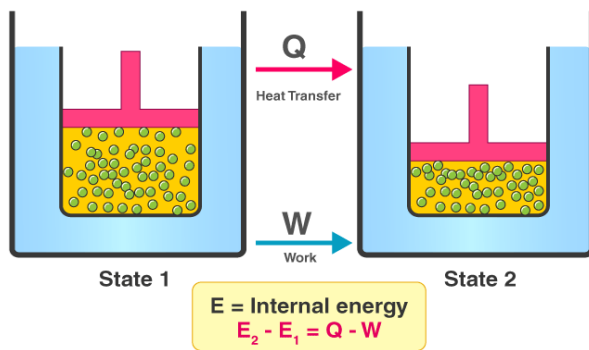
Internal energy, U.   (First law)

*law of energy conservation applied to a thermal system.

*Energy cannot be created or destroyed.

*Energy can change form and location.

*The total amount of energy remains constant.

*An energy balance or an accounting statements of the quantity of energy.

$$\textit{Net change of energy in system}$$
$$= \sum \textit{energy input} - \sum \textit{energy output}$$

*A system undergoing a transformation from a state A to a state B is considered. Assuming that the system is macroscopically at rest in states A and B, energy conservation gives:

$\Delta U = U_B - U_A =$ [energy received by the system between A and B]

*If the energy received ΔU is positive, the system receives energy. If the energy received ΔU is negative, the system gives away energy.

Energy gains are classified into two categories, **_The work_** received **_W_** and the heat **_received._**

During a transformation, we have

*$\Delta U = W + Q$

*U is internal energy

*W is work received

*Q is heat received

*(the three quantities W, Q, and ΔU can be positive, negative or zero).

$dU = dW + dQ$

H.W: A gas has constant pressure in a system. There is a loss of 45 J of heat in the surroundings around the system. 450 J of work is done onto the system. Find the system's internal energy?

Second law of thermodynamics

-The second law of thermodynamics states that as energy is transferred or transformed, more and more of it is wasted. The second law of thermodynamics states that **the total entropy can only increase over time for an isolated system**, meaning a system which neither energy nor matter can enter or leave. that heat does not spontaneously flow from **a colder body to a hotter body**." This became the basis for the Second Law.

*Specifies the direction that a certain energy transformation can follow:

*Heat energy flows down a gradient naturally; the reverse is not possible without additional input of energy.

*Thermal energy flows from hot to cold.

*Entropy tends to go from order to disorder.

*Entropy is measure of how evenly distributed heat within a system.

*A system tends to go from order to disorder.

*For each system, there is a quantity S defined at equilibrium, called ***Entropy*** , which is : A state function the value of S

depends only on the (macroscopic) state of the system, not on its history. In simple case, we write S.
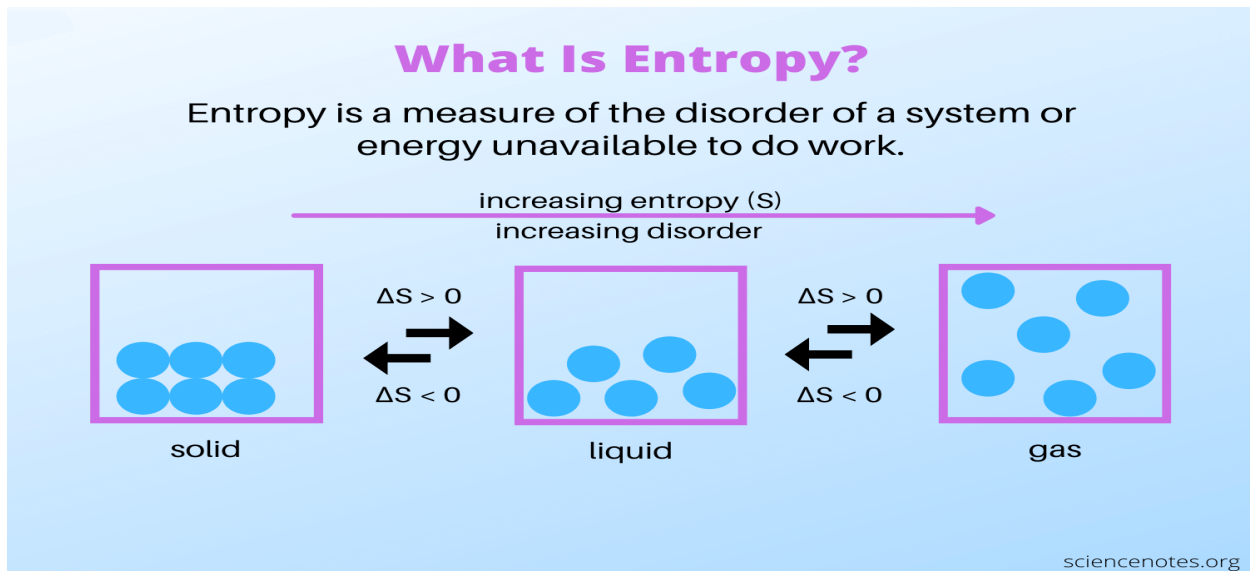
Or,

Entropy, **the measure of a system's thermal energy per unit temperature**.

$$dS = \frac{dQ}{T}$$

Entropy: a measure of amount of energy which is unavailable to do work.

Entropy: a measure of the disorder of a system.

H.W/ Does entropy affect the universe?

Second low Limitations

*it is impossible to extract an amount of heat dQH from a hot reservoir and use it to all to do work. Some amount of heat dQc must be exhausted to a cold reservoir.

*In any cyclic process the entropy will either increase or remain the same.

Q/ What is the relationship between entropy and microstates?

The Ideal Gases

*Is an ideal thermodynamic system where the interactions between particles are neglected. For a classical ideal gas (where quantum effects are neglected),the equation of state (ideal gas law) is:

$$PV=NRT$$

According to the ideal gas law, when a gas is compressed into a smaller volume, the number and velocity of molecular collisions increase, raising the gas's temperature and pressure.

An ideal gas is a theoretical gas composed of a set of randomly-moving point particles that interact only through elastic collisions.
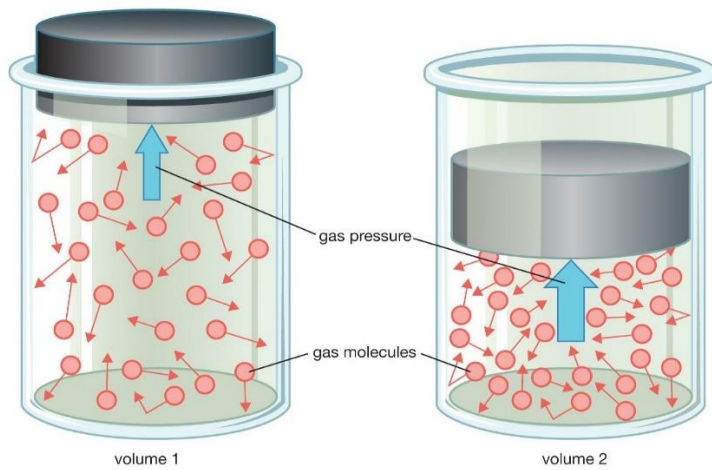
$$p = nRT / V$$

V = volume in units of m³

n = number of moles

T = temperature in units of °K

R = 8.31J/moles · °K ←———   Called the gas constant

p = pressure(absolute) in units of Pa(N/m²)

The van der waals gas

*when matter density increases and the ideal gas approximation is no longer satisfactory, one needs to take into account the interaction potential. The main two effects are the following:

*Because of the repulsive part of the potential, the volume that the gas can occupy is effectively smaller by an amount which is proportional to the numbers of the particles.

*Because of the attractive part of the potential, the particles heading towards the boundaries are slowed down by the rest of the gas; one shows that this has the effect of reducing the pressure by an amount proportional to the square of the matter density. To take these two effects into account; van der waals wrote in 1873 an equation of state,

$$(P+\frac{a}{V^2})(V - b) = nRT$$

*Where **a** and **b** are to two gas dependent constants. As opposed to the ideal gas equation is gas-dependent.

Pressure

***pressure** is force exerted by a fluid per unit area.

$$Pressure = \frac{Force}{Area} \ldots\ldots \frac{N}{m^2} = Pa$$

*the unit of **pressure** are force per unit area.
*the **SI** unit is the **(pa):**

$$1pa = 1\frac{N}{m^2} = 1\frac{kg}{ms^2} \qquad\qquad 1bar = 10^5 Pa$$

$$1atm = 1.01325 \times 10^5 Pa1$$