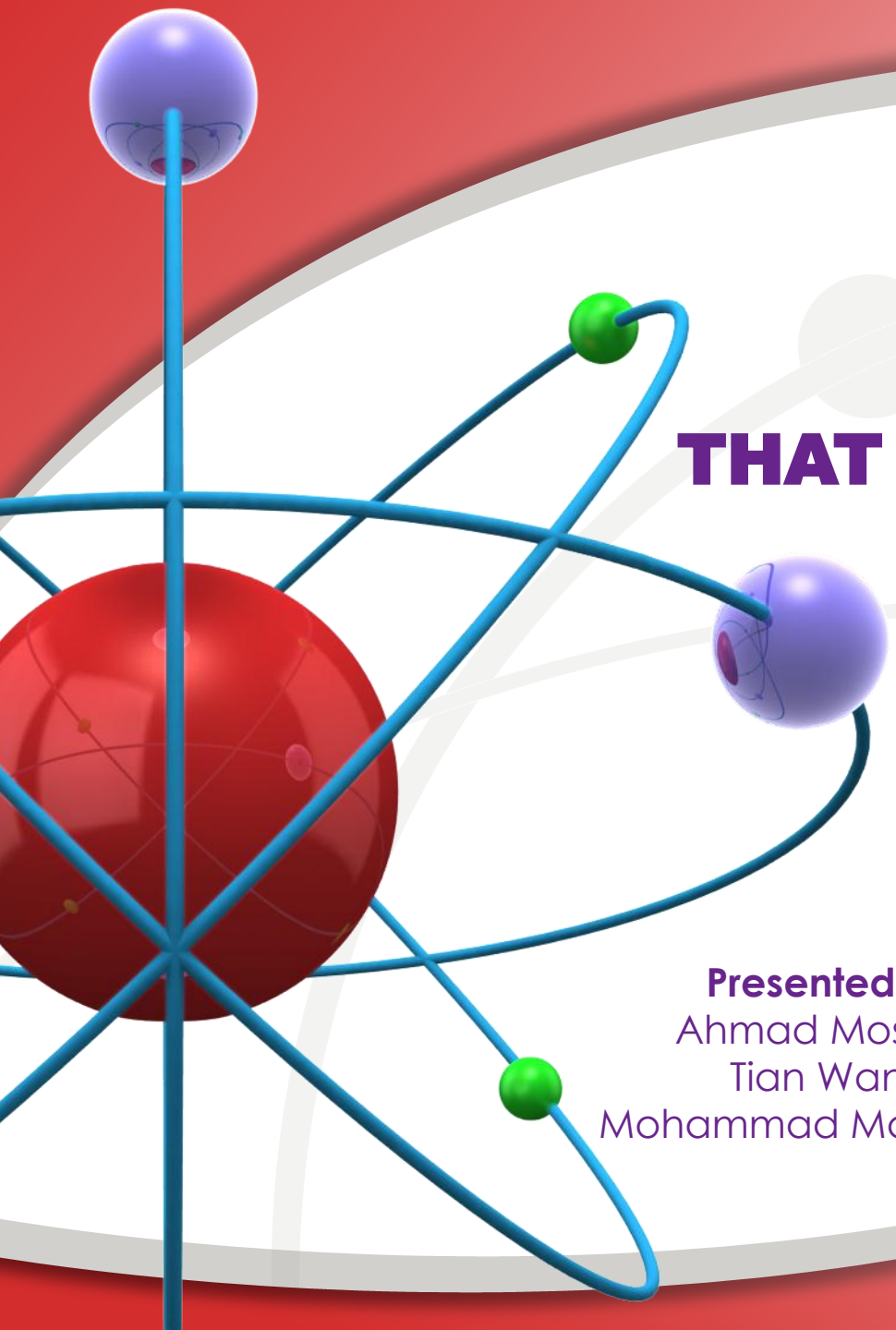
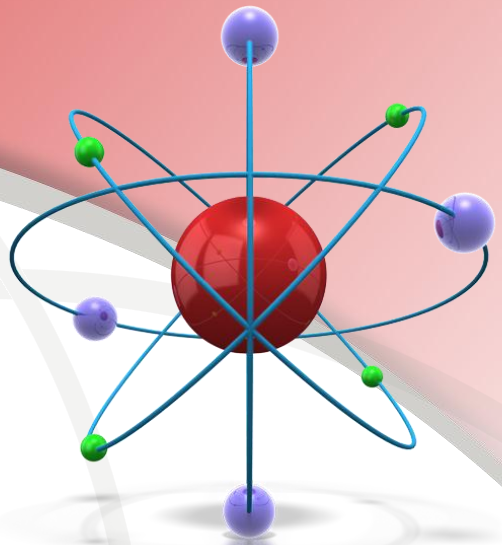


FOUR LAWS THAT DRIVE THE UNIVERSE

PETER ATKINS

Presented by
Ahmad Mostafa
Tian Wang
Mohammad Mahdipoor

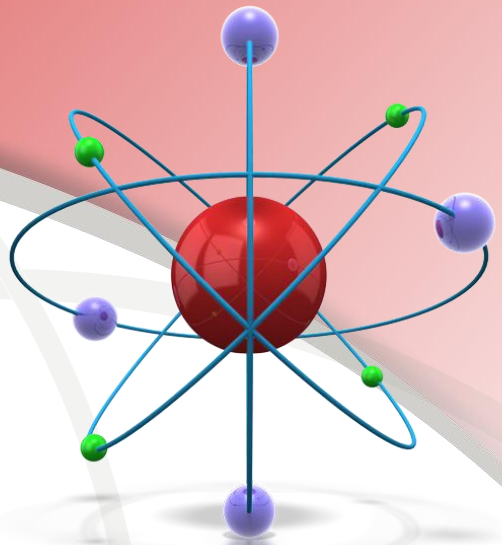
• Introduction



- **The laws of thermodynamics** are the laws which summarize the properties of energy and its transformation from one form to another.
- The title of the book does not contain the word of **thermodynamics** because of the boundlessly important and fascinating aspect of nature of the role of the energy in the world.
- From this book you will know what drives the universe.

Do not think that thermodynamics is only about steam engines!!!! It is about almost **EVERYTHING**

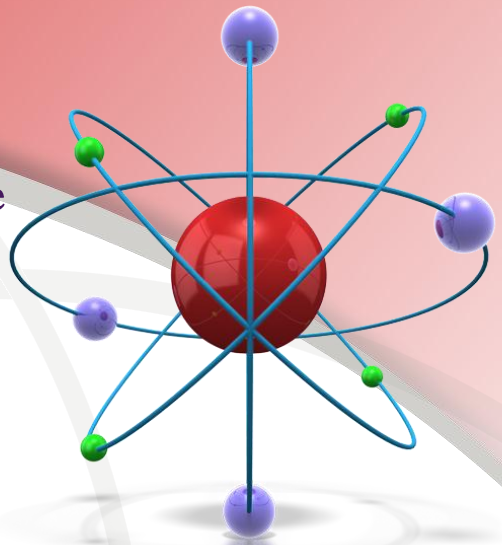
• Introduction



- The mighty handful consists of four laws, with the numbering starting at zero and ending at three.
- The first and second laws (the zeroth and the first), introduce two familiar properties, the temperature and the energy.
- The third law (the second), introduces the most enigmatic property, the entropy, it is a great law because it illustrates why ANYTHING from the cooling of hot matter happens at all.
- The fourth law (the third), a barrier prevents us to reach absolute zero. There is a world that lies below zero.

we consider first the observational aspects of each law, then dive below the surface of bulk matter and discover the interpretation of the laws in terms of concepts that inhabit the underworld of atoms.

• The Zeroth Law- The concept of temperature



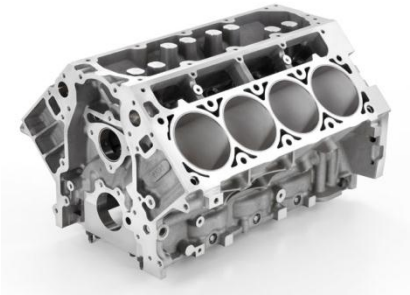
The zeroth term:

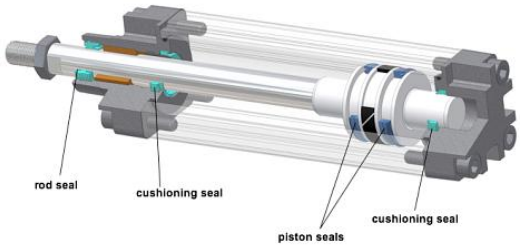
It was not dignified with a name and number until early in the twentieth century. By then, the first and second laws were established and no hope of going back and numbering them again.

Although the zeroth law establishes the meaning of the most familiar property, but in fact it is the most enigmatic: temperature.

Thermodynamics, takes terms with an everyday meaning and sharpens them, to give the exact meanings

The system: is the part of the universe that is at the centre of attention in thermodynamics.





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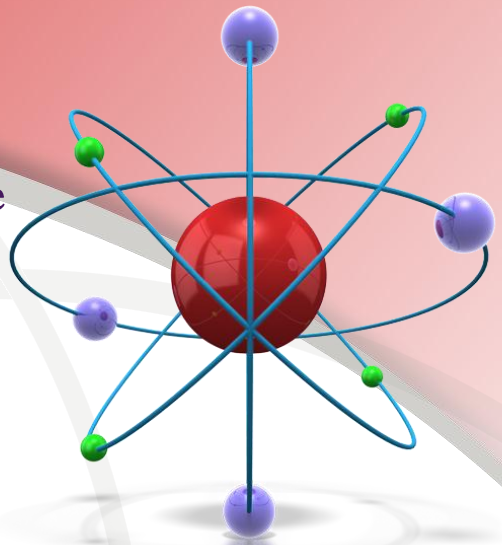
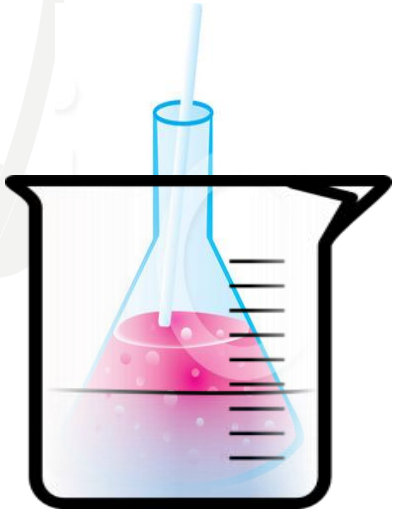


The Surroundings: the container which circumscribes each of the system entities. The surroundings are where we stand to make observations on the system and its properties.

Let us consider the surrounding is a water bath maintained at constant temperature, this will be more controllable than the true surroundings, the rest of the world.

The universe: is the system and its surroundings joined to each others. For example, it might be a beaker of water (the system) immersed in a water bath (the surrounding).

Universe



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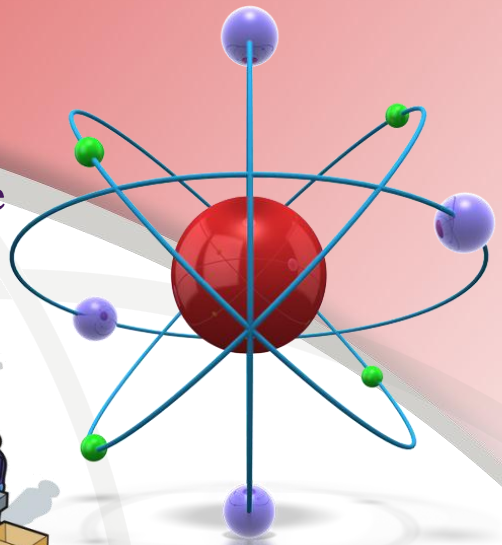
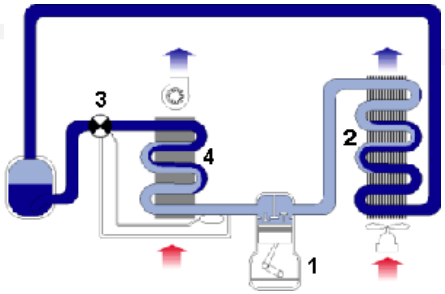


A system is defined by its boundary. If matter can be added to or removed from the system, then it is said to be **open**.

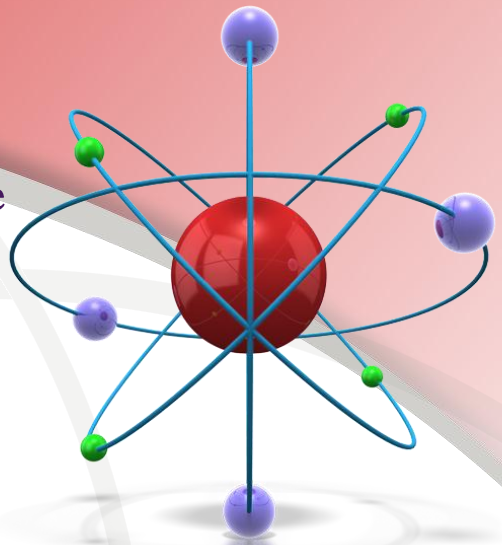
A system with a boundary that is impervious to matter is called **closed**. The system will always contain the same amount of matter.



A system with a boundary that impervious everything in the sense that the system remains **UNCHANGED** regardless of anything that happens in the surrounding is called **isolated.**

The properties of the system depend on the prevailing conditions. For instance, the pressure of a gas depends on the volume it occupies, the effect of changing the volume can be seen if the system has flexible walls.

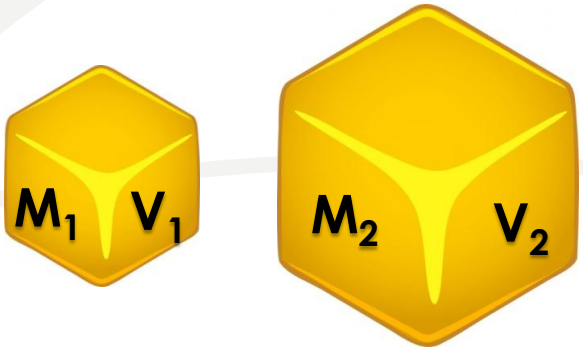
• The Zeroth Law- The concept of temperature



Properties are divided into two classes. An extensive property depends on the quantity of matter in the system, such as the mass and the volume of the system.

An extensive property ⇨

$(M_1, V_1) \neq (M_2, V_2)$

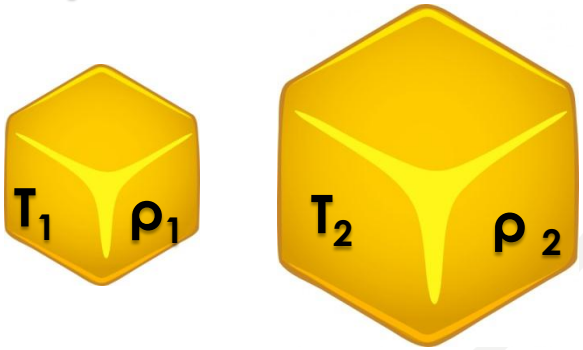


2 kg of iron occupies twice the volume of 1 kg of iron; whereas, the density of the iron is 7.8 g/cm^3 regardless or whether we have a 1 kg block or 2 kg block.

An intensive property is independent of the amount of matter present, such as the temperature and the density.

An intensive property ⇨

$(T_1, \rho_1) = (T_2, \rho_2)$



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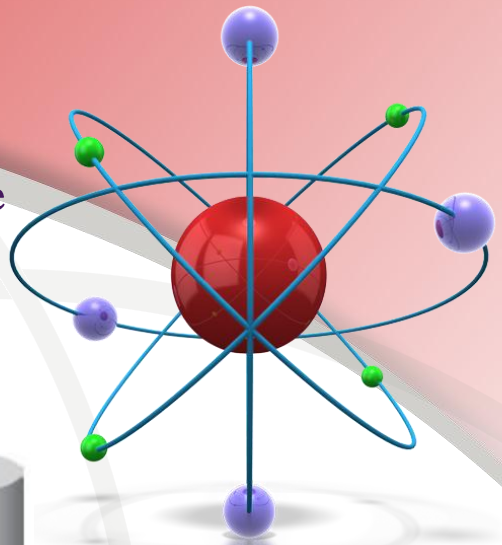
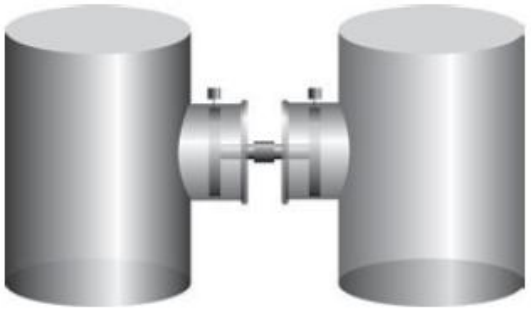


Two pistons are connected to each others so as if one moves in the other will moves out.

If the pin removed and one of the pistons drives the other, then we can say that the pressure is higher in the driving piston.



The system is mechanically in **equilibrium** if the pressure is the same in both pistons.

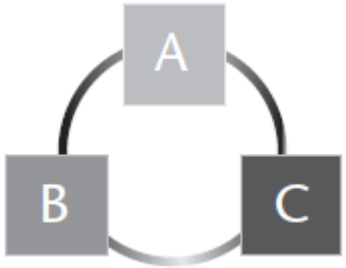
"Thermodynamicists get very excited, or at least get very interested, when nothing happens" [Page 6].

Thermal equilibrium

Both have the same temperature

Zeroth law of thermodynamics:

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C will be in thermal equilibrium with A.



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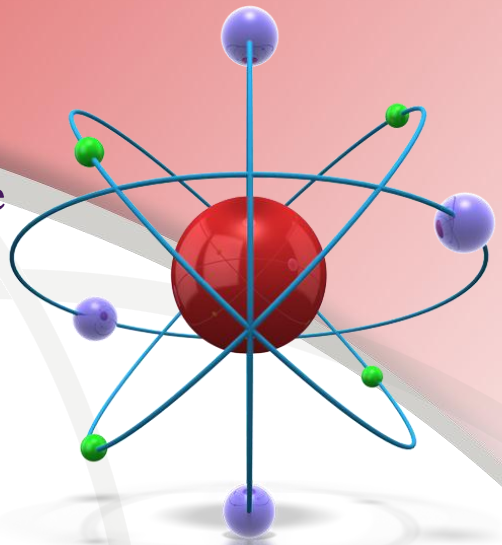
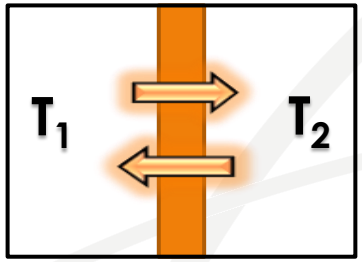
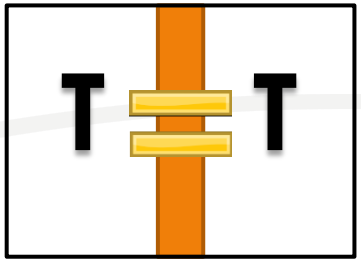


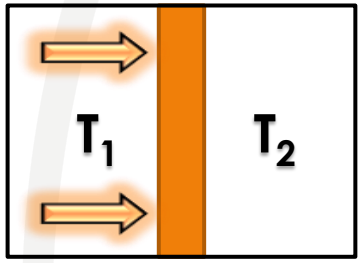
Two new words added to thermodynamic vocabulary:

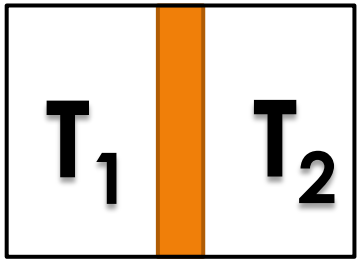
Diathermic (through) and (warm): any wall permits conducting of heat.





Adiabatic (impassable): if no change occurs and the temperatures are still the same on both sides of the wall.

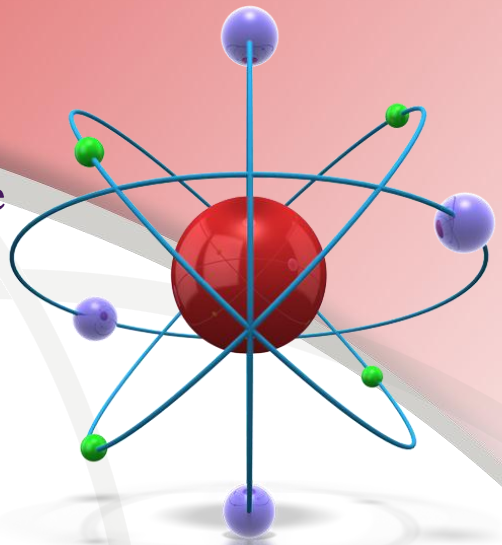




Examples:

An example on diathermic system is the copper wall. Whereas, the adiabatic system is represented as if the system is embedded in foamed polystyrene.

• The Zeroth Law- The concept of temperature

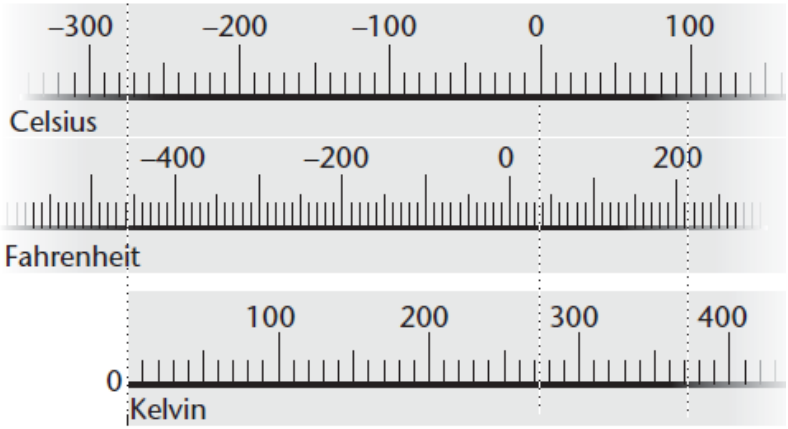


Simply, the zeroth law basis can be observed in the thermometer used to measure the temperature of the room.

The thermal expansion of the mercury takes place due to heat exchange between the system (thermometer) and the surrounding (the room).

There are different temperature scales were developed such as Celsius and Fahrenheit scales . The temporary advantage of Fahrenheit`s scale is the need for some negative values.

Thermodynamic temperatures are denoted by the scale of absolute temperature (Kelvin scale), which is the lowest possible temperature.



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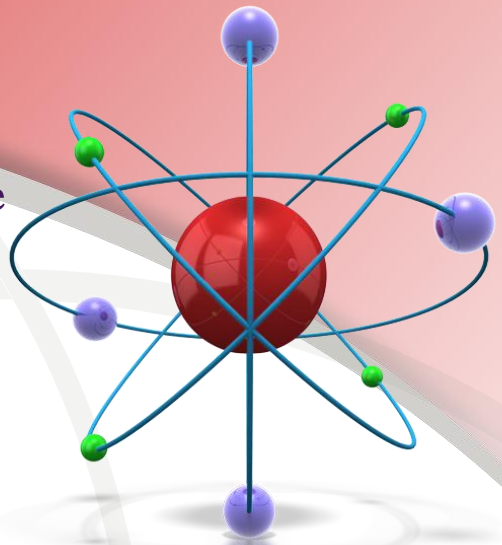
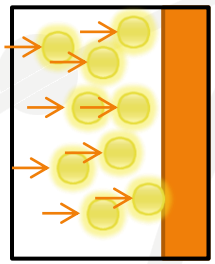
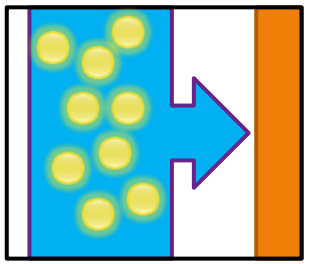


Classical thermodynamics is a part of thermodynamics that used before accepting the atoms.

Statistical thermodynamics. We do not need to think about the behavior of individual atoms, but we need to think about the average behavior of infinite number of atoms.

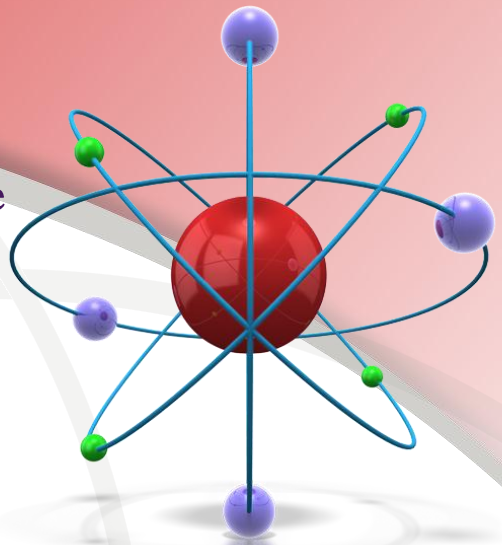




The pressure exerted due to the impact of the average of the storm of molecules on the wall.

The statistical thermodynamics expression was derived by **Boltzmann**. That was no long before he committed suicide, because many oppositions who were not convinced about the reality of atoms.

• The Zeroth Law- The concept of temperature



To understand the nature of Boltzmann expression, imagine a series of shelves at different heights on a wall, the shelves representing the allowed energy states and their heights the allowed energy. Then one think of pelting balls at the shelves and noting where they land. The most probable distribution of the population for the large number of throws is then taken into account, this parameter is β.

$$\frac{\text{Population of state of energy } E}{\text{Population of state of energy } 0} = e^{-\beta E}$$

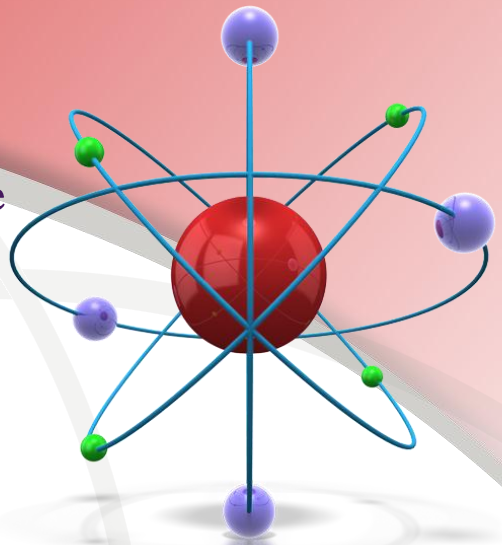
If the parameter β increases (throwing the balls weakly), then the relative population of a state of given energy decreases and the balls sink down to lower shelves. Because it is an exponential relationship.

$$\beta = 1/kT$$

K: is Boltzmann constant 1.38×10^{-23} J/k

The precise form of the distribution of the molecules over their allowed states, or the balls over the shelves is called Boltzmann distribution.

• The Zeroth Law- The concept of temperature



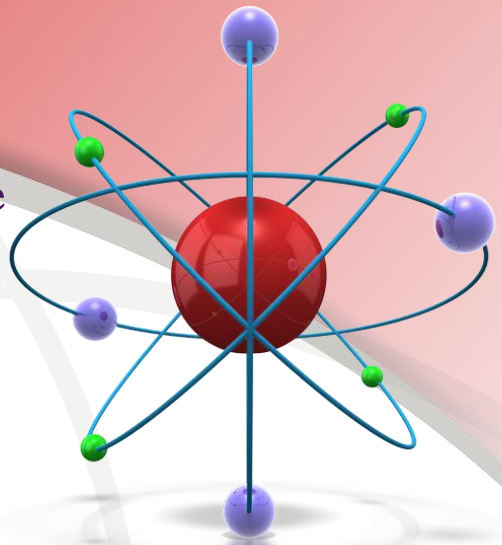
The molecular Significance of temperature based on Boltzmann distribution is:

1. Temperature is the parameter that tells us the most probable distribution of populations of molecules over the available states of a system at equilibrium.
2. β is a more natural parameter for expressing temperature than T itself; because of the difficulty to attain absolute zero (T=0).
3. The existence and value of the fundamental constant k.

β is a parameter that expresses the equilibrium distribution of the molecules of a system over their available energy states.

"Although Boltzmann's constant k is commonly listed as a fundamental constant, it is actually only a recovery from a historical mistake. If Ludwig Boltzmann had done his work before Fahrenheit and Celsius had done theirs, then it would have been seen that β was the natural measure of temperature". [Page 16]

• The Zeroth Law- The concept of temperature



In summary, Boltzmann distribution can be used to express through:

1. The distribution of the molecules over their possible energy states.
2. Their distribution of speeds.
3. Relation of distribution of speeds to the temperature.

The resulting expression is called the **Maxwell-Boltzmann distribution** of speeds.

The Average speed of molecules in the air on a warm day is greater by 4% than their average on a cold day.

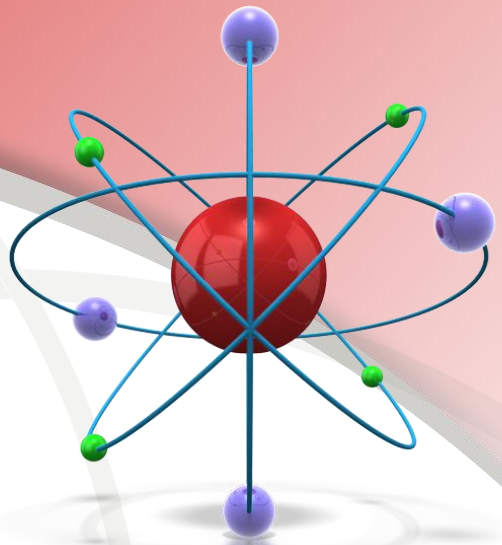
The temperature is raised means that more and more molecules are moving, rotating, or vibrating more vigorously.

The average speed of the molecules increases as the square root of the absolute temperature.

25°C, 298 K

0°C, 273 K

• The First Law- The conservation of energy



The first law:
The energy can be neither created nor destroyed.

Work: is motion against an opposing force. Work is the primary foundation of thermodynamics and in particular of the first law.

$$W=F.d$$

W: Work (N.m (J))
F: Force (N)
d: Displacement (m)

The capacity of a system to do work is termed as *energy*.

Any system has the capacity to do work.

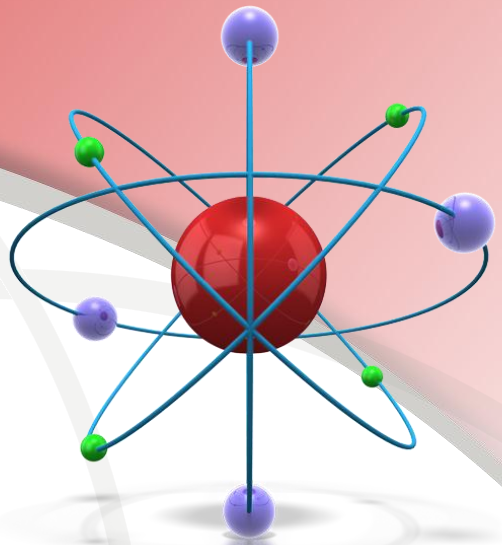
The spring can produce work; therefore, the fully stretched spring has a greater capacity to do work than the slightly stretched spring.

E_{s1} 

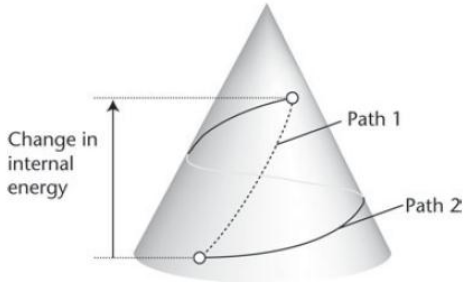
E_{s2} 

$(E_{s1}) > (E_{s2})$

• The First Law- The conservation of energy



The **state function** is a thermodynamic property of a system that depends only on the current state of the system and independent of how the state was prepared; such as the internal energy (U).



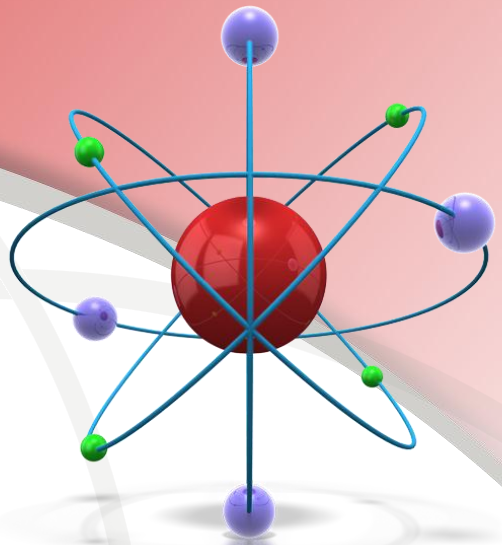
The work required which represents the initial and final values of the internal energy = U final – U initial

The observation that different ways of doing work on a system and thereby changing its state between fixed endpoints required the same amount of work of different paths resulted in the same altitude (Internal energy).

Heat: is the transfer of energy as a result of a temperature difference.

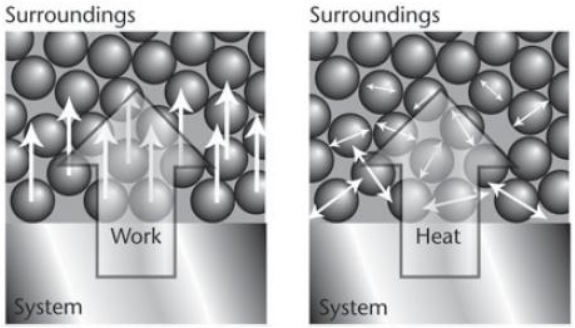
heat is a mode of transfer of energy. It is not a form of energy, or a fluid of some kind. Heat is the transfer of energy by virtue of a temperature difference.

• The First Law- The conservation of energy



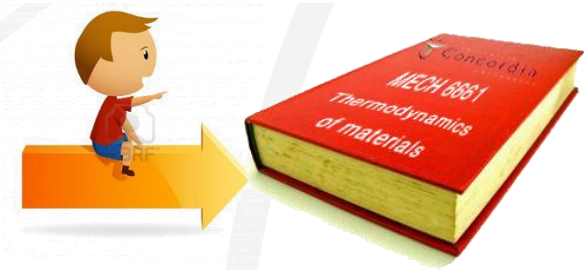
Work is the transfer of energy that makes use of the uniform motion of atoms in the surrounding.

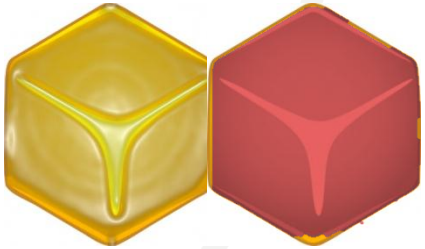
Heat is the transfer of energy that makes use of the random motion of atoms in the surrounding.



The molecular distinguish between the transfer of energy as work and heat

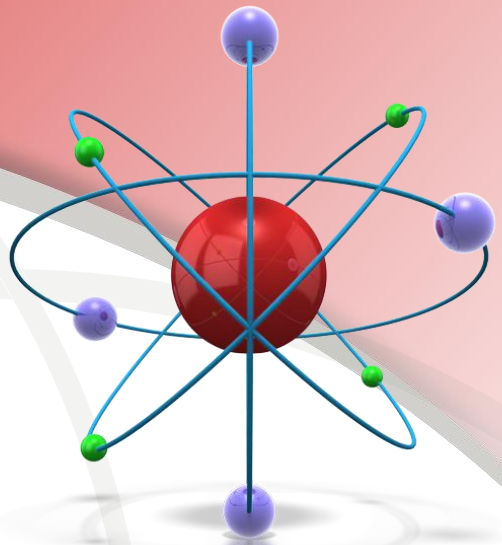
Doing work results in the uniform motion of atoms in the surroundings; heating stimulates their disorderly motion.





Once the energy is inside the system, either by making use of the uniform motion of atoms in the surroundings or of randomly oscillating atoms, there is no memory of how it was transferred.

• The First Law- The conservation of energy



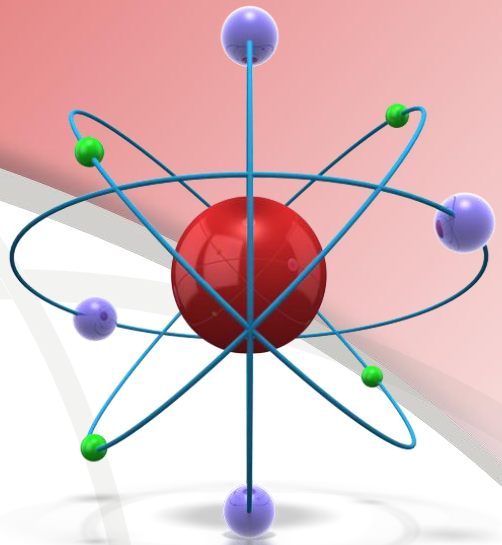
A reversible process is one that is reversed by infinitesimal modification of the condition in the surroundings.

If a piston is in equilibrium within the environment, then any infinitesimal change will affect the piston motion, either expands or retracts to compensate for the amount of the exerted change.

No greater work can be done, because if at any stage the external pressure is increased even infinitesimally, then the piston will move in rather than out

By ensuring that at every stage the expansion is reversible in the thermodynamic sense, the system does the maximum work.
When the fuel burns in a certain container. The generated energy will drive the piston. This expansion requires work.

• The First Law- The conservation of energy



Enthalpy: it is a Greek word means "heat inside".

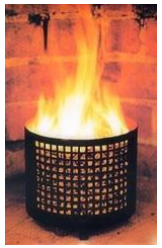
$$H = U + pV$$

H: is the enthalpy
U: is the internal energy
p: is the pressure
V: is the volume

The differences between changes in internal energy and enthalpy must always be borne in mind.

The enthalpy is the basis of a kind of accounting trick, which keeps track invisibly of the work that is done by the system, and reveals the amount of energy that is released only as heat, provided the system is free to expand in an atmosphere that exerts a constant pressure on the system.

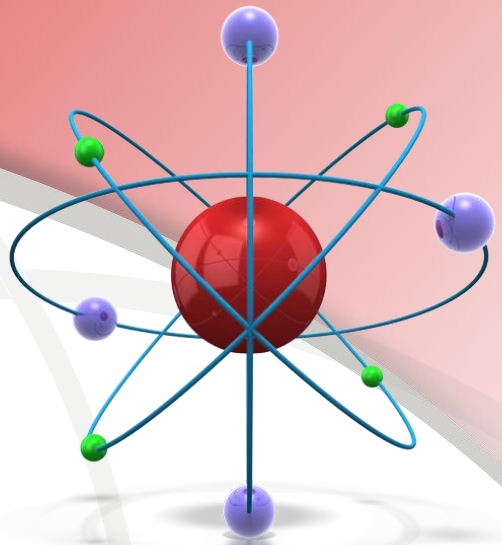
In fact, if the combustion occurs in an open container, the change in enthalpy (ΔH) is used through thermodynamics to denote the change in a quantity.



In combustion, the system has to do about 130 kJ of work to make room for the gases that are generated, but that energy is not available to us as heat.

The 130 kJ, which is enough to heat about half a litre of water from room temperature to its boiling point, if we prevent the gases from expanding so that all the energy released in the combustion is liberated as heat.

• The First Law- The conservation of energy



Latent heat (Enthalpy of vaporization), is the amount of heat required to separate the molecules from one another.

The enthalpy of vaporization of 1gm of water is close to 2kJ. Then the condensation of 1gm of steam will release 2kJ.

Enthalpy of fusion, is the amount of heat required to melt a solid.

Enthalpy of fusion << Enthalpy of vaporization

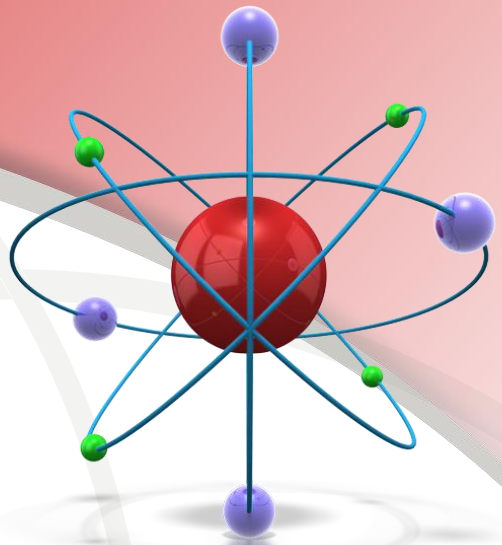
Heat Capacity (C), is the slope of a graph of the value of the internal energy plotted against temperature.

C= zero when T=0

Substances with a high heat capacity (water is an example) require a larger amount of heat to bring about a given rise in temperature than those with a small heat capacity (air is an example).

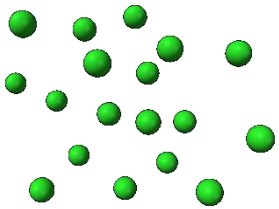
The difference between heat capacities of a system at constant volume and at constant pressure is of most practical significance for gases, which undergo large changes in volume as they are heated in vessels that are able to expand.

• The First Law- The conservation of energy



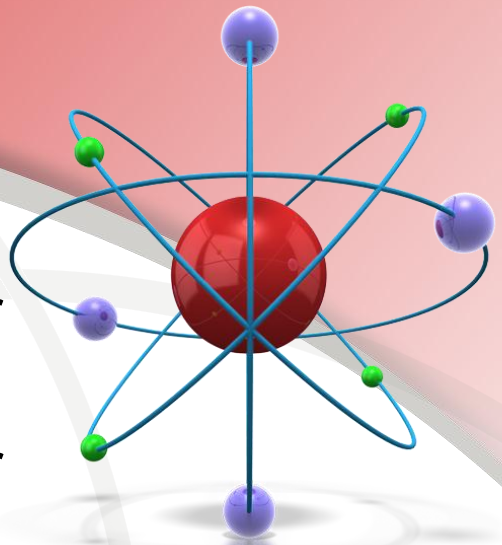
When all the molecules of a system are in a single state, there is no spread of populations and the 'fluctuation' in population is zero; correspondingly the heat capacity of the system is zero.

At higher temperatures, the populations are spread over a range of states and hence the heat capacity is non-zero, as is observed.



Substances with a high heat capacity (water is an example) require a larger amount of heat to bring about a given rise in temperature than those with a small heat capacity (air is an example).

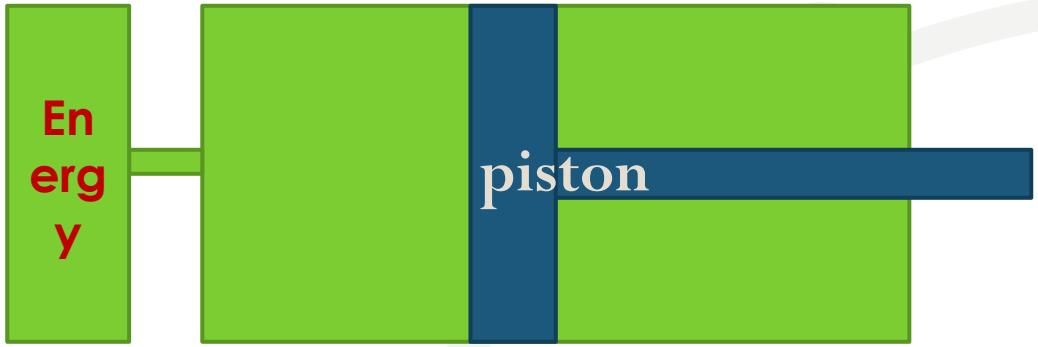
Water has a very high heat capacity, which means that to raise its temperature takes a lot of energy. Conversely, hot water stores a lot of energy, which is why it is such a good medium for central heating systems (as well as being cheap), and why the oceans are slow to heat and slow to cool, with important implications for our climate



- The second law is of central importance in the whole of science, and hence in our rational understanding of the universe, because it provides a foundation for understanding why *any* change occurs.

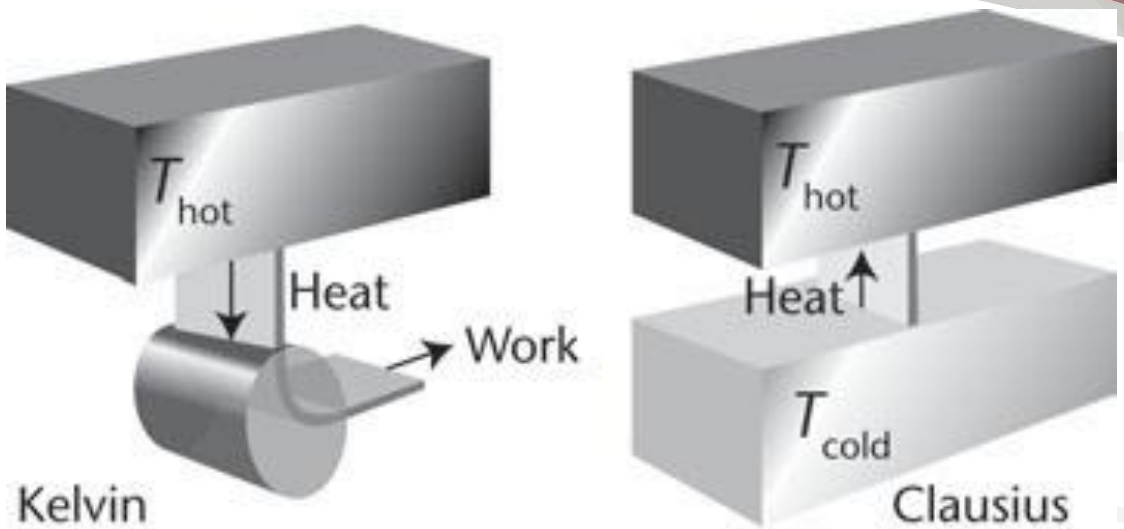
- Thus, not only is it a basis for understanding why engines run and chemical reactions occur, but it is also a foundation for understanding those most exquisite consequences of chemical reactions, the acts of literary, artistic, and musical creativity that enhance our culture

• Steam engine



A young French engineer Sadi Carnot (1796–1832) analysing the constraints on the efficiency of a steam engine found that heat was a kind of imponderable fluid that, as it flowed from hot to cold, was able to do work, just as water flowing down a gradient can turn a water mill that the efficiency of a perfect steam engine is independent of the working substance and depends only on the temperatures at which heat is supplied from the hot source and discarded into the cold sink.

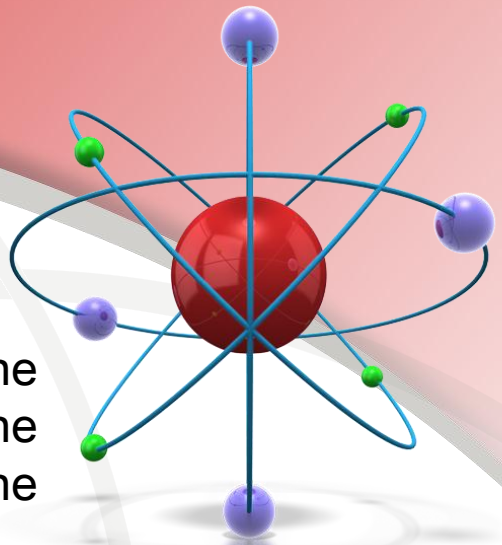
Efficiency(ε) = 1 − *T*sink/*T*source



- Kelvin realized that to take away the surroundings would stop the heat engine in its tracks. To be more precise, the Kelvin statement of the second law of thermodynamics is as follows: no cyclic process is possible in which heat is taken from a hot source and converted completely into work.

- Clausius went on to realize that although energy has a tendency to migrate as heat from hot to cold, the reverse migration is not spontaneous. He formulated into what is now known as the Clausius statement of the second law of thermodynamics: heat does not pass from a body at low temperature to one at high temperature without an accompanying change elsewhere.

• Entropy (S)



Clausius defined a change in entropy of a system as the result of dividing the energy transferred as heat by the (absolute, thermodynamic) temperature at which the transfer took place:

$$\text{Change in entropy} = \frac{\text{heat supplied reversibly}}{\text{temperature}}$$

Clausius's definition of the change in entropy is that of sneezing in a busy street or in a quiet library. A quiet library is the metaphor for a system at low temperature, with little disorderly thermal motion. Busy street is a metaphor for a system at high temperature, with a lot of thermal motion.

The entropy of the universe increases in the course of any spontaneous change.

absolute entropy of any system could be calculated from a very simple formula:

$$S = k \log W$$

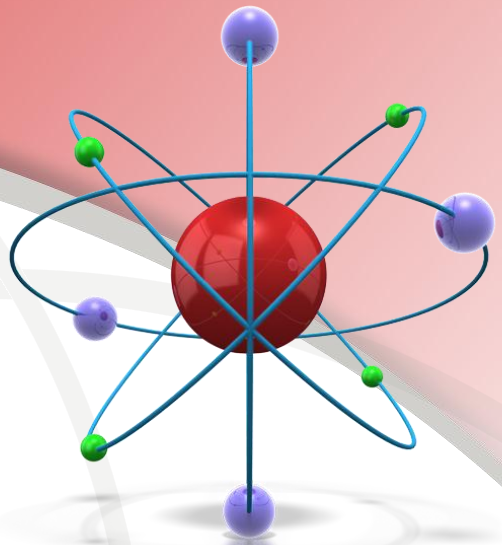
Boltzmann's formula can be used to calculate both the absolute entropies of substances, especially if they have simple structures, like a gas, and changes in entropy that accompany various changes, such as expansion and heating.

The concept of entropy is the foundation of the operation of heat engines, heat pumps, and refrigerators.

A *refrigerator* is a device for removing heat from an object and transferring that heat to the surroundings. This process does not occur spontaneously because it corresponds to a reduction in total entropy.

Thus, when a given quantity of heat is removed from a cool body, there is a large decrease in entropy. When that heat is released into warmer surroundings, there is an increase in entropy, but the increase is smaller than the original decrease because the temperature is higher. Therefore, overall there is a net decrease in entropy.

Refrigerators don’t work unless you turn them on.



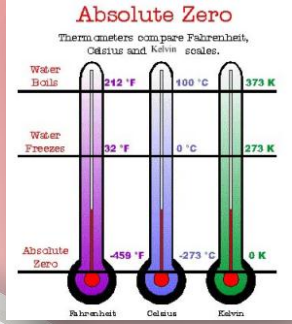
Our body is also like “steam engine”, an increase in entropy is the metabolism of the food and the dispersal of energy and matter that metabolism releases. Thus, as we eat, so we grow.

Moreover, the greatest steam engine is in the sky, the Sun. We all live off the spontaneous dissipation of its energy, and as we live so we spread disorder into our surroundings: we could not survive without our surroundings.

John Donne’s unknowingly expression of second law (two centuries before Carnot, Joule, Kelvin, and Clausius):

no man is an island

The third law: Unattainability of zero



- The temperature, the internal energy, and the entropy have been introduced as previous laws. Essentially the whole of thermodynamics can be expressed in terms of these three quantities.
- The third law of thermodynamics is not really in the same league as the first three, For one thing, it does not inspire the introduction of a new thermodynamic function. However, it does make possible their application.
- The coefficient of performance of a refrigerator depends on the temperature of the body we are seeking to cool and that of the surroundings ($c=1/(T_{surronding}/T_{cold} -1)$).

$T_{cold}=0 \longrightarrow c=0$, needing to do an ever increasing, and ultimately infinite, amount of work to remove energy from the body as heat as its temperature approaches absolute zero.

- Definition of Entropy:

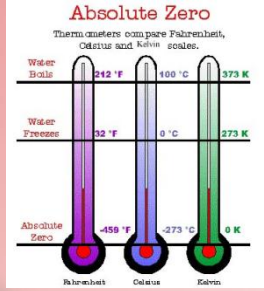
Third law

Clausius's definition

A system in its nondegenerate ground state has zero entropy regardless of the chemical composition of the subs

Statistical expressed by Boltzmann's formula

Entropy has a value other than zero at T = 0 and different substances have different entropies at that temperature



The third law: Unattainability of zero

- Classical thermodynamics, observations made outside the system.

  Classical thermodynamics ⟶ wholly phenomenologically

  Original version of properties in the very low temperatures, superconductivity & superfluidity

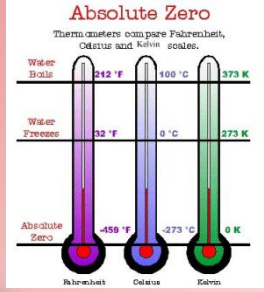
Challenges !!?

1. cooling matter to absolute zero
2. cool matter to temperatures below absolute zero

Experiments to cool matter to absolute zero proved to be very difficult.

It is impossible to attain absolute zero using a conventional thermal technique (a refrigerator based on the heat engine design). This empirical observation is the content of the phenomenological version of the third law of thermodynamics

No finite sequence of cyclic processes can succeed in cooling a body to absolute zero.



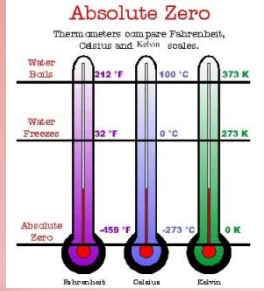
The third law: Unattainability of zero

- To consider how the third law impinges on the thermodynamic definition of entropy, we need to think about how low temperatures are achieved ..
- **System**, molecules, electron → having the property of spin

Spins states: ↑↓

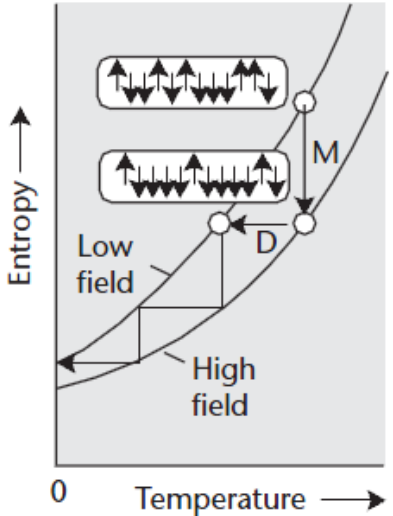
- At room temperature there will be slightly more lower energy ↓ spins than higher energy ↑ spins. If somehow (using magnetic field) we could contrive to convert some of the ↑ into ↓ spins, then the population difference will correspond to a lower temperature, and we shall have cooled the sample. If we could contrive to make all the spins ↓, then we shall have reached absolute zero.

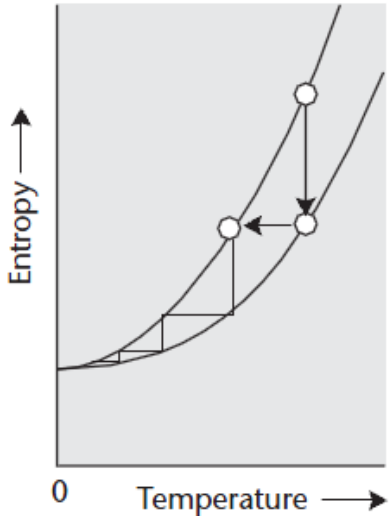
So, we can reach absolute zero !!?



The third law: Unattainability of zero

1. A matter at room temperature and in the absence of magnetic field, ↓↓↑↓↑↑↓↓↑↓ (random distribution of ↓ and ↑ spins)
2. Increasing the magnetic field with the sample in thermal contact with its surroundings. The sample becomes ↑↓↓↑↓↓↓↓↑↓↓ with a small preponderance of ↓ spins over ↑ spins.
3. Isolating the sample thermally from its surroundings and gradually reduce the applied field to zero, adiabatic demagnetization. (Same as step 2 ↑↓↓↑↓↓↓↓↑↓↓), constant entropy → lower temperature
4. Repeat the process



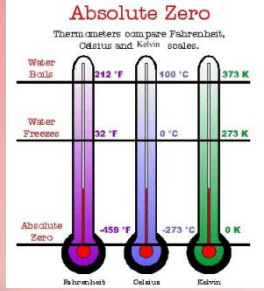


Other cyclic process to reach absolute zero:

✓compress a gas isothermally, expand adiabatically to its initial volume and repeat this process to reach T=0

✓using a reactant A to form a product B, finding an adiabatic path to recreate A, and continuing this cycle.

All Failed !!



The third law: Unattainability of zero

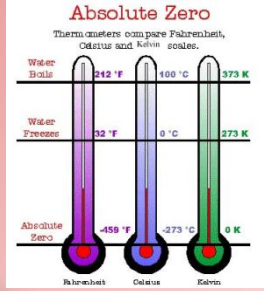
- The common feature of this collective failure is traced to the convergence of the substances entropies to a common value as T approaches zero. So, we can replace the phenomenological statement of the third law with a slightly more sophisticated version expressed in terms of the entropy:

The entropy of every pure, perfectly crystalline substance approaches the same value as the temperature approaches zero.

- Note that the experimental evidence and the third law do not tell us the absolute value of the entropy of a substance at $T = 0$. All the law implies is that all substances have the same entropy at $T = 0$ provided they have nondegenerate ground states. However, it is expedient and sensible to choose the common value for the entropy of all perfectly crystalline substances as zero, and thus we arrive at the conventional 'entropy' statement of the third law:

The entropy of all perfectly crystalline substances is zero at $T = 0$.

So, entropy can be expressed on an absolute scale.

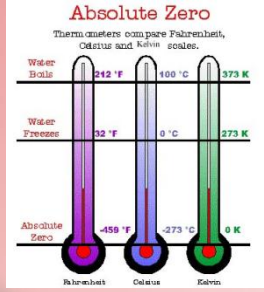


The third law: Unattainability of zero

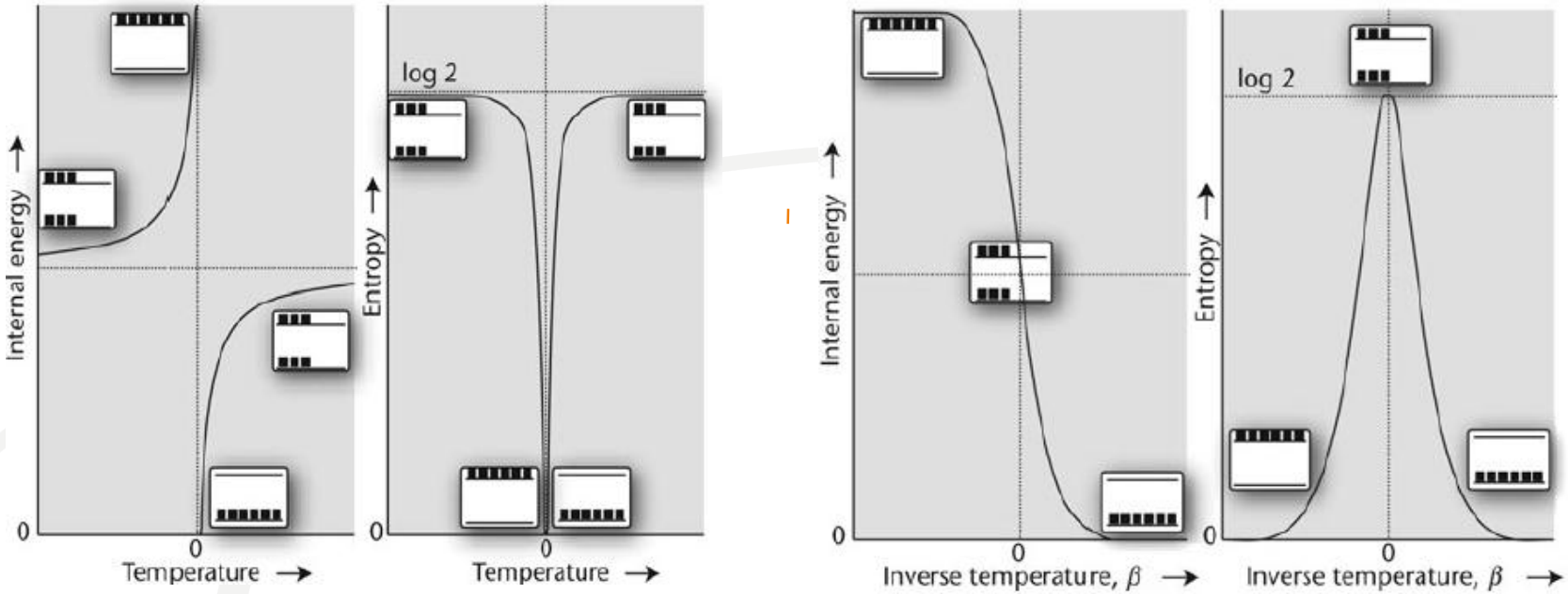
- **At first sight, the law would seem to be irrelevant to the everyday world, unlike the other three laws of thermodynamics. As a matter of fact, there are serious consequences of third law for those who inhabit laboratories.**

1. It eliminates one of science's most cherished idealizations, that of a perfect gas. However, a perfect gas is taken to be the starting point for many discussions and theoretical formulations in thermodynamics, the third law rules out its existence at T = 0.
2. One major application of thermodynamics to chemistry lies in the use of thermal data, specifically heat capacities measured over range of temperatures, to calculate the equilibrium composition of reactions and thus to decide whether a reaction is likely to be successful or not and to optimize the conditions for its using in industry. The third law provides the key to this application of , which could not be done if the entropies of substances were different at absolute zero.

The third law: Unattainability of zero



- **Intriguing consequential question, Its possible to contrive special technique to take a sample at negative temperature !?**



More entropy & ratio of ↑ : ↓

More entropy & ratio of ↓ : ↑

- ∞ ← → **+ ∞**

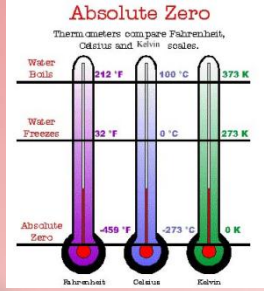
Ratio of ↑ : ↓ = 1

Maximum population of upper state (↑)

T

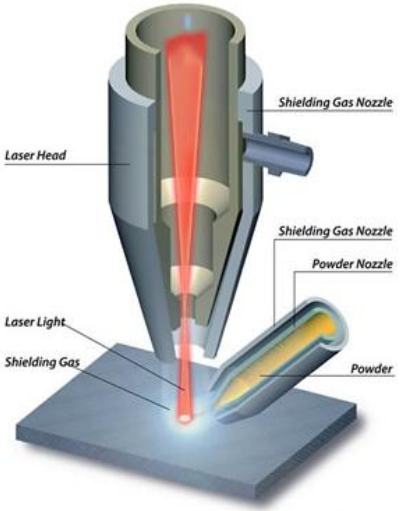
Maximum population of lower state (↓)

Ratio of ↓ : ↑= 1

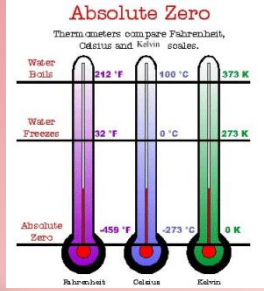


The third law: Unattainability of zero

- The big question is whether the inversion of a thermal equilibrium population can be contrived. It can, but not by thermodynamic procedures. There are a variety of experimental techniques available for polarizing, as it is called, a collection of electron or nuclear spins that use pulses of radiofrequency energy.
- In fact, there is an everyday device that makes use of negative temperatures: the laser. All the laser-equipped devices we use around the home, as in CD and DVD players, operate at temperatures below zero.

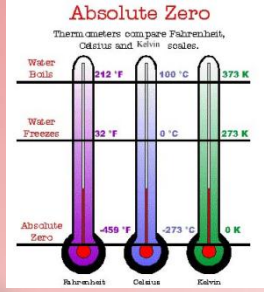


(Picture: non-coaxial powder feed)



The third law: Unattainability of zero

- The first law is independent of how populations are distributed. So, in a region of negative temperature, energy is conserved and the internal energy may be changed by doing work or making use of a temperature difference.
- The second law survives because the definition of entropy survives, but its implications are different.
  - One system with negative temperature and one system with positive temperature, there is an overall increase in entropy when heat is transferred from a region of negative temperature to one of positive temperature. The only difference between this discussion and the conventional one is that, the heat flows from the system with the lower (negative) temperature to the one with the higher (positive) temperature.
  - If both systems have a negative temperature, heat flows spontaneously from the system with the higher (less negative) temperature to the system with the lower (more negative) temperature.

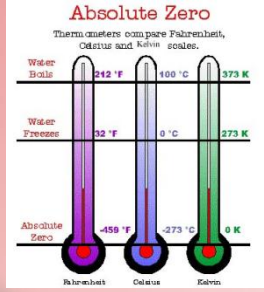


The third law: Unattainability of zero

- The efficiency of a heat engine, direct consequence of the second law, is defined by the Carnot expression. ($\varepsilon = 1 - T_{sink}/T_{source}$)
- However, if the temperature of the cold reservoir is negative, the efficiency of the engine may be greater than 1 !!
- **Example:**

Extracting heat (q) from a source at a temperature 300 K, the entropy decreases by q/(300 K). Also withdraw heat (q´) from the sink at −200 K, its entropy increases by q´ /(200 K). The total change is positive provided that q´ /(200 K) is at least equal to q/(300 K). Both contributions can be converted into work without changing the entropy, so the work we can get is equal to q + q´. The efficiency is (work done)/(heat absorbed from the hot source), or (q + q´)/q = 1 + (200 K/300 K) = 1.67.

- If both the source and the sink of a heat engine are at negative temperatures, the efficiency is less than 1, and the work done is the conversion of the energy withdrawn as heat from the 'warmer', less negative, sink.



The third law: Unattainability of zero

- **The third law requires a slight amendment on account of the discontinuity of the thermal properties of a system across T = 0.**
  - **On the 'normal' side of zero, we simply have to change the law to read 'it is impossible in a finite number of cycles to cool any system down to zero'.**
  - **On the other side of zero, the law takes the form that 'it is impossible in a finite number of cycles to heat any system up to zero.'**

The writer suspects anyone would wish to try !

Thank you