

Zeroth Law of Thermodynamics

Objectives :

1. Understand what is Zeroth law of thermodynamics ?
2. Why the Law is given unusual name and its significance
3. Identify major implications of the Zeroth Law of Thermodynamics
4. Zeroth Law- applications in Thermometry

1 Introduction :

Thermodynamics is the branch of science that deals with energetics of reacting systems. Any finite part of the universe represents a thermodynamic system. So, a living cell can be considered as a physicochemical system. The study of the biological processes involves a variety of thermodynamic aspects of living organisms in which energy extracted, channeled and utilized. Almost all processes in nature are accompanied by energy changes. This energy changes manifest into various forms eg. mechanical, electrical. Therefore, thermodynamics gives us a way to describe or characterize the energy changes in any biochemical reaction. Several technical terms which are often used in thermodynamics and some of these terms are:

2 Terminology

System - can be a chemical reaction or a natural process or a cell

Universe - consists of the system and surroundings

Surroundings- the space that encloses the system

Open system - that exchanges both energy and matter with its surroundings ex. biological systems in particular are all open systems.

Closed system – that exchanges only energy with its surroundings ex.

Heat energy – that can do work by causing a change in temperature or pressure.

Internal energy of a substance - the energy stored within a substance, E.

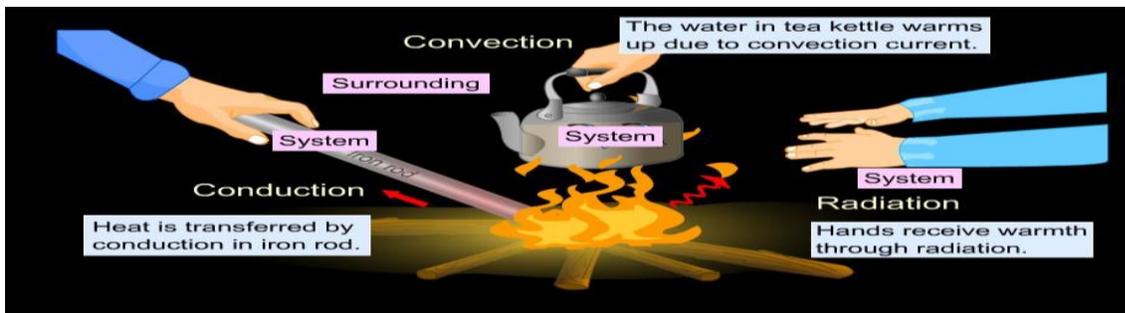
Work- the force, F multiplied by the displacement, dl and is given by $w = Fx dl$.

Universe is an open system. Similarly, cells are open systems where energy and matter can cross the membrane. In thermodynamics, a system in a definite state, i , is characterized by specific values of the state variables, namely of its composition n , its pressure p_i , and temperature T and by the strengths of imposed external fields (gravitational, electric, magnetic). Thus, biological processes usually occur under isobaric (P , a constant is atmospheric pressure) and isothermic (T is constant) conditions. A function of the state variables is a “state function”. If its value depends on the actual values of the variables only, and not on the path of the system, i.e. on the way it has reached the specific state Then, $F = F (V, p, T, n (i))$ is a state function, and $\Delta F = f_1^2 dF = (V_2, p_2, T_2, n (2)) - F (V_1, p_1, T_1, n (1))$

Most thermodynamic properties are either ‘extensive’ which means proportional to the amount of matter, or ‘intensive,’ i.e. ‘independent’ of it. Examples for extensive qualities are weight, volume, energy content, and for intensive qualities, temperature, pressure, refractive index and all molar or molal quantities.

Slide 8 (after objectives)

3 Different ways of heat transfer:



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4 What are the 4 laws of thermodynamics ?

- Zeroth law
- First Law
- Second Law
- Third law

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5 Zeroth law :

Definition : The Zeroth Law of Thermodynamics states that systems in thermal equilibrium are at the same temperature.

The Zeroth law is incredibly important as it allows us to define the concept of a temperature scale. *If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other.* For example, consider two separate cups of boiling water. If we place a thermometer into the first cup, it gets warmed up by the water until it reads 100°C. We now say that the thermometer is in **thermal equilibrium** with the first cup of water. Next, we move the thermometer into the second cup of boiling water, and it continues to read 100°C. The thermometer is therefore also in thermal equilibrium with the second cup of water. Using the logic of the Zeroth law, we can conclude that the two separate cups of boiling water are in thermal equilibrium *with each other*. The Zeroth law therefore enables us to use thermometers to compare the temperatures of any objects we like.

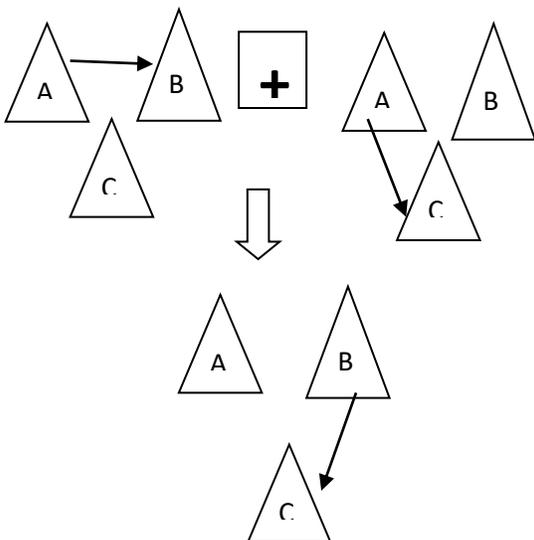
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6 Why the law is given a very unusual name ? "zeroth" law ?

The fact is that the other thermodynamic laws (the first, second, and third) had already been Why the law is given a very unusual name ? "zeroth" law named by the time this one was formulated. However, scientists thought that it was so important that it should go before all the others, and hence it was termed the Zeroth law.

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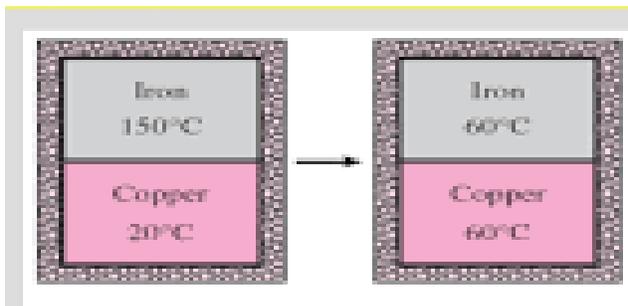
The Zeroth law of thermodynamics is also known as the “law of thermal equilibrium”. It simply states that “when two bodies A and B are separately in thermal equilibrium with a third body C, then they are all in turn are in thermal equilibrium with each other.”



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7 Temperature and the Zeroth Law

The Zeroth law of thermodynamics is an observation. *When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.* As an illustration, suppose we have three objects as shown above. Object #1 and object #2 are in physical contact and in thermal equilibrium. Object #2 is also in thermal equilibrium with object #3. There is initially no physical contact between object #1 and object #3. But, if object #1 and object #3 are brought into contact, it is observed that they are in thermal equilibrium. This simple observation allows us to create a **thermometer**. We can **calibrate** the change in a thermal property, such as the length of a column of mercury, by putting the thermometer in thermal equilibrium with a known physical system at several reference points. Celsius thermometers have the reference points fixed at the freezing and boiling point of pure water. If we then bring the thermometer into thermal equilibrium with any other system, such as the bottom of your tongue, we can determine the temperature of the other system by noting the change in the thermal property. Objects in thermodynamic equilibrium have the same temperature.



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8 Applications of Zeroth Law :

8.1 Thermometers

There are different types of thermometers . But The most common one being the classical mercury clinical thermometer.

1. **Liquid-in-glass thermometers,**
2. **Constant volume gas thermometers,**
3. **Platinum resistance thermometers,**
4. **Thermocouples,**
5. **Radiation thermometers**

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Zeroth Law of Thermodynamics, Example



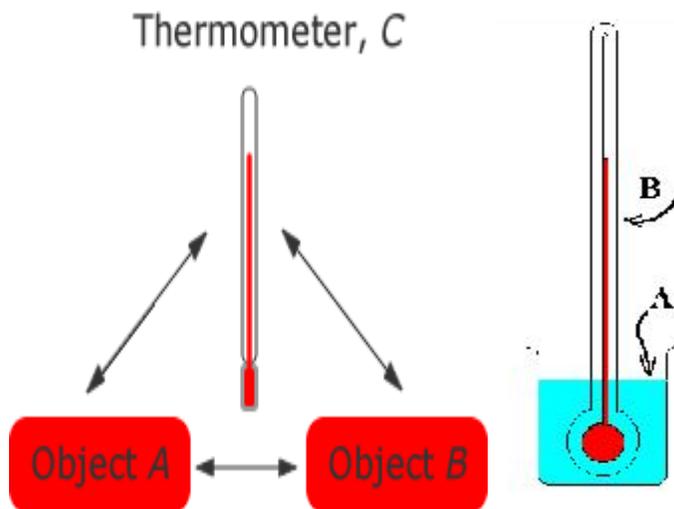
- ▶ Object C (thermometer) is placed in contact with A until they achieve thermal equilibrium
 - The reading on C is recorded
- ▶ Object C is then placed in contact with object B until they achieve thermal equilibrium
 - The reading on C is recorded again
- ▶ If the two readings are the same, A and B are also in thermal equilibrium

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a Mercury Stick Thermometer:

This is a good example of application of Zeroth Law in day to day life.



This is used in everyday life. Please note that the

Thermometric Property = Length of Column of Hg in Stick's Bore

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b Constant Volume Gas Thermometer

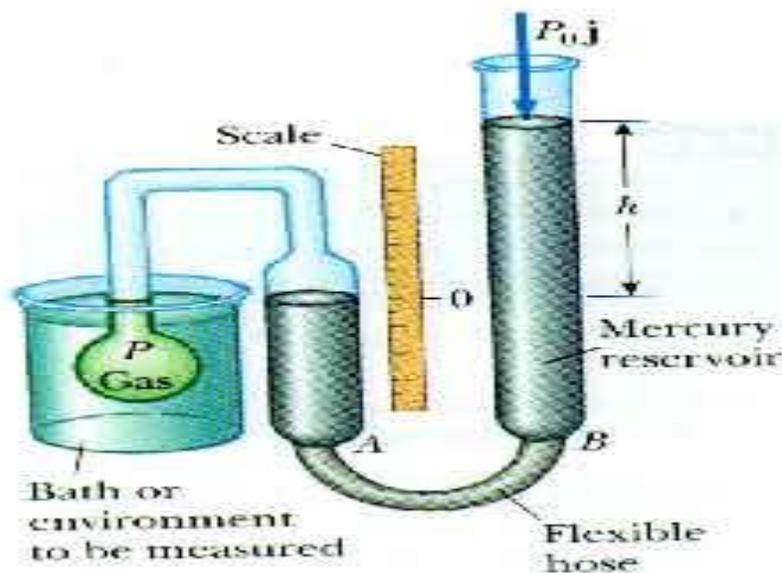
The gas thermometers can be classified into two based on the method by which the gas can be heated. They are,

- ✚ Constant Pressure Gas Thermometer
- ✚ Constant Volume Gas Thermometer.

The constant pressure gas thermometer is not used in practice because of the errors which arise due to the non – uniformity of tube bore.

The constant volume gas thermometer is the most accurate laboratory thermometer and is used for the calibration of other thermometers.

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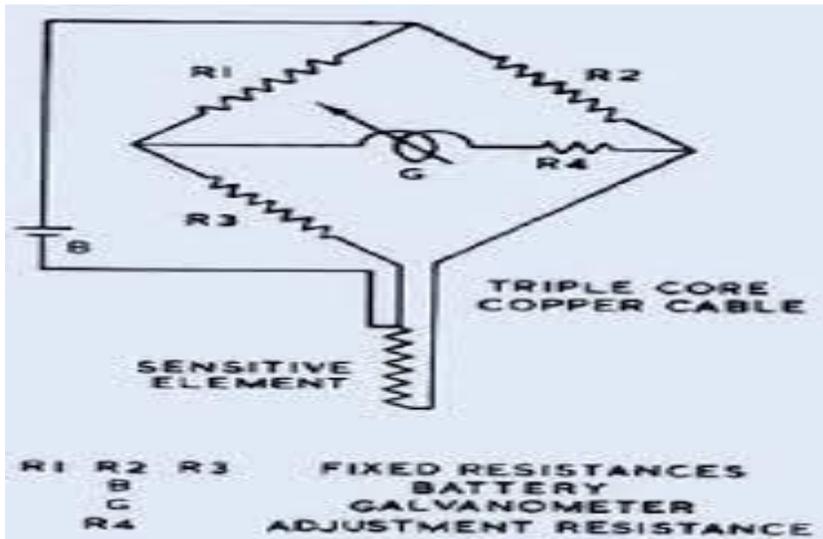
Const Volume Gas Cell : the Thermometric Property = Pressure of Gas

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c Platinum Resistance Thermometers

- The platinum resistance thermometer is a versatile instrument for temperature measurement in the range from — 200° to 1000°C.

- It is used both for precision measurements of the highest accuracy and for routine industrial work. The development and construction of resistance thermometers finds its uses in a wide range of industries.
- **Thermometric Property = Resistance of Resistor**



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Therefore each thermometer works on a thermometric property, as shown below

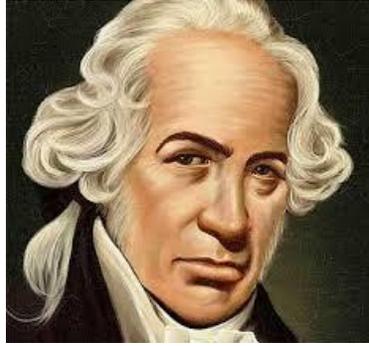
Type of Thermometer	Thermometric Property
liquid-in-glass thermometer	length of mercury in a capillary tube
Resistance thermometer	resistance of platinum wire
Thermocouple thermometer	EMF of a copper-constantan thermocouple
constant volume gas thermometer	pressure of a fixed mass of gas at constant volume

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9 Different Scales of Temperature:

9.1 Fahrenheit Scale

Fahrenheit Scale, established by Daniel Gabriel Fahrenheit in 1724, used three fixed points; a Brine Sol'n (0° F), the Ice Point (32° F) and Body Temperature (96° F)



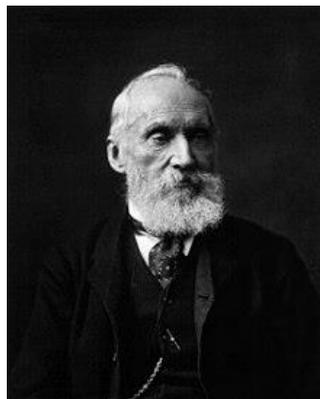
9.2 Centigrade or Celsius

The later scale of Anders Celsius, established in 1742, used two fixed points; the Ice Point (100°C) and the Steam Point (0°C). Each was established using a Mercury stick thermometer; the linear expansion of a narrow column of Mercury being the thermometric property.



9.3 Kelvin scale

The Ideal Gas Temperature Scale is established using a single fixed point, the Triple Point of Water set at 273.16 Kelvin, and a constant volume gas thermometer.



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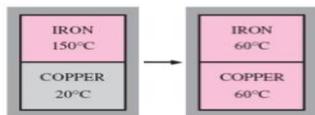
10 Physical meaning of the Zeroth law :

This Law was not enunciated until almost ~1930. The observations were considered obvious. However as pointed out above, its statement is needed to complete the thermodynamic framework. As mentioned this is because it establishes that a property we call "temperature" exists. Since the measurement of the temperature of thermodynamic systems is central to establishing the other Laws of thermodynamics, this Law really should have been established first. And, it really was. It was simply not codified until much later.

Now, how do these observations concerning thermal equilibrium establish that a property called "temperature" exists?

Zeroth Law of Thermodynamics

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



Two bodies reaching thermal equilibrium after being brought into contact in an isolated enclosure.

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Historical developments:

Nevertheless, the usual statement perhaps does not explicitly convey the full physical meaning that underlies it. The underlying physical meaning was perhaps first clarified by Maxwell in his 1871 textbook.

In Carathéodory's (1909) theory, it is postulated that there exist walls "permeable only to heat", though heat is not explicitly defined in that paper. This postulate is a physical postulate of existence. It does not, however, as worded just previously, say that there is only one kind of heat. This paper of Carathéodory states as proviso 4 of its account of such walls: "Whenever each of the systems S_1 and S_2 is made to reach equilibrium with a third system S_3 under identical conditions, systems S_1 and S_2 are in mutual equilibrium".^[11] It is the function of this statement in the paper, not there labeled as the Zeroth law, to provide not only for the existence of transfer of energy other than by work or transfer of matter, but further to provide that such transfer is unique in the sense that there is only one kind of such wall, and one kind of such transfer. This is signaled in the postulate of this paper of Carathéodory that precisely one non-deformation variable is needed to complete the specification of a thermodynamic state, beyond the necessary deformation variables, which are not restricted in number. It is therefore not exactly clear what

Carathéodory means when in the introduction of this paper he writes "*It is possible to develop the whole theory without assuming the existence of heat, that is of a quantity that is of a different nature from the normal mechanical quantities.*"

Maxwell (1871) discusses at some length ideas which he summarizes by the words "**All heat is of the same kind.** This may be expressed by the statement that there is only one kind of temperature, regardless of the variety of scales in which it is expressed. Another modern expression of this idea is that "**All diathermal walls are equivalent**".^[13] This might also be expressed by saying that there is precisely one kind of non-mechanical, non-matter-transferring contact equilibrium between thermodynamic systems. These ideas may be regarded as helping to clarify the physical meaning of the usual statement of the Zeroth law of thermodynamics. *Thus the idea remains open to consideration that the existence of heat and temperature are needed as coherent primitive concepts for thermodynamics, as expressed, for example, by Maxwell and Planck.* On the other hand, Planck in 1926 clarified how the second law can be stated without reference to heat or temperature, by referring to the irreversible and universal nature of friction in natural thermodynamic processes, invented the title '*the Zeroth law of thermodynamics*' when he was discussing the 1935 text of Saha and Srivastava. They write on page 1 that "every physical quantity must be measurable in numerical terms". They presume that temperature is a physical quantity and then deduce the statement "If a body A is in temperature equilibrium with two bodies B and C, then B and C themselves will be in temperature equilibrium with each other". They then in a self-standing paragraph italicize as if to state their basic postulate: "*Any of the physical properties of A which change with the application of heat may be observed and utilised for the measurement of temperature.*" They do not themselves here use the term 'Zeroth law of thermodynamics'. There are very many statements of these physical ideas in the physics literature long before this text, in very similar language. What was new here was just the label '**Zeroth law of thermodynamics**'. Fowler, with co-author [Edward A. Guggenheim](#), wrote of the Zeroth law as follows: "...we introduce the postulate: *If two assemblies are each in thermal equilibrium with a third assembly, they are in thermal equilibrium with each other.*"

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11 Why is the temperature measurement crucial ?

Several thermometric properties change with change in temperature. For example, temperature increases, the volume increases, pressure increases, and also the electrical resistance. That's why temperature measurement has a greatest application.

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The important point to remember that, the Zeroth Law implies that a property called "temperature" exists, **but it does not establish how to measure the temperature. This must be done independently using a process called Thermometry.**

Summary

- *Assuming A, B, and C are three systems, if A and C are in thermal equilibrium, and A and B are in thermal equilibrium, then B and C are in thermal equilibrium.*
- *The Zeroth Law of Thermodynamics implies that temperature is a quantity worth measuring.*
- *Zeroth Law of Thermodynamics can be stated in different ways, but , but the simplest is as follows: systems that are in thermal equilibrium exist at the same temperature.*
- *Two systems are in thermal equilibrium if they could transfer heat between each other, But it does not establish how to measure the temperature. This must be done independently using a process called Thermometry.*

Second law of Thermodynamics

1. To able to describe the second law of thermodynamics, which asserts that processes occur in a certain direction and that energy has quality as well as quantity.
2. Describe the Kelvin-Planck and Clausius statements of the second law of thermodynamics.
3. Discuss the concepts of perpetual-motion machines.
4. Describe the Carnot cycle/ engine.
5. Able to define entropy

1. Introduction

The second law of thermodynamics states that processes occur in a certain direction, not in just any direction. Physical processes in nature can proceed toward equilibrium spontaneously for example water flows down a waterfall, gases expand from a high pressure to a low pressure, heat flows from a high temperature to a low temperature. Once it has taken place, a spontaneous process can be reversed, but it will not reverse itself spontaneously. Some external inputs, energy, must be expended to reverse the process. As it falls down the waterfall, water can be collected in a water wheel, cause a shaft to rotate, coil a rope onto the shaft, and lift a weight. So the energy of the falling water is captured as potential energy increase in the weight, and the first law of thermodynamics is satisfied. However, there are losses associated with this process (friction). Allowing the weight to fall, causing the shaft to rotate in the opposite direction, will not pump all of the water back up the waterfall. Spontaneous processes can proceed only in a particular direction. The first law of thermodynamics gives no information about direction; it states only that when one form of energy is converted into another, identical quantities of energy are involved regardless of the feasibility of the process. We know by experience that heat flows spontaneously from a high temperature to a low temperature. But heat flowing from a

low temperature to a higher temperature with no expenditure of energy to cause the process to take place would not violate the first law.

The first law is concerned with the conversion of energy from one form to another. Joule's experiments showed that energy in the form of heat could not be completely converted into work; however, work energy can be completely converted into heat energy. Evidently heat and work are not completely interchangeable forms of energy. Furthermore, when energy is transferred from one form to another, there is often a degradation of the supplied energy into a less “useful” form. We shall see that it is the second law of thermodynamics that controls the direction processes may take and how much heat is converted into work. A process will not occur unless it satisfies both the first and the second laws of thermodynamics.

2. Thermodynamic cycle

A system has completed a thermodynamic cycle when the system undergoes a series of processes and then returns to its original state, so that the properties of the system at the end of the cycle are the same as at its beginning.

Thus, for whole numbers of cycles

$$P_f = P_i, T_f = T_i, u_f = u_i, v_f = v_i, \text{ etc}$$

2.1 Heat Engine

A heat engine is a thermodynamic system operating in a thermodynamic cycle to which net heat is transferred and from which net work is delivered. The system, or working fluid, undergoes a series of processes that constitute the heat engine cycle.

The following figure illustrates a steam power plant as a heat engine operating in a thermodynamic cycle.

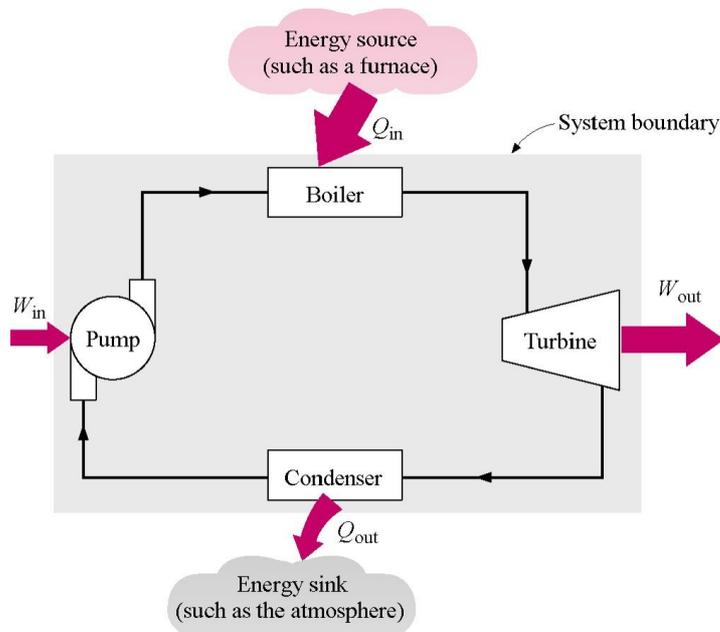


Figure 1: Heat Engine

2.2 Heat (thermal) reservoir

A heat reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of heat can be transferred without any change in its temperature. A high temperature heat reservoir from which heat is transferred is sometimes called a heat source. A low temperature heat reservoir to which heat is transferred is sometimes called a heat sink.

2.3 Work reservoir

A work reservoir is a sufficiently large system in stable equilibrium to which and from which finite amounts of work can be transferred adiabatically without any change in its pressure.

2.4 Thermal Efficiency η_{th}

The thermal efficiency is the index of performance of a work-producing device or a heat engine and is defined by the ratio of the net work output (the desired result) to the heat input (the costs to obtain the desired result).

$$\eta_{th} = \frac{\text{Desired Result}}{\text{Required Input}}$$

For a heat engine the desired result is the net work done and the input is the heat supplied to make the cycle operate. The thermal efficiency is always less than 1 or less than 100 percent.

$$\eta_{th} = \frac{W_{net, out}}{Q_{in}}$$

Where,

$$W_{net, out} = W_{out} - W_{in}$$

$$Q_{in} - Q_{out} = Q_{net}$$

Here the use of the *in* and *out* subscripts means to use the magnitude (take the positive value) of either the work or heat transfer and let the minus sign in the net expression take care of the direction.

Now apply the first law to the cyclic heat engine.

$$Q_{net, in} - W_{net, out} = \Delta U$$

$$W_{net, out} = Q_{net, in}$$

$$W_{net, out} = Q_{in} - Q_{out}$$

The cycle thermal efficiency may be written as

$$\eta_{th} = \frac{W_{net, out}}{Q_{in}}$$

$$= \frac{Q_{in} - Q_{out}}{Q_{in}}$$

$$= 1 - \frac{Q_{out}}{Q_{in}}$$

Cyclic devices such as heat engines, refrigerators, and heat pumps often operate between a high-temperature reservoir at temperature T_H and a low-temperature reservoir at temperature T_L .

The thermal efficiency of the above device becomes

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

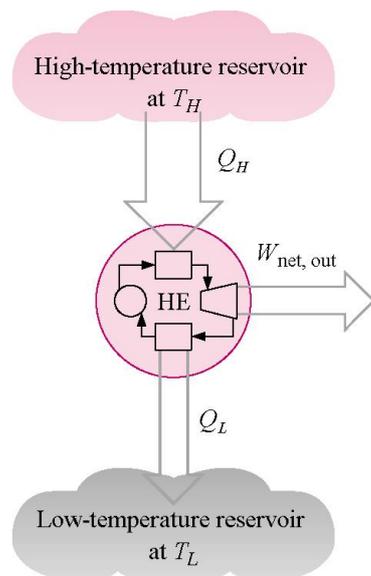


Figure 2: heat cycle process

3. Kelvin-Planck statement of the second law

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. The Kelvin-Planck statement of the second law of thermodynamics states that no heat engine can produce a net amount of work while exchanging heat with a single reservoir only. In other words, it is **impossible to build a 100% efficient heat engine.**

$$\eta_{th} < 100\%$$

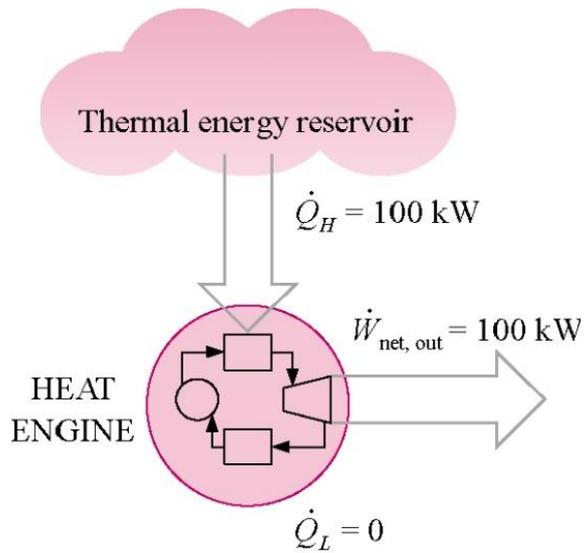


Figure 3: Heat engine that violates the Kelvin-Planck statement of the second law

4: Clausius statement of the second law

The Clausius statement of the second law states that it is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.

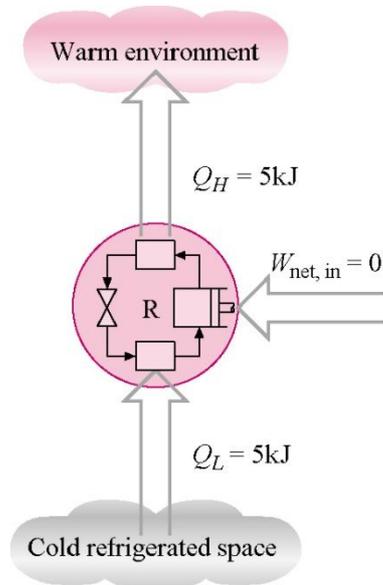


Figure 4: Heat pump that violates the Clausius statement of the second law

A violation of either the Kelvin-Planck or Clausius statements of the second law implies a violation of the other. Assume that the heat engine shown below is violating the Kelvin-Planck statement by absorbing heat from a single reservoir and producing an equal amount of work W . The output of the engine drives a heat pump that transfers an amount of heat Q_L from the low-temperature thermal reservoir and an amount of heat $Q_H + Q_L$ to the high-temperature thermal reservoir. The combination of the heat engine and refrigerator in the left figure acts like a heat pump that transfers heat Q_L from the low-temperature reservoir without any external energy input. This is a violation of the Clausius statement of the second law.

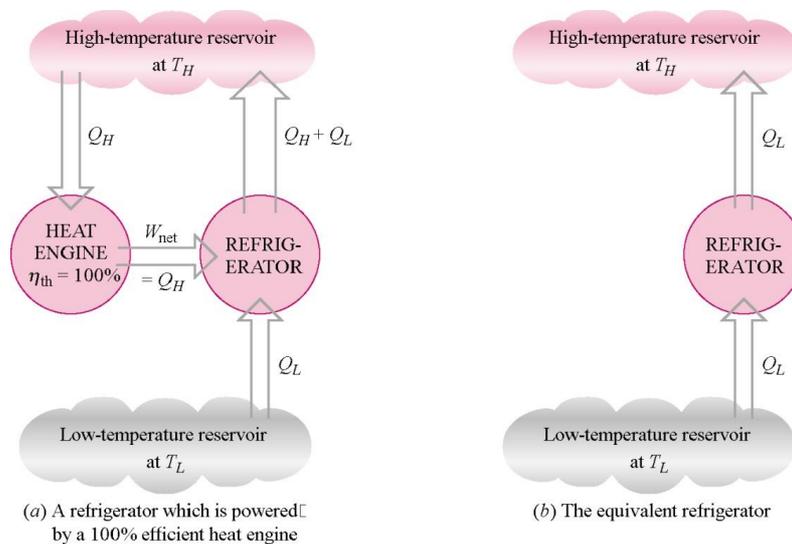


Figure 5: Violation of second law of thermodynamics

6. Perpetual-Motion Machines

A perpetual motion machine is a hypothetical machine that can do work indefinitely without an energy source. This kind of machine is impossible, as it would violate the first or second law of thermodynamics.

6.1 Classification of perpetual motion machine:

One classification of perpetual motion machines refers to the particular law of thermodynamics the machines purport to violate:

6.1.1 A **perpetual motion machine of the first kind** produces work without the input of energy. It thus violates the first law of thermodynamics: the law of conservation of energy.

6.1.2 A **perpetual motion machine of the second kind** is a machine which spontaneously converts thermal energy into mechanical work. When the thermal energy is equivalent to the work done, this does not violate the law of conservation of energy. However, it does violate the more subtle second law of thermodynamics (see also entropy). The signature of a perpetual motion machine of the second kind is that there is only one heat reservoir involved, which is being spontaneously cooled without involving a transfer of heat to a cooler reservoir. This conversion of heat into useful work, without any side effect, is impossible, according to the second law of thermodynamics.

6.1.2 A **perpetual motion machine of the third kind** is usually (but not always) defined as one that completely eliminates friction and other dissipative forces, to maintain motion forever (due to its mass inertia). (*Third* in this case refers solely to the position in the above classification scheme, not the third law of thermodynamics.) It is impossible to make such a machine, as dissipation can never be completely eliminated in a mechanical system, no matter how close a system gets to this ideal.

7. Carnot heat engine

A **Carnot heat engine** is an engine that operates on the reversible Carnot cycle. The basic model for this engine was developed by Nicolas Léonard Sadi Carnot in 1824. The Carnot engine model was graphically expanded upon by Benoît Paul Émile Clapeyron in 1834 and mathematically elaborated upon by Rudolf Clausius in 1857 from which the concept of entropy emerged.

Every thermodynamic system exists in a particular state. A thermodynamic cycle occurs when a system is taken through a series of different states, and finally returned to its initial state. In the process of going through this cycle, the system may perform work on its surroundings, thereby acting as a heat engine.

A heat engine acts by transferring energy from a warm region to a cool region of space and, in the process, converting some of that energy to mechanical work. The cycle may also be reversed. The system may be worked upon by an external force, and in the process, it can transfer thermal energy from a cooler system to a warmer one, thereby acting as a refrigerator or heat pump rather than a heat engine.

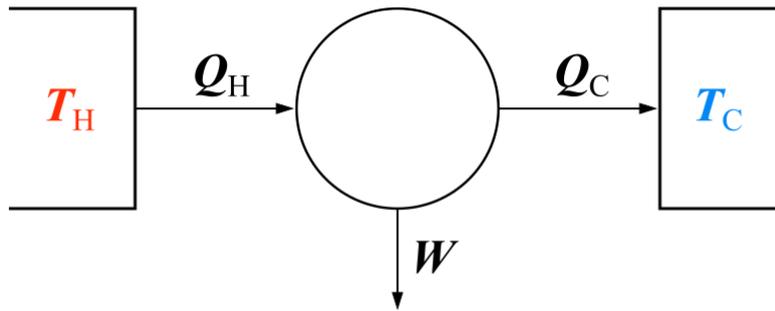


Figure 6: Carnot engine diagram (modern) - where an amount of heat Q_H flows from a high temperature T_H furnace through the fluid of the "working body" (working substance) and the remaining heat Q_C flows into the cold sink T_C , thus forcing the working substance to do mechanical work W on the surroundings, via cycles of contractions and expansions.

7.1 The Carnot Cycle

Process 1-2: Reversible isothermal heat addition at high temperature, $T_H > T_L$, to the working fluid in a piston-cylinder device that does some boundary work.

Process 2-3: Reversible adiabatic expansion during which the system does work as the working fluid temperature decreases from T_H to T_L .

Process 3-4: The system is brought in contact with a heat reservoir at $T_L < T_H$ and a reversible isothermal heat exchange takes place while work of compression is done on the system.

Process 4-1: A reversible adiabatic compression process increases the working fluid temperature from T_L to T_H .

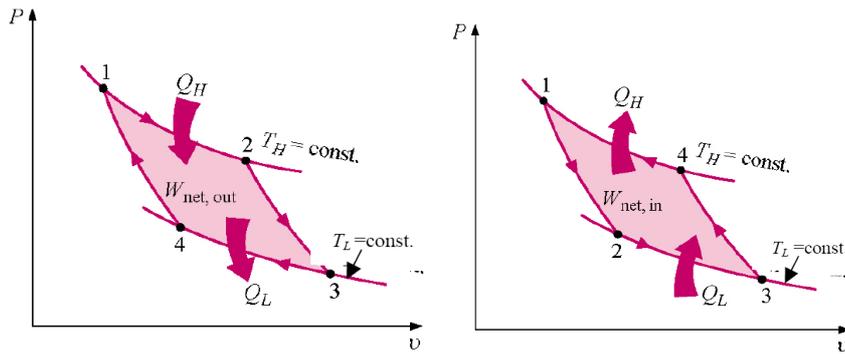


Figure 7: Carnot cycle.

8. The second law of thermodynamics and Entropy

The first law of thermodynamics provides the basic definition of internal energy, associated with all thermodynamic systems, and states the rule of conservation of energy. The second law is concerned with the direction of natural processes. It asserts that a natural process runs only in one sense, and is not reversible. For example, heat always flows spontaneously from hotter to colder bodies, and never the reverse, unless external work is performed on the system. Its modern definition is in terms of entropy.

In a fictive reversible process, an infinitesimal increment in the entropy (dS) of a system is defined to result from an infinitesimal transfer of heat (δQ) to a closed system divided by the common temperature (T) of the system and the surroundings which supply the heat:^[6]

Different notations are used for infinitesimal amounts of heat (δ) and infinitesimal amounts of entropy (d) because entropy is a function of state, while heat, like work, is not. For an actually possible infinitesimal process without exchange of matter with the surroundings, the second law requires that the increment in system entropy be greater than that:

This is because a general process for this case may include work being done on the system by its surroundings, which must have frictional or viscous effects inside the system, and because heat transfer actually occurs only irreversibly, driven by a finite temperature difference.

The change in entropy ΔS of a system when an amount of thermal energy Q is **added** to a system by a reversible process at constant **absolute temperature** T is given by:

$$\Delta S = Q / T$$

The units of the change in entropy are JK^{-1}

Numerical:

Q. A heat engine removes 100 J each cycle from a heat reservoir at 400 K and exhausts 85 J of thermal energy to a reservoir at 300 K. Compute the change in entropy for each reservoir.

Solution

Since the hot reservoir loses heat, we have that:

$$\Delta S = Q / T = -100 \text{ J} / 400 \text{ K} = \mathbf{-0.25 \text{ JK}^{-1}}$$

For the cold reservoir we have:

$$\Delta S = Q / T = 85 \text{ J} / 300 \text{ K} = \mathbf{0.283 \text{ JK}^{-1}}$$

Therefore:

The increase in entropy of the cold reservoir is greater than the decrease for the hot reservoir.

In this example and all other cases, it has been found that the total entropy increases. This infers that total entropy increases in all natural systems. The entropy of a given system can increase or decrease

but the change in entropy of the system ΔS , plus the change in entropy of the environment ΔS_{env} must be greater than or equal to zero.

Thus

$$\Delta S = \Delta S_{\text{S}} + \Delta S_{\text{env}} \geq 0$$

Summary:

1. When energy changes from one form to another form, or matter moves freely, entropy (disorder) increases. Differences in temperature, pressure, and density tend to even out horizontally after a while.
2. Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.
3. It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.
4. **Entropy** in an isolated system – the combination of a subsystem under study and its surroundings – increases during all spontaneous chemical and physical processes.

The Third Law of Thermodynamics

Objectives :

1. Understand what is 3rd law of thermodynamics ?
2. Significance of third Law
3. Understand the terms, Absolute zero,
4. Specific heat
5. Thermal expansion coefficient
6. Applications of third Law

Introduction:

“It is interesting to note that the pioneers in the area of thermodynamics, Helmholtz and Julios von Mayer, were actually clinicians. Mayer a German Physicist, is best known for enunciating in 1841 one of the original statements of the conservation of energy or what is now known as one of the first versions of the first law of thermodynamics. Dr. Helmholtz is known for his theories on the conservation of energy, work in electrodynamics, chemical thermodynamics, and on a mechanical foundation of thermodynamics.”(Shaha Dolev and Avshalom C. Elitzur).



Julios von Mayer
(1814 – 1882)



Hermann Ludwig Ferdinand von Helmholtz (1821 – 1894)

It is appropriate to remember these two great scientists before we go into other topics of the thermodynamics and its applications

Thermodynamics studies the transformations of energy, and such transformations ceaselessly take place in all living systems (probably with important differences between the states of health and disease). Moreover, thermodynamics studies the elusive notions of order and disorder, which

are also, respectively, the very hallmarks of life and death. These similarities suggest that thermodynamics might provide a unifying paradigm for many life sciences, explaining the multitude of life's manifestations on the basis of a few basic physical principles.

What is the Third Law of Thermodynamics ?

The **third law of thermodynamics** is sometimes stated as follows, regarding the properties of systems in equilibrium at absolute zero temperature: The entropy of a perfect crystal at absolute zero is exactly equal to zero. At absolute zero (zero kelvin), the system must be in a state with the minimum possible energy, and the above statement of the third law holds true provided that the perfect crystal has only one minimum energy state. Entropy is related to the number of accessible microstates, and for a system consisting of many particles, quantum mechanics indicates that there is only one unique state (called the ground state) with minimum energy.^[1] If the system does not have a well-defined order (if its order is glassy, for example), then in practice there will remain some finite entropy as the system is brought to very low temperatures as the system becomes locked into a configuration with non-minimal energy. The constant value is called the residual entropy of the system.

In the year 1848, Lord Kelvin devised the scale for absolute zero temperature and he concluded that absolute zero temperature meant -273.15 degree Celsius. Later, by the international agreement a new temperature scale was found by the name Kelvin. As per this scale absolute meant 0K or 0 degree Kelvin on Kelvin scale.

The relation between Kelvin and Celsius temperature scale is: $K = \text{degree Celsius} + 273$.

The Third law of thermodynamics

The Third Law of Thermodynamics is the lesser known of the three major thermodynamic laws. The Third Law of Thermodynamics refers to a state known as "absolute zero." This is the lowest temperature in the Kelvin temperature scale. In actuality, no object or system can have a temperature of zero Kelvin, because of the Second Law of Thermodynamics. The Second Law, in part, implies that heat can never spontaneously move from a colder body to a hotter body. So, as a system approaches absolute zero, it will eventually have to draw energy from whatever systems are nearby. If it draws energy, it can never obtain absolute zero. So, this state is not physically possible, but is a mathematical limit of the universe. In short the Third Law of Thermodynamics says: "The entropy of a pure perfect crystal is zero (0) at zero Kelvin (0° K)." Entropy is a property of matter and energy discussed by the Second Law of Thermodynamics. The Third Law of Thermodynamics means that as the temperature of a system approaches absolute zero, its entropy approaches a constant (for pure perfect crystals, this constant is zero). A pure perfect crystal is one in which every molecule is identical, and the

molecular alignment is perfectly even throughout the substance. For non-pure crystals, or those with less-than perfect alignment, there will be some energy associated with the imperfections, so the entropy cannot become zero. There is no entropy and there is no mixing since the crystal is pure. For a mixed crystal containing the atomic or molecular species A and B, there are many possible arrangements of A and B and entropy is associated with the arrangement of the atoms/molecules. Most of the direct use of the Third Law of Thermodynamics occurs in ultra-low temperature chemistry and physics. The applications of this law have been used to predict the response of various materials to temperature changes.

A) Single possible configuration for a system at absolute zero, i.e., only one microstate is accessible.

Thus $S = k \ln W = 0$.

b) At temperatures greater than absolute zero, multiple microstates are accessible due to atomic vibration (exaggerated in the figure).

Since the number of accessible microstates is greater than 1, $S = k \ln W > 0$.

$$S = \int^T \frac{dQ}{T} + S_0$$

As long as we deal in differences in entropy, knowledge of S_0 is unnecessary. However, absolute entropy IS important, e.g.

$$\mathbf{F = U - TS}$$
$$\mathbf{G = H - TS}$$

Statement of Third Law : By different ways by different scientists

1 Gibbs-Helhotz

2 Nernst and 3 Plank

Statements of the third law

•The Gibbs-Helmholtz equation:

$$G = H + T \left(\frac{\partial G}{\partial T} \right)_P$$

•For an isothermal process:

$$\Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P$$

•These equations imply:

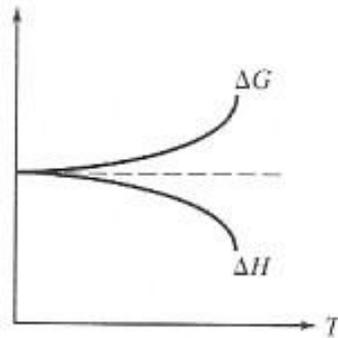
$$\lim_{T \rightarrow 0} G = \lim_{T \rightarrow 0} H$$

$$\lim_{T \rightarrow 0} \Delta G = \lim_{T \rightarrow 0} \Delta H$$

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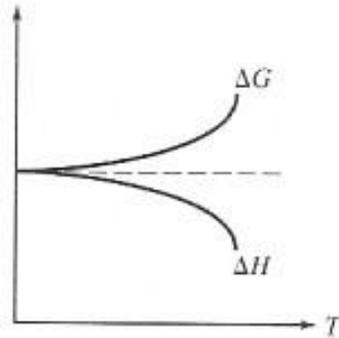
•Nernst postulate implies that:

$$\lim_{T \rightarrow 0} \left[\frac{\partial(G_2 - G_1)}{\partial T} \right]_P = \lim_{T \rightarrow 0} \left[\frac{\partial G_2}{\partial T} - \frac{\partial G_1}{\partial T} \right] = \lim_{T \rightarrow 0} [S_1 - S_2] = 0$$

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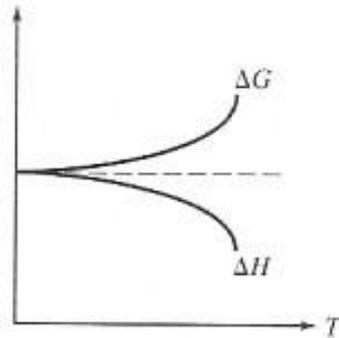
•The Nernst formulation of the Third Law:

'All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero.'

Statements of the third law

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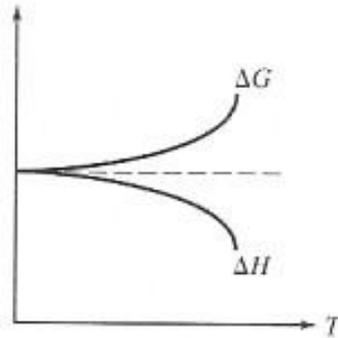
•Planck later postulated that:

$$\lim_{T \rightarrow 0} \left(\frac{\partial G}{\partial T} \right)_P = 0, \quad \lim_{T \rightarrow 0} \left(\frac{\partial H}{\partial T} \right)_P = 0 \quad \Rightarrow \quad \lim_{T \rightarrow 0} S = 0$$

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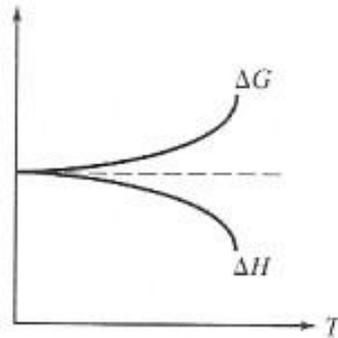
• Planck's statement of the Third Law:

'The entropy of a true equilibrium state of a system at absolute zero is zero.'

Statements of the third law

$$\lim_{T \rightarrow 0} G = \lim_{T \rightarrow 0} H$$

$$\lim_{T \rightarrow 0} \Delta G = \lim_{T \rightarrow 0} \Delta H$$



• Another statement of the Third Law is:

'It is impossible to reduce the temperature of a system to absolute zero using a finite number of processes.'

Significance of entropy in biological reactions

In biological systems, very complex but well defined structures arise with high three-dimensional order and, correspondingly, low entropy and high information content. As discussed earlier, water has a strong tendency to form hydrogen bonded structures which make

biomolecules to arrange themselves in “tertiary structures” with their polar, hydrophilic groups turned towards the surrounding water. And the hydrophobic, aliphatic groups and tails pack closely together to protect against water contacts. Therefore, it must be remembered that the $T\Delta S$ is the dominant term in ΔG for the protein folding reaction. In small systems, surface energies also contribute markedly to the free energy. The spatial fixation of one single amino acid group in chain poly peptide molecule (see proteins in chapter 5) diminishes its entropy by about $0.05 \text{ eV} \approx 1.2 \text{ kcal mol}^{-1}$ at 25° C . Similarly, considerable entropy effects arise due to formation of base pairing in DNA in the cell.

Evolution and Thermodynamics :

To comprehend the evolution from the thermodynamic aspect of energy efficiency:

The ability of living systems to increase complexity is not accidental. Complexity is vital for efficiency. Life was therefore compelled to increase complexity as organisms fought for survival. The course of evolution can be rephrased as “Survival of the most efficient.”

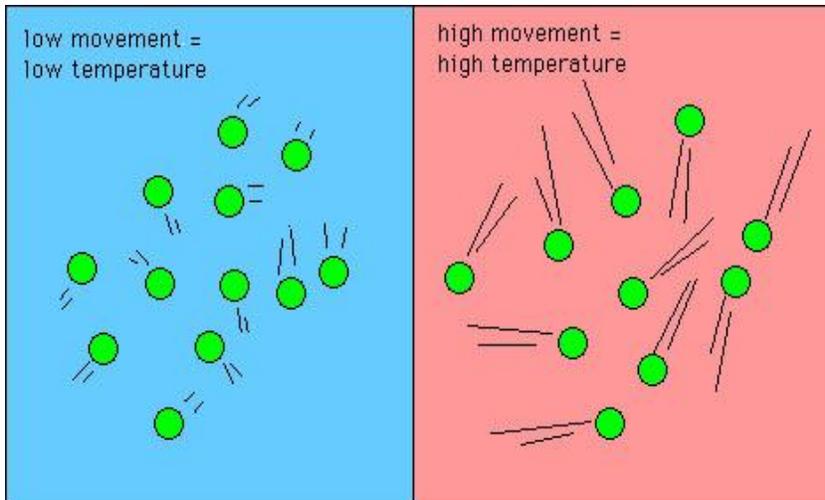
Applications Of Third Law :

1 Response of materials to Temperature changes

Most of the direct use of the Third Law of Thermodynamics occurs in ultra-low temperature chemistry and physics. The applications of this law have been used to predict the response of various materials to temperature changes. These relationships have become core to many science disciplines, even though the Third Law of Thermodynamics is not used directly nearly as much as the other two.

Specific Heat and Heat capacity:

Specific heat is another physical property of matter. All matter has a temperature associated with it. The temperature of matter is a direct measure of the motion of the molecules: The greater the motion the higher the temperature.



The temperature of an object on gain or loss of heat energy is given by:

The specific heat (S) of the object :

Therefore, the specific heat of an object is defined as: **mass m, x the heat and the temperature rise, then S is given by**

$$S = \frac{\text{Heat (in Joules or cal)}}{\text{mass} \times \Delta T}$$

ΔT = change in temperature

Some common specific heats and heat capacities:

Substance	S (J/g 0C)	C (J/0C) for 100 g
Air	1.01	101
Aluminum	0.902	90.2
Copper	0.385	38.5
Gold	0.129	12.9
Iron	0.450	45.0
Mercury	0.140	14.0
NaCl	0.864	86.4
Ice	2..03	203
Water	4.179	417.9

Vapor pressure(v_p)	0.0212 atm at 20°C	
Heat of vaporization, (C_r)	40.63 kJ/mol	High value gives resistance to dehydration
Heat Capacity (C_p)	4.22 kJ/kg.K	High value helps in thermal regulation in the body
Specific heat	4180 J kg ⁻¹ K ⁻¹ (T=293...373 K)	

Thermal Expansion :

Thermal expansion is the tendency of matter to change in shape, area, and volume in response to a change in temperature. Temperature is a monotonic function of the average molecular kinetic energy of a substance. When a substance is heated, the kinetic energy of its molecules increases.

Therefore, the molecules begin vibrating/moving more and usually maintain a greater average separation. Materials which contract with increasing temperature are unusual; this effect is limited in size, and only occurs within limited temperature ranges. The relative expansion or strain divided by the change in temperature is called the material's coefficient of thermal expansion and generally varies with temperature.

Coefficient of Thermal Expansion :

The **coefficient of thermal expansion**(α) describes how the size of an object changes with a change in temperature. Specifically, it measures the fractional change in size per degree change in temperature at a constant pressure. Several types of coefficients have been developed: volumetric, area, and linear. Which is used depends on the particular application and which dimensions are considered important. For solids, one might only be concerned with the change along a length, or over some area. The volumetric thermal expansion coefficient is the most basic thermal expansion coefficient, and the most relevant for fluids. In general, substances expand or contract when their temperature changes, with expansion or contraction occurring in all directions. Substances that expand at the same rate in every direction are called isotropic. For isotropic materials, the area and volumetric thermal expansion coefficient are, respectively, approximately twice and three times larger than the linear thermal expansion coefficient. Mathematical definitions of these coefficients are defined below for solids, liquids, and gases.

General volumetric thermal expansion coefficient

In the general case of a gas, liquid, or solid, the volumetric coefficient of thermal expansion is given by

Volume Thermal Expansion Coefficient Formula

$$\alpha_v = \frac{1}{V} \frac{\Delta V}{\Delta T}$$

α_v – volume thermal expansion coefficient

V – area of the object in m^3

ΔV – change in volume in m^3

ΔT – change in temperature in kelvin

2 Gives support to the implications of the first two laws.

The 3rd Law basically affirms the first two laws. The Third Law of Thermodynamics demonstrates another detectable, absolute, all-encompassing, important natural law. The Laws of Thermodynamics demonstrate very ordered rules of energy interactions, which the entire universe must obey. Why is the Third Law of Thermodynamics true? Why are there no exceptions in the entire universe? This law cannot be an accident, since none of the thermodynamic laws are random.

SUMMARY

The **third law of thermodynamics** is sometimes stated as follows, regarding the properties of systems in equilibrium at absolute zero temperature: The entropy of a perfect crystal at absolute zero is exactly equal to zero. At absolute zero (zero Kelvin), the system must be in a state with the minimum possible energy, and the above statement of the third law holds true provided that the perfect crystal has only one minimum energy state. The relation between Kelvin and Celsius temperature scale is: $K = \text{degree Celsius} + 273$.

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Entropy of a true equilibrium state of a system at absolute zero is zero .

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Applications Of Third Law :

- 1 Response of materials to Temperature changes and it explains the behavior of solids at very low temperature
- 2 Specific heat, Thermal expansion Coefficient
- 3 Gives support to the implications of the first two laws
- 4 It helps in calculating the thermodynamic properties.

- 5) It is helpful in measuring chemical affinity. Because of this it is known as Nernst theorem.

- 6) It helps in analyzing chemical and phase equilibrium.