Laws of Thermodynamics

- The first law, also known as Law of Conservation of Energy, states that energy cannot be created or destroyed in an isolated system.
- The second law of thermodynamics states that the entropy of any isolated system always increases.
- The third law of thermodynamics states that the entropy of a system approaches a constant value as the temperature approaches absolute zero.

  Example: Heat is energy can be converted from one form to another, or transferred from one object to another. For example, a stove burner converts electrical energy to heat and conducts that energy through the pot to the water. This increases the kinetic energy of the water molecules, causing them to move faster and faster. At a certain temperature (the boiling point), the atoms have gained enough energy to break free of the molecular bonds of the liquid and escape as vapor.

System or Surroundings

- In order to avoid confusion, scientists discuss thermodynamic values in reference to a system and its surroundings. Everything that is not a part of the system constitutes its surroundings. The system and surroundings are separated by a boundary. For example, if the system is one mole of a gas in a container, then the boundary is simply the inner wall of the container itself. Everything outside of the boundary is considered the surroundings, which would include the container itself.
- The boundary must be clearly defined, so one can clearly say whether a given part of the world is in the system or in the surroundings. If matter is not able to pass across the boundary, then the system is said to be *closed*; otherwise, it is *open*. A closed system may still exchange energy with the surroundings unless the system is an isolated one, in which case neither matter nor energy can pass across the boundary.

The First Law of Thermodynamics

The first law of thermodynamics, also known as Law of Conservation of Energy, states that energy can neither be created nor destroyed; energy can only be transferred or changed from one form to another. For example, turning on a light would seem to produce energy; however, it is electrical energy that is converted.

A way of expressing the first law of thermodynamics is that any change in the internal energy (ΔE) of a system is given by the sum of the heat (q) that flows across its boundaries and the work (w) done on the system by the surroundings:

[latex]\Delta E = q + w[/latex]

This law says that there are two kinds of processes, heat and work, that can lead to a change in the internal energy of a system. Since both heat and work can be measured and quantified, this is the same as saying that any change in the energy of a system must result in a corresponding change in the energy of the surroundings outside the system. In other words, energy cannot be created or destroyed. If heat flows into a system or the surroundings do work on it, the internal energy increases and the sign of q and w are positive. Conversely, heat flow out of the system or work done by the system (on the surroundings) will be at the expense of the internal energy, and q and w will therefore be negative.

The Second Law of Thermodynamics

The second law of thermodynamics says that the entropy of any isolated system always increases. Isolated systems spontaneously evolve towards thermal equilibrium—the state of maximum entropy of the system. More simply put: the entropy of the universe (the ultimate isolated system) only increases and never decreases.

A simple way to think of the second law of thermodynamics is that a room, if not cleaned and tidied, will invariably become more messy and disorderly with time – regardless of how careful one is to keep it clean. When the room is cleaned, its entropy decreases, but the effort to clean it has resulted in an increase in entropy outside the room that exceeds the entropy lost.

The Third Law of Thermodynamics

The third law of thermodynamics states that the entropy of a system approaches a constant value as the temperature approaches absolute zero. The entropy of a system at absolute zero is typically zero, and in all cases is determined only by the number of different ground states it has. Specifically, the entropy of a pure crystalline substance (perfect order) at absolute zero temperature is zero. This statement holds true if the perfect crystal has only one state with minimum energy.

Heat

Thermodynamics, then, is concerned with several properties of matter; foremost among these is heat. Heat is energy transferred between substances or systems due to a temperature difference between them, according to Energy Education. As a form of energy, heat is conserved, i.e., it cannot be created or destroyed. It can, however, be transferred from one place to another. Heat can also be converted to and from other forms of energy. For example, a steam turbine can convert heat to kinetic energy to run a generator that converts kinetic energy to electrical energy. A light bulb can convert this electrical energy to electromagnetic radiation (light), which, when absorbed by a surface, is converted back into heat.

Temperature

The amount of heat transferred by a substance depends on the speed and number of atoms or molecules in motion, according to Energy Education. The faster the atoms or molecules move, the higher the temperature, and the more atoms or molecules that are in motion, the greater the quantity of heat they transfer.

Temperature is "a measure of the average kinetic energy of the particles in a sample of matter, expressed in terms of units or degrees designated on a standard scale," according to the American Heritage Dictionary. The most commonly used temperature scale is Celsius, which is based on the freezing and boiling points of water, assigning respective values of 0 degrees C and 100 degrees C. The Fahrenheit scale is also based on the freezing and boiling points of water which have assigned values of 32 F and 212 F, respectively.

Newton's Law of Cooling

In 1701, Sir Isaac Newton first stated his Law of Cooling in a short article titled "Scala graduum Caloris" ("A Scale of the Degrees of Heat") in the Philosophical Transactions of the Royal Society. Newton's statement of the law translates from the original Latin as, "the excess of the degrees of the heat ... were in geometrical progression when the times are in an arithmetical progression." Worcester Polytechnic Institute gives a more modern version of the law as "the rate of change of temperature is proportional to the difference between the temperature of the object and that of the surrounding environment."

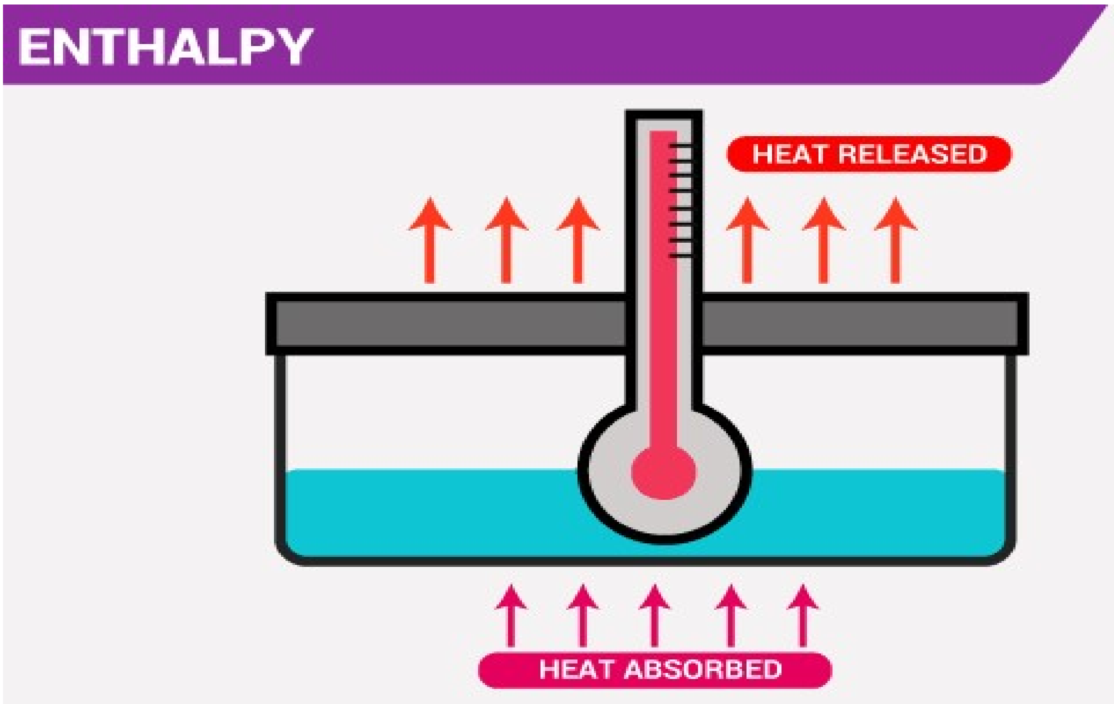
Entropy

All thermodynamic systems generate waste heat. This waste results in an increase in entropy, which for a closed system is "a quantitative measure of the amount of thermal energy not available to do work," according to the American Heritage Dictionary. Entropy in any closed system *always* increases; it *never* decreases. Additionally, moving parts produce waste heat due to friction, and radiative heat inevitably leaks from the system.

This makes so-called perpetual motion machines impossible. Siabal Mitra, a professor of physics at Missouri State University, explains, "You cannot build an engine that is 100 percent efficient, which means you cannot build a perpetual motion machine. However, there are a lot of folks out there who still don't believe it, and there are people who are still trying to build perpetual motion machines."

Entropy is also defined as "a measure of the disorder or randomness in a closed system," which also inexorably increases. You can mix hot and cold water, but because a large cup of warm water is more disordered than two smaller cups containing hot and cold water, you can never separate it back into hot and cold without adding energy to the system. Put another way, you can't unscramble an egg or remove cream from your coffee. While some processes appear to be completely reversible, in practice, none actually are. Entropy, therefore, provides us with an arrow of time: forward is the direction of increasing entropy.

Enthalpy



What is Enthalpy?

When a process takes place at constant pressure, the heat absorbed or released is equal to the Enthalpy change. Enthalpy is sometimes known as "heat content", but "enthalpy" is an interesting and unusual word, so most people like to use it. Etymologically, the word "entropy" is derived from the Greek, meaning "turning" and "enthalpy" is derived from the Greek meaning "warming". As for pronunciation, Entropy is usually stressed on its first syllable, while enthalpy is usually stressed on the second. Enthalpy(H) is nothing but the sum of the internal energy(U) and the product of pressure(P) and volume(V).

Enthalpy H can be written as,

H = U + pV

Where, H = Enthalpy of the system

U = Internal energy of the system

p = Pressure of the system

V = Volume of the system

Enthalpy is not measured directly, however, the change in enthalpy (ΔH) is measured, which is the heat added or lost by the system. It is entirely dependent on the state functions T, p and U.

Enthalpy can also be written as

$$\Delta H=\Delta U+\Delta PV$$

At constant temperature, for the process heat flow(q) is equal to the change in enthalpy, this is represented as

$$\Delta H=q$$

Enthalpy Units

The Enthalpy is expressed as,

H = Energy/Mass

Any physical quantity can be represented by dimensions. The arbitrary magnitudes allocated to the dimensions are called units. There are two types of dimensions namely primary or fundamental and secondary or derived dimensions.

Primary dimensions are: mass, m; length, L; time, t; temperature, T

Secondary dimensions are the ones that can be derived from primary dimensions such as velocity(m/s2), pressure (Pa = kg/m.s2).

There are two unit systems currently available SI (International System) and USCS (United States Customary System) or English system. We, however, will use SI units exclusively in this course. The SI units are based on the decimal relationship between units.

SI Prefixes:

Factor	**Name**	**symbol**
10^{12}	**Tera**	**T**
10^{9}	**Giga**	**G**
10^{6}	**Mega**	**M**
10^{3}	**Kilo**	**k**
10^{2}	**Hecto**	**h**
10^{-2}	**Centi**	**c**
10^{-3}	**Milli**	**m**
10^{-6}	**Micro**	μ
10^{-9}	**Nano**	**n**
10^{-12}	**Pico**	**p**

What is Thermodynamics?

Thermodynamics is the branch of physics that deals with the relationships between heat and other forms of energy. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter. First law of thermodynamics: one of the most fundamental laws of nature is the conservation of energy principle.

It simply states that during an interaction, energy can change from one form to another but the total amount of energy remains constant. The second law of thermodynamics: energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy. Whenever there is an interaction between energy and matter, thermodynamics is involved. Some examples include heating and air-conditioning systems, refrigerators, water heaters, etc.