Laws of Thermodynamics

By

Dr.Vinod Kumar Singh

Associate Professor Physics K .S. Saket P G College Ayodhya

Email: vks423272@gmail.com

Thermodynamics, science of the relationship between heat, work, temperature, and energy. In broad terms, thermodynamics deals with the transfer of energy from one place to another and from one form to another. The key concept is that heat is a form of energy corresponding to a definite amount of mechanical work.

Zeroth Law of Thermodynamics:

Zeroth law of thermodynamics helps us in defining the temperature. It states that if out of three systems A, B and C, A and B are separately in thermal equilibrium with C, then A and B are also in thermal equilibrium with each other.

Thermodynamic Equilibrium:

A system in thermodynamic equilibrium must fulfill the following conditions –

(i) **Mechanical Equilibrium:** For a system to be in mechanical equilibrium, there should be no unbalanced forces between different parts of the system or between the system and surroundings.

(ii) **Thermal Equilibrium:** For a system to be in thermal equilibrium, the temperature of all parts of the system be same and should be identical with that of surroundings.

(iii) **Chemical Equilibrium:** For a system to be in chemical equilibrium, the composition of the system should remain fixed and definite.

The First Law Of Thermodynamics

The laws of thermodynamics are deceptively simple to state, but they are far-reaching in their consequences. The first law asserts that if heat is recognized as a form of energy, then the total energy of a system plus its surroundings is conserved; in other words, the total energy of the universe remains constant.

The first law is put into action by considering the flow of energy across the boundary separating a system from its surroundings. Consider the classic example of a gas enclosed in a cylinder with a movable piston. The walls of the cylinder act as the boundary separating the gas inside from the world outside, and the movable piston provides a mechanism for the gas to do work by expanding against the force holding the piston (assumed frictionless) in place. If the gas does work W as it expands, and/or absorbs heat Q from its surroundings through the walls of the cylinder, then this corresponds to a net flow of energy $W - Q$ across the boundary to the surroundings. In order to conserve the total energy U, there must be a counterbalancing change$\Delta U = Q - W$ (1)in the internal energy of the gas. The first law provides a kind of strict energy accounting system in which the change in the energy account (ΔU) equals the difference between deposits (Q) and withdrawals (W).

There is an important distinction between the quantity ΔU and the related energy quantities Q and W. Since the internal energy U is characterized entirely by the quantities (or parameters) that uniquely determine the state of the system at equilibrium, it is said to be a state function such that any change in energy is determined entirely by the initial (i) and final (f) states of the system: $\Delta U = U_f - U_i$. However, Q and W are not state functions. Just as in the example of a bursting balloon, the gas inside may do no work at all in reaching its final expanded state, or it could do maximum work by expanding inside a cylinder with a movable piston to reach the same final state. All that is required is that the change in energy (ΔU) remain the same. By analogy, the same change in one's bank account could be achieved by many different combinations of deposits and withdrawals. Thus, Q and W are not state functions, because their values depend on the particular process (or path) connecting the same initial and final states. Just as it is more meaningful to speak of the balance in one's bank account than its deposit or withdrawal content, it is only meaningful to speak of the internal energy of a system and not its heat or work content.

From a formal mathematical point of view, the incremental change dU in the internal energy is an exact differential, while the corresponding incremental changes $d'Q$ and $d'W$ in heat and work are not, because the definite integrals of these quantities are path-dependent. These concepts can be used to great advantage in a precise mathematical formulation of thermodynamics.

Heat engines

The classic example of a heat engine is a steam engine, although all modern engines follow the same principles. Steam engines operate in a cyclic fashion, with the piston moving up and down once for each cycle. Hot high-pressure steam is admitted to the cylinder in the first half of each cycle, and then it is allowed to escape again in the second half. The overall effect is to take heat Q_1 generated by burning a fuel to make steam, convert part of it to do work, and exhaust the remaining heat Q_2 to the environment at a lower temperature. The net heat energy absorbed is then $Q = Q_1 - Q_2$. Since the engine returns to its initial state, its internal energy U does not change ($\Delta U = 0$). Thus, by the first law of thermodynamics, the work done for each complete cycle must be $W = Q_1 - Q_2$. In other words, the work done for each complete cycle is just the difference between the heat Q_1 absorbed by the engine at a high temperature and the heat Q_2 exhausted at a lower temperature. The power of thermodynamics is that this conclusion is completely independent of the detailed working mechanism of the engine. It relies only on the overall conservation of energy, with heat regarded as a form of energy.

Different Types of Thermodynamic Process:

Isothermal Process:

The equation of a gas for isothermal process is –

$\boxed{PV = RT = \text{Constant}}$

In isothermal process, there is no change in temperature so no change in internal energy i.e. $dU = 0$

So, from 1st law of thermodynamics – $dQ = dW$

Adiabatic Process: In adiabatic process no exchange of heat takes place between it and surroundings, then the process is called.

For adiabatic change in perfect gas – $dQ = 0$

So, from 1st law of thermodynamics – $0 = dU + dW$

OR $dU =- dW$

In an adiabatic process, the gas follows the equation –

$$\boxed{PV^{\gamma} = \text{constant}}$$

Equation (1) is called 'Poisson's law'.

Isobaric Process: The process in which pressure remains constant is called isobaric process.

Isochoric Process: The process in which volume remains constant is called isochoric process.

The Second Law Of Thermodynamics

The first law of thermodynamics asserts that energy must be conserved in any process involving the exchange of heat and work between a system and its surroundings. A machine that violated the first law would be called a perpetual motion machine of the first kind because it would manufacture its own energy out of nothing and thereby run forever. Such a machine would be impossible even in theory. However, this impossibility would not prevent the construction of a machine that could extract essentially limitless amounts of heat from its surroundings (earth, air, and sea) and convert it entirely into work. Although such a hypothetical machine would not violate conservation of energy, the total failure of inventors to build such a machine, known as a perpetual motion machine of the second kind, led to the discovery of the second law of thermodynamics. The second law of thermodynamics can be precisely stated in the following two forms, as originally formulated in the 19th century by the Scottish physicist William Thomson (Lord Kelvin) and the German physicist Rudolf Clausius, respectively:

A cyclic transformation whose only final result is to transform heat extracted from a source which is at the same temperature throughout into work is impossible.

A cyclic transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible.

The two statements are in fact equivalent because, if the first were possible, then the work obtained could be used, for example, to generate electricity that could then be discharged through an electric heater installed in a body at a higher temperature. The net effect would be a flow of heat from a lower temperature to a higher temperature, thereby violating the second (Clausius) form of the second law. Conversely, if the second form were possible, then the heat transferred to the higher temperature could be used to run a heat engine that would convert part of the heat into work. The final result would be a conversion of heat into work at constant temperature—a violation of the first (Kelvin) form of the second law.

Central to the following discussion of entropy is the concept of a heat reservoir capable of providing essentially limitless amounts of heat at a fixed temperature. This is of course an idealization, but the temperature of a large body of water such as the Atlantic Ocean does not materially change if a small amount of heat is withdrawn to run a heat engine. The essential point is that the heat reservoir is assumed to have a well-defined temperature that does not change as a result of the process being considered.

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.

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.

Third Law Of Thermodynamics Examples:

Let us consider steam as an example to understand the third law of thermodynamics step by step:

1. The molecules within it move freely and have high entropy.

2. If one decreases the temperature below 100 °C, the steam gets converted to water, where the movement of molecules is restricted, decreasing the entropy of water.

3. When water is further cooled below 0 °C, it gets converted to solid ice. In this state, the movement of molecules is further restricted and the entropy of the system reduces more.

4. As the temperature of the ice further reduces, the movement of the molecules in them are restricted further and the entropy of the substance goes on decreasing.

5. When the ice is cooled to absolute zero, ideally, the entropy should be zero. But in reality, it is impossible to cool any substance to zero.