CHAPTER 2

Thermodynamics – I

❖ Brief Resume of First and Second Law of Thermodynamics

There are four laws of thermodynamics that define the fundamental physical quantities like temperature, energy, and entropy that characterize thermodynamic systems at thermal equilibrium. These laws describe how these quantities behave under different conditions and rule out the possibility of some phenomena the perpetual motion. The zeroth law of thermodynamics states that If two systems are each in thermal equilibrium with a third system, they are in thermal equilibrium with each other; therefore, this law helps to define the concept of temperature. In this section, we will discuss the elementary ideas and mutual correlation between the first and second laws of thermodynamics.

➢ *First Law of Thermodynamics*

The first law of thermodynamics states that the energy can neither be created nor destroyed, but can be converted from one form to another.

The first law of thermodynamics is obtained on the experimental basis. In other words, we can say that the energy of an isolated system is always constant, which means that whenever some energy disappears from the system, an equal amount of energy in some other form is also produced. In 1847, Helmholtz explained this situation in his famous words, "it is impossible to construct a perpetual machine". The term perpetual machine refers to a device that can work continuously without any energy consumption. Furthermore, we all know that heat is always produced whenever some mechanical work is done. These correlations were studied by Joule (1840 – 1880); and he found that mechanical work is directly proportional to the heat produced. Mathematically, we can say that

$$W \propto Q \quad or\ W = JQ \tag{1}$$

Where J represents the proportionality constant and is called as "Joule's mechanical equivalent of heat". If $Q = 1$, $W = J$; making J as the amount of mechanical work required to produce one calorie of heat. The experimental value for J was found to be 4.184 joules, which is a very popular relation (1 calorie = 4.184 joule). The first law of thermodynamics can also be deduced from the equivalence of heat and work. Suppose there is now an equivalence between the work and heat; and let Q heat is converted into work. Now when the same amount of work is done to produce the heat Q'; considering $Q \neq Q'$, we can say that Q is either greater or less than Q'. This would eventually mean that a certain amount of energy has been destroyed or created in this process, which is against the first law of thermodynamics.

The mathematical formulation of the first law thermodynamics can be obtained from the increase in the internal energy of the system. The internal energy of the system can be increased in two ways; one is doing work on the system, and the second one involves the supply of heat. Suppose that the initial internal energy of the system is E_1, after supplying heat q and doing work w on the system, the final amount of internal energy can be formulated as:

$$E_2 = E_1 + q + w \tag{2}$$

$$E_2 - E_1 = q + w \tag{3}$$

$$\Delta E = q + w \tag{4}$$

$$q = \Delta E - w \tag{5}$$

If the work is done by the system, putting $w = -P\Delta V$ in equation (5), we get

$$q = \Delta E - (-P\Delta V) \tag{6}$$

$$q = \Delta E + P\Delta V \tag{7}$$

The physical significance of the equation (7) is that heat absorbed by a given system is converted work done by the system and to raise its internal energy.

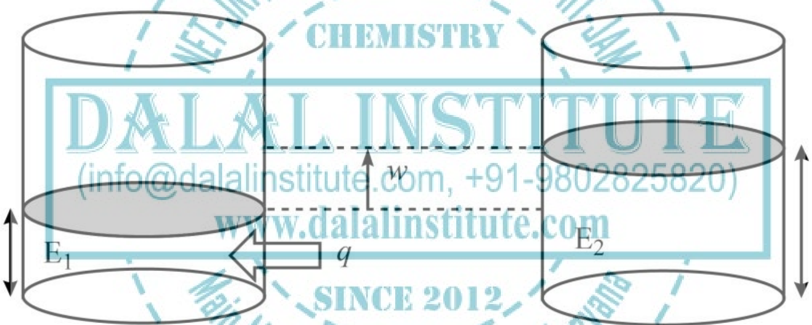

Figure 1. The pictorial representation of the first law of thermodynamics.

It is also worthy to note that the general form of the first law of thermodynamics is applicable only in the case of chemical thermodynamics or physical processes. In 1905, Albert Einstein showed that energy and mass are just the faces of the coin, and can be transformed within each other. In other words, his findings showed that the mass can be converted into energy and the energy can back be converted into mass. Mathematically, the formulation is

$$E = mc^2 \tag{8}$$

Where m is the mass and c is the velocity of light. Since the velocity of light is a very large quantity (so the square), even the small disappearance of mass would generate a huge amount of energy. Such observations are pretty common in case of nuclear reactions and can be neglected here. Therefore, in a broad sense, it is the "law of energy-mass conservation".

➢ ***Second Law of Thermodynamics***

The second law of thermodynamics states that it is impossible to convert the heat completely into work without leaving some effect elsewhere.

The second law of thermodynamics is actually a rational solution to the limitations of the first law. For instance, the first law talks about the exact equivalence between heat and work, but it is quite far from reality. In 1824, a French scientist Sadi Carnot showed that for every heat engine there is an upper limit to the efficiency of conversion of heat to work. In order to illustrate Carnot's conclusion, consider a locomotive engine that is supplied with a certain amount of heat; however, all of that heat will not be used to move the train but a part of it will always be consumed in some other processes like overcoming the friction. Let q_2 be the heat absorbed by the heat engine at temperature T_2, and w is the amount of the work done by the system; while q_1 is the heat returned to the sink at temperature T_1, then the Carnot's formulation can be given as:

$$\eta = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad (9)$$

Where η is the efficiency of the heat engine and is always less than one. Ideally, $\eta = 1$, which means that such a heat engine would convert 100% of the heat absorbed into work.

One more limitation of the first law is that it does not tell about the feasibility of the process, like whether the heat can flow from cold terminal to the hot one or not. It simply talks if the heat gained or heat lost but not the direction of the process. The second law of thermodynamics states that all the spontaneous processes are thermodynamically irreversible. The word "spontaneous" simply means a process that occurs by itself and external drive is required. In other words, we can also say that heat cannot flow from a cold body to hot, the water cannot uphill without any external drive.

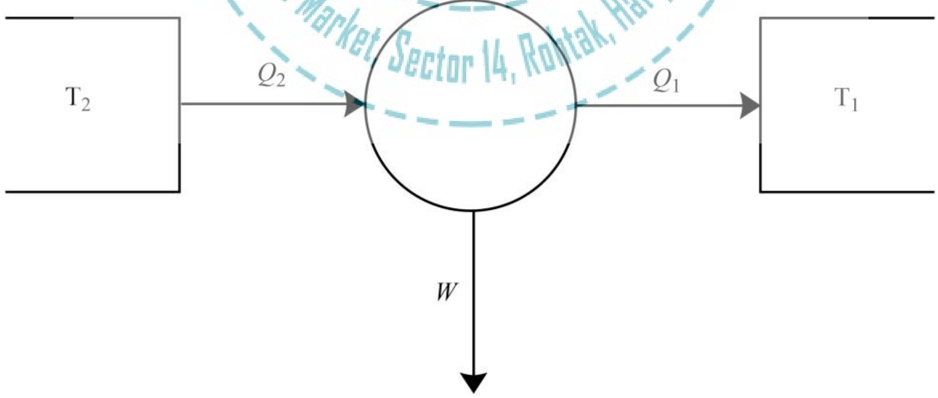

Figure 2. The pictorial representation of the second law of thermodynamics.

The 2nd law of thermodynamics also states that the total entropy of an isolated system can never decline with time; in other words, combined entropy of a system and surroundings remains constant in ideal cases where the system is undergoing a reversible process. In all processes, including spontaneous processes, that occur, the total entropy of the system and surroundings increases and the process is irreversible in the thermodynamic frame. The entropy-increase accounts for the irreversibility of all the natural processes, and the asymmetry between the past and the future. Overall, the 2nd law of thermodynamics can be labeled as an empirical finding that was accepted as a truism of thermodynamic theory. The microscopic origin of the law can be explained by statistical mechanics.

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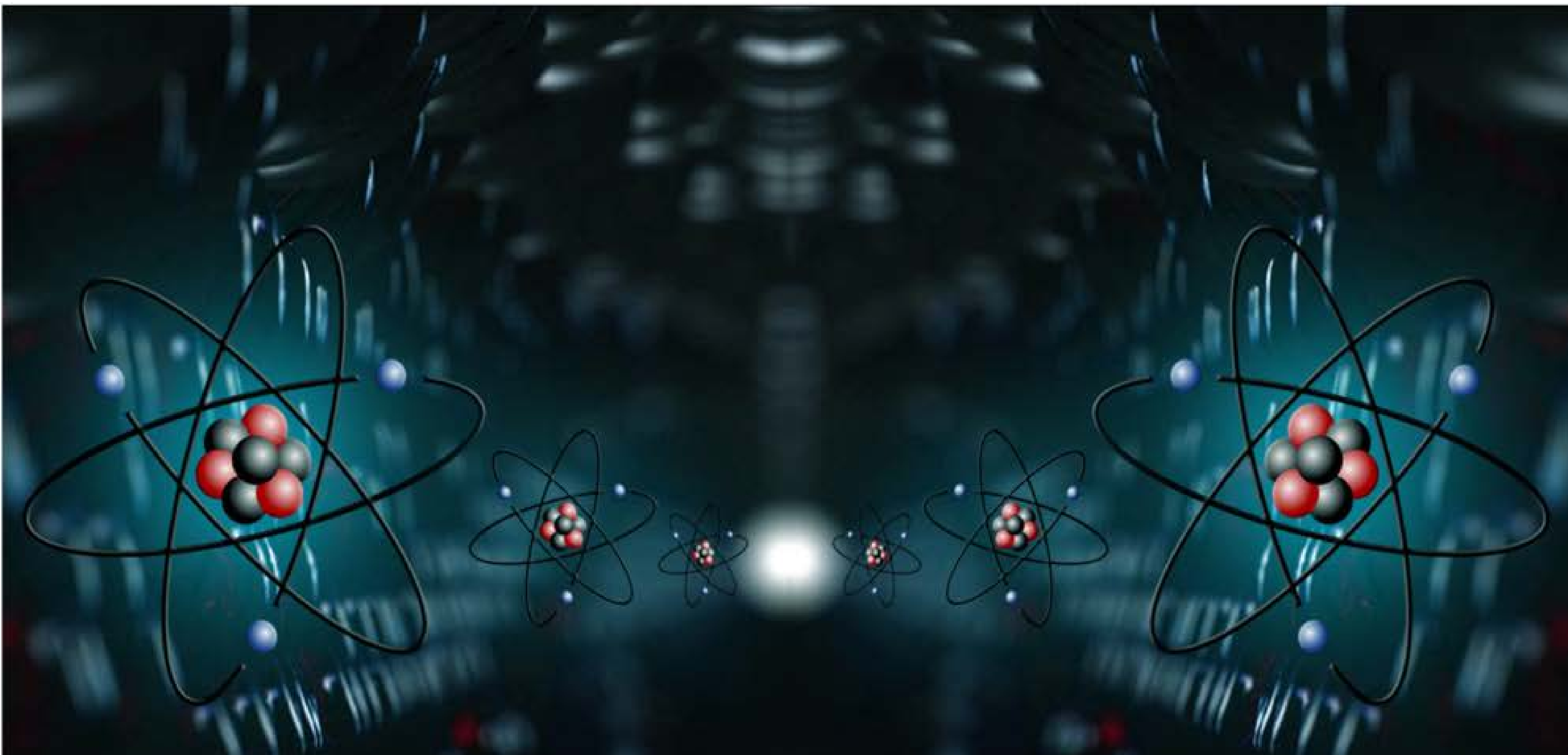

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