

AN INTROCUCTION TO THERMODYNAMICS

Thermodynamics, in general, is concerned with those physical and chemical phenomena which involve heat and temperature. From the practical definition, thermodynamics is the phenomenological theory of converting heat to work and understanding the role of energy and other properties of matter in this conversion process. Equilibrium thermodynamics is confined to the equilibrium states of matter. Change of one equilibrium state to another is infinitely slow and as a result it is independent of time. Concepts of heat, work, energy, and properties of matter exist in public vocabulary of every language. Thermodynamic laws which govern the relations between these concepts originate from ordinary experiences in our daily lives. Statistical thermodynamics, in general, is concerned with the atomic or molecular structure of matter and the relationship between microscopic structure and the macroscopic thermodynamic behavior of substances.

Historically, thermodynamics took its name from the study of efficiency of heat engines by Carnot. In his 1824 thesis Carnot stated that the efficiency of a heat engine depended only on the temperature difference between its heat source and heat sink, and not on the working substance. A decade was passed when Clapeyron developed the relationship between vapor pressure and an unknown function of empirical temperature scale. Clausius later identified this unknown function as the absolute temperature scale. The equation relating the vapor pressure to the absolute temperature is known as the Clausius-Clapeyron equation. It was in 1850 when Clausius published his thesis on the Second Law of thermodynamics which is known as "the Clausius statement." It was this statement that marked the beginning of thermodynamics as a science as it was stated by Gibbs in the late nineteenth century. A year after publication of this thesis, Thomson formulated explicitly the First and Second Laws of thermodynamics. Thomson had already defined an absolute temperature scale in 1848 and was aware of the 1845 publication by Joule in which Joule had demonstrated the equivalence of heat and work.

It was 1865 when Clausius introduced the term "entropy" and stated "The energy of universe is constant. The entropy of universe tends towards a maximum". Introduction of the term entropy resulted in a new formulation of the Second Law by Clausius.

Since the findings of Clausius many other investigators have contributed to the science of thermodynamics. The thesis by Gibbs published in 1875 entitled "On the equilibrium of heterogeneous substances" and his other publications have a special place in thermodynamics of mixtures and phase equilibria. Gibbs extended the science of thermodynamics in a general form to heterogeneous systems with and without chemical reactions. He is also credited for derivation and formulation of completely general equilibrium conditions for various cases. Other early contributors to this branch of thermodynamics are the following: Helmholtz, who in 1882 independent of Gibbs, introduced the concept of free energy and derived the relationship now known as the Gibbs-Helmholtz equation, Duhem, who in 1886, derived the Gibbs-Duhem equation, Planck, who in 1887, divided the changes of state into two classes of thermodynamic processes, namely reversible and irreversible processes, Nerst, who in 1906, published his heat theorem, and Caratheodory, who in 1909, developed a new axiomatic basis of thermodynamics.