

CHAPTER 1

INTRODUCTION

1.1 ORIGINS OF CHEMICAL THERMODYNAMICS

An alert young scientist with only an elementary background in his or her field might be surprised to learn that a subject called “thermodynamics” has any relevance to chemistry, biology, material science, and geology. The term *thermodynamics*, when taken literally, implies a field concerned with the mechanical action produced by heat. Lord Kelvin invented the name to direct attention to the *dynamic* nature of *heat* and to contrast this perspective with previous conceptions of heat as a type of fluid. The name has remained, although the applications of the science are much broader than when Kelvin created its name.

In contrast to mechanics, electromagnetic field theory, or relativity, where the names of Newton, Maxwell, and Einstein stand out uniquely, the foundations of thermodynamics originated from the thinking of over half a dozen individuals: Carnot, Mayer, Joule, Helmholtz, Rankine, Kelvin, and Clausius [1]. Each person provided crucial steps that led to the grand synthesis of the two classic laws of thermodynamics.

Eighteenth-century and early nineteenth-century views of the nature of heat were founded on the principle of conservation of caloric. This principle is an eminently attractive basis for rationalizing simple observations such as temperature changes that occur when a cold object is placed in contact with a hot one. The cold object seems to have extracted something (caloric) from the hot one. Furthermore,

if both objects are constituted of the same material, and the cold object has twice the mass of the hot one, then we observe that the increase in temperature of the former is only half the decrease in temperature of the latter. A conservation principle develops naturally. From this principle, the notion of the flow of a substance from the hot to the cold object appears almost intuitively, together with the concept that the total quantity of the caloric can be represented by the product of the mass multiplied by the temperature change. With these ideas in mind, Black was led to the discovery of specific heat, heat of fusion, and heat of vaporization. Such successes established the concept of caloric so solidly and persuasively that it blinded even the greatest scientists of the early nineteenth century. Thus, they missed seeing well-known facts that were common knowledge even in primitive cultures, for example, that heat can be produced by friction. It seems clear that the earliest of the founders of thermodynamics, Carnot, accepted conservation of caloric as a basic axiom in his analysis [2] of the heat engine (although a few individuals [3] claim to see an important distinction in the contexts of Carnot's uses of "calorique" versus "chaleur").

Although Carnot's primary objective was to evaluate the mechanical efficiency of a steam engine, his analysis introduced certain broad concepts whose significance goes far beyond engineering problems. One of these concepts is the reversible process, which provides for thermodynamics the corresponding idealization that "frictionless motion" contributes to mechanics. The idea of "reversibility" has applicability much beyond ideal heat engines. Furthermore, it introduces continuity into the visualization of the process being considered; hence, it invites the introduction of the differential calculus. It was Clapeyron [4] who actually expounded Carnot's ideas in the notation of calculus and who thereby derived the vapor pressure equation associated with his name as well as the performance characteristics of ideal engines.

Carnot also leaned strongly on the analogy between a heat engine and a hydrodynamic one (the water wheel) for, as he said:

we can reasonably compare the motive power of heat with that of a head of water.

For the heat engine, one needs two temperature levels (a boiler and a condenser) that correspond to the two levels in height of a waterfall. For a waterfall, the quantity of water discharged by the wheel at the bottom level is the same as the quantity that entered originally at the top level, with the work being generated by the drop in gravitational level. Therefore, Carnot postulated that a corresponding thermal quantity, "calorique," was carried by the heat engine from a high temperature to a low one; the heat that entered at the upper temperature level was conserved and exited in exactly the same quantity at the lower temperature, with work having been produced during the drop in temperature level. Using this postulate, he was able to answer in a general way the long-standing question of whether steam was suited uniquely for a heat engine; he did this by showing that in the ideal engine any other substance would be just as efficient. It was also from this construct that Kelvin subsequently realized that one could establish an absolute temperature scale independent of the properties of any substance.

When faced in the late 1840s with the idea of conservation of (heat plus work) proposed by Joule, Helmholtz, and Mayer, Kelvin at first rejected it (as did the Proceedings of the Royal Society when presented with one of Joule's manuscripts) because conservation of energy (work plus heat) was inconsistent with the Carnot analysis of the fall of an *unchanged* quantity of heat through an ideal thermal engine to produce work. Ultimately, however, between 1849 and 1851, Kelvin and Clausius, each reading the other's papers closely, came to recognize that Joule and Carnot could be made concordant if it was assumed that only *part* of the heat entering the Carnot engine at the high temperature was released at the lower level and that the *difference* was converted into work. Clausius was the first to express this in print. Within the next few years, Kelvin developed the mathematical expression $\Sigma Q/T = 0$ for "the second fundamental law of the dynamical theory of heat" and began to use the word *thermodynamic*, which he had actually coined earlier. Clausius's analysis [5] led him, in turn, to the mathematical formulation of $\int dQ/T \geq 0$ for the second law; in addition, he invented the term *entropy* (as an alternative to Kelvin's "dissipation of energy"), for, as he says,

I hold it better to borrow terms for important magnitudes from the ancient languages so that they may be adopted unchanged in all modern languages.

Thereafter, many individuals proceeded to show that the two fundamental laws, explicitly so-called by Clausius and Kelvin, were applicable to all types of macroscopic natural phenomena and not just to heat engines. During the latter part of the nineteenth century, then, the scope of thermodynamics widened greatly. It became apparent that the same concepts that allow one to predict the maximum efficiency of a heat engine apply to other energy transformations, including transformations in chemical, biological, and geological systems in which an energy change is not obvious. For example, thermodynamic principles permit the computation of the maximum yield in the synthesis of ammonia from nitrogen and hydrogen under a variety of conditions of temperature and pressure, with important consequences to the chemical fertilizer industry. Similarly, the equilibrium distribution of sodium and potassium ions between red blood cells and blood plasma can be calculated from thermodynamic relationships. It was the observation of deviations from an equilibrium distribution that led to a search for mechanisms of active transport of these alkali metal ions across the cell membrane. Also, thermodynamic calculations of the effect of temperature and pressure on the transformation between graphite and diamond have generated hypotheses about the geological conditions under which natural diamonds can be made.

For these and other phenomena, thermal and work quantities, although controlling factors, are only of indirect interest. Accordingly, a more refined formulation of thermodynamic principles was established, particularly by Gibbs [6] and, later, independently by Planck [7], that emphasized the nature and use of several special functions or potentials to describe the state of a system. These functions have proved convenient and powerful in prescribing the rules that govern chemical and physical transitions. Therefore, in a sense, the name "energetics" is more descriptive than is

“thermodynamics” insofar as applications to chemistry are concerned. More commonly, one affixes the adjective “chemical” to thermodynamics to indicate the change in emphasis and to modify the literal and original meaning of thermodynamics.

1.2 OBJECTIVES OF CHEMICAL THERMODYNAMICS

In practice, the primary objective of chemical thermodynamics is to establish a criterion for determining the feasibility or spontaneity of a given physical or chemical transformation. For example, we may be interested in a criterion for determining the feasibility of a spontaneous transformation from one phase to another, such as the conversion of graphite to diamond, or the spontaneous direction of a metabolic reaction that occurs in a cell. On the basis of the first and second laws of thermodynamics, which are expressed in terms of Gibbs’s functions, several additional theoretical concepts and mathematical functions have been developed that provide a powerful approach to the solution of these questions.

Once the spontaneous direction of a natural process is determined, we may wish to know how far the process will proceed before reaching equilibrium. For example, we might want to find the maximum yield of an industrial process, the equilibrium solubility of atmospheric carbon dioxide in natural waters, or the equilibrium concentration of a group of metabolites in a cell. Thermodynamic methods provide the mathematical relations required to estimate such quantities.

Although the main objective of chemical thermodynamics is the analysis of spontaneity and equilibrium, the methods also are applicable to many other problems. For example, the study of phase equilibria, in ideal and nonideal systems, is basic to the intelligent use of the techniques of extraction, distillation, and crystallization; to metallurgical operations; to the development of new materials; and to the understanding of the species of minerals found in geological systems. Similarly, the energy changes that accompany a physical or chemical transformation, in the form of either heat or work, are of great interest, whether the transformation is the combustion of a fuel, the fission of a uranium nucleus, or the transport of a metabolite against a concentration gradient. Thermodynamic concepts and methods provide a powerful approach to the understanding of such problems.

1.3 LIMITATIONS OF CLASSIC THERMODYNAMICS

Although descriptions of chemical change are permeated with the terms and language of molecular theory, the concepts of classic thermodynamics are independent of molecular theory; thus, these concepts do not require modification as our knowledge of molecular structure changes. This feature is an advantage in a formal sense, but it is also a distinct limitation because we cannot obtain information at a molecular level from classic thermodynamics.

In contrast to molecular theory, classic thermodynamics deals only with measurable properties of matter in bulk (for example, pressure, temperature, volume, cell potential,

magnetic susceptibility, and heat capacity). It is an empirical and phenomenological science, and in this sense, it resembles classic mechanics. The latter also is concerned with the behavior of macroscopic systems, with the position and the velocity of a body as a function of time, without regard to the body's molecular nature.

Statistical mechanics (or *statistical thermodynamics*) is the science that relates the properties of individual molecules and their interactions to the empirical results of classical thermodynamics. The laws of classic and quantum mechanics are applied to molecules; then, by suitable statistical averaging methods, the rules of macroscopic behavior that would be expected from an assembly of many such molecules are formulated. Because classical thermodynamic results are compared with statistical averages over very large numbers of molecules, it is not surprising that fluctuation phenomena, such as Brownian motion, the "shot effect," or certain turbidity phenomena, cannot be treated by classical thermodynamics. Now we recognize that all such phenomena are expressions of local microscopic fluctuations in the behavior of a relatively few molecules that deviate randomly from the average behavior of the entire assembly. In this submicroscopic region, such random fluctuations make it impossible to assign a definite value to properties such as temperature or pressure. However, classical thermodynamics is predicated on the assumption that a definite and reproducible value always can be measured for such properties.

In addition to these formal limitations, limitations of a more functional nature also exist. Although the concepts of thermodynamics provide the foundation for the solution of many chemical problems, the answers obtained generally are not definitive. Using the language of the mathematician, we might say that classical thermodynamics can formulate *necessary* conditions but not *sufficient* conditions. Thus, a thermodynamic analysis may rule out a given reaction for the synthesis of some substance by indicating that such a transformation cannot proceed spontaneously under any set of available conditions. In such a case, we have a definitive answer. However, if the analysis indicates that a reaction may proceed spontaneously, no statement can be made from classical thermodynamics alone indicating that it will do so in any finite time.

For example, classic thermodynamic methods predict that the *maximum* equilibrium yield of ammonia from nitrogen and hydrogen is obtained at low temperatures. Yet, under these optimum thermodynamic conditions, the rate of reaction is so slow that the process is not practical for industrial use. Thus, a smaller equilibrium yield at high temperature must be accepted to obtain a suitable reaction rate. However, although the thermodynamic calculations provide no assurance that an equilibrium yield will be obtained in a finite time, it was as a result of such calculations for the synthesis of ammonia that an intensive search was made for a catalyst that would allow equilibrium to be reached.

Similarly, specific catalysts called enzymes are important factors in determining what reactions occur at an appreciable rate in biological systems. For example, adenosine triphosphate is thermodynamically unstable in aqueous solution with respect to hydrolysis to adenosine diphosphate and inorganic phosphate. Yet this reaction proceeds very slowly in the absence of the specific enzyme adenosine triphosphatase. This combination of thermodynamic control of direction and enzyme control of rate makes possible the finely balanced system that is a living cell.

In the case of the graphite-to-diamond transformation, thermodynamic results predict that graphite is the stable allotrope at a fixed temperature at all pressures below the transition pressure and that diamond is the stable allotrope at all pressures above the transition pressure. But diamond is not converted to graphite at low pressures for kinetic reasons. Similarly, at conditions at which diamond is the thermodynamically stable phase, diamond can be obtained from graphite only in a narrow temperature range just below the transition temperature, and then only with a catalyst or at a pressure sufficiently high that the transition temperature is about 2000 K.

Just as thermodynamic methods provide only a *limiting value* for the yield of a chemical reaction, so also do they provide only a limiting value for the work obtainable from a chemical or physical transformation. Thermodynamic functions predict the work that may be obtained if the reaction is carried out with infinite slowness, in a so-called reversible manner. However, it is impossible to specify the actual work obtained in a real or natural process in which the time interval is finite. We can state, nevertheless, that the real work will be less than the work obtainable in a reversible situation.

For example, thermodynamic calculations will provide a value for the *maximum* voltage of a storage battery—that is, the voltage that is obtained when no current is drawn. When current is drawn, we can predict that the voltage will be less than the maximum value, but we cannot predict how much less. Similarly, we can calculate the *maximum* amount of heat that can be transferred from a cold environment into a building by the expenditure of a certain amount of work in a heat pump, but the actual performance will be less satisfactory. Given a nonequilibrium distribution of ions across a cell membrane, we can calculate the *minimum* work required to maintain such a distribution. However, the actual process that occurs in the cell requires much more work than the calculated value because the process is carried out irreversibly.

Although classical thermodynamics can treat only limiting cases, such a restriction is not nearly as severe as it may seem at first glance. In many cases, it is possible to approach equilibrium very closely, and the thermodynamic quantities coincide with actual values, within experimental error. In other situations, thermodynamic analysis may rule out certain reactions under any conditions, and a great deal of time and effort can be saved. Even in their most constrained applications, such as limiting solutions within certain boundary values, thermodynamic methods can reduce materially the amount of experimental work necessary to yield a definitive answer to a particular problem.

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