

THERMODYNAMIC SYSTEMS AND STATE FUNCTIONS

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Summary

In this article, the most relevant thermodynamic functions are introduced, as well as the three fundamental laws of thermodynamics and the most important relationships existing among these functions. The approach followed to derive all these thermodynamic relationships is the axiomatic one, through which the three fundamental laws are stated. The thermodynamic functions examined here are internal energy, enthalpy, entropy, heat capacity, and Gibbs and Helmholtz free energies, as well as the partial molar functions, such as the chemical potential. Applications to thermodynamic cyclic transformations are also presented. In addition, all the differential

expressions are derived as a function of pressure and temperature, suitable for the calculations of all the state functions above.

1. Introduction and Historical Perspectives

The common definition of thermodynamics is “the science that deals with the transformations of heat into mechanical work and the opposite ones that transform mechanical work into heat.” Obviously, when chemical systems are of interest, other forms of work can be taken into account besides the purely mechanical one, such as electrical or chemical ones. On a more general basis, thermodynamics deals with transformations of systems, establishing relations between the initial status of the system before its transformation starts and the final one reached at the end of the considered transformation. No limitations are applied to the transformations that can occur—both spontaneous or forced ones by a transfer of heat, mass, or work from and to the external surroundings can be considered.

In a classical framework and from a macroscopic point of view, the time evolution of systems is examined by means of the definition of several functions called the “state functions,” representing averaged microscopic properties of the system. Moreover, the fundamental laws are assumed as postulates based on experimental evidence, and conclusions are derived from them without entering into the microscopic description of the involved phenomena. The advantage of this classical procedure is the possibility of deriving highly accurate relationships among the different state functions in a quite simple mathematical framework. Obviously, nowadays the description of any chemical system’s transformation without any reference to the molecular scale is somewhat unsatisfactory, and thus it is often important to complete the classical thermodynamics results with their microscopic explanation. The link between macroscopic and microscopic descriptions is the object of statistical thermodynamics. Then, for example, the state-function temperature—macroscopic description—can be viewed as the average velocity of the species constituting the system. Again, the state-function pressure can be linked to the number of collisions between the species at the atomic scale and the walls surrounding the system. The above examples evidence what is in general true—a meaning in terms of the microphysical world can always be associated with all the state functions and the relationships among them (see *Statistical Thermodynamics*).

In this section, the system transformations and the relationships among the different state functions will be derived in a classical framework without the link to the atomic world. All these relationships can then be derived from only three postulates called the three fundamental laws of thermodynamics. The first one deals with the conservation of energy. The second one deals with the existing limitation of the transformations between heat and work, and in general to the direction of spontaneous transformations. Finally, the third one is related to the absolute value of the state functions’ entropy (see *Energy Balance of Reacting Systems* and *Statistical Thermodynamics*).

Historically, classical thermodynamics was mostly developed during the nineteenth century. Actually, the second law was developed before the first one, while the third one was stated only at the beginning of the twentieth century. The story started with the invention of the steam engine by James Watt in 1769, and dealt with the practical

transformation of heat into mechanical work. It was clear almost immediately that such a transformation has some limitations and that the entire amount of heat could not be converted into work. The efficiency of such a transformation was first stated in 1824 by a young engineer named Sadi Carnot, from whom the two classical enunciations of the second law can be derived. These two equivalent postulates were enunciated by William Thomson (Lord Kelvin) and Rudolf J.E. Clausius. It is interesting to note that the second law could still be stated without an understanding of the physical nature of heat. These studies and the extension of the energy conservation law to heat were defined between 1840 and 1848, notably in the works of Julius Robert von Mayer, James Prescott Joule, and Hermann von Helmholtz. The first postulate for the third law was stated by Walther Nernst in 1906, in the form of a theorem whose meaning was extended by Max Planck by linking entropy to its microphysical meaning. Despite this, it is of interest that the first fully satisfactory enunciation for the third law was the one reported in 1926 by Gilbert Newton Lewis and Merle Randall in their fundamental textbook.

Besides the formulation of the three fundamental laws, many state functions typical of thermodynamics were introduced in the meantime. For example, entropy was introduced by Rudolf Clausius in 1855 during the reformulation of the second law enunciation. Enthalpy was defined as heat content at constant pressure during the development of thermochemistry by Germain Henri Hess and Hermann von Helmholtz in the years 1840–1869. Finally, the free energies were named in honor of Josiah Willard Gibbs and Hermann von Helmholtz (see *History of Chemistry and Energy Balance of Reacting Systems*). Some of the scientists mentioned above are illustrated in Figure 1.

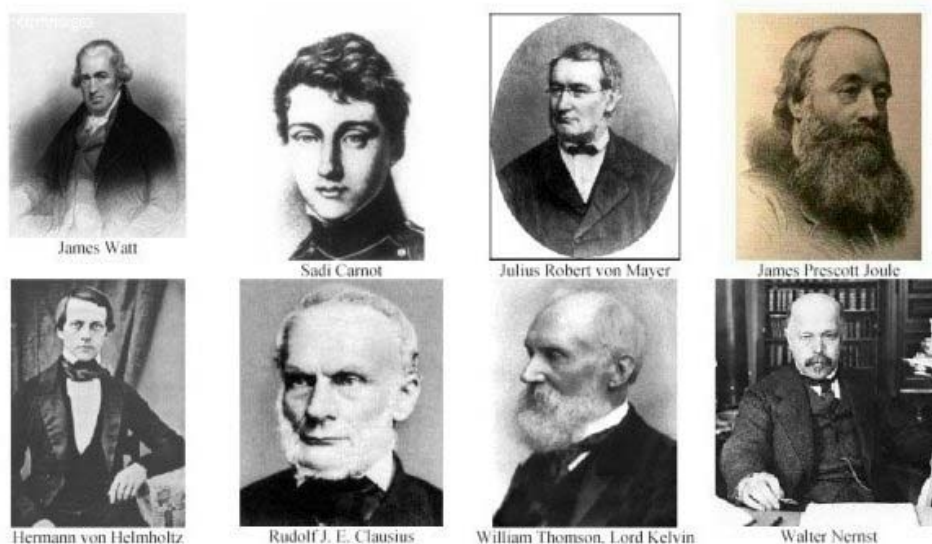


Figure 1. Scientists whose work was relevant to the development of the three fundamental laws of thermodynamics

2. Thermodynamic Systems

A “thermodynamic system” is a part of the physical world constituted by a significantly large number of particles (i.e., atoms or molecules). Examples are the gases, liquids, and

solids, and their mixtures. The system is divided by what is called the “external ambient” or the “surroundings” by means of a well-defined boundary surface. These boundaries can be permeated or not by streams of mass, heat, and work. If any streams are not allowed, then the system is called “isolated.” Accordingly, a system can be described as depicted in Figure 2 where the boundary surfaces are open to the exchange of mass, heat, and work with the surroundings. A system like this is called “open.” Generally, the features of the walls surrounding the systems define the constraints existing on the system. Thus, a wall that inhibits or allows the exchange of heat is called “adiabatic” or “diathermal,” respectively, while one that inhibits the exchange of mechanical work is called “rigid.” A classification of the thermodynamic systems as a function of their interaction with their surroundings is summarized in Table 1.

System type	Exchange of mass	Exchange of heat	Exchange of work
open	yes	yes	yes
closed	no	yes	yes
thermally isolated	no	no	yes
isolated	no	no	no

Table 1. Classification of thermodynamic systems

The state of a system is completely defined from a mechanical point of view when the position and the velocity of any mass point of the system are known at a given instant of time. Thus, for a system formed by a number NP of mass points, $6NP$ variables should be known (i.e., three velocity components and three coordinates). If a system constituted by a large numbers of points, such as a chemical one, is examined, the mechanical approach immediately evidences its limits. Hence, the classical thermodynamic approach introduces a simpler concept for the state of a system, given that it is identified through functions representing average properties. Then, the detailed knowledge of the motion of each mass point (e.g., molecules or atoms) would be superfluous.

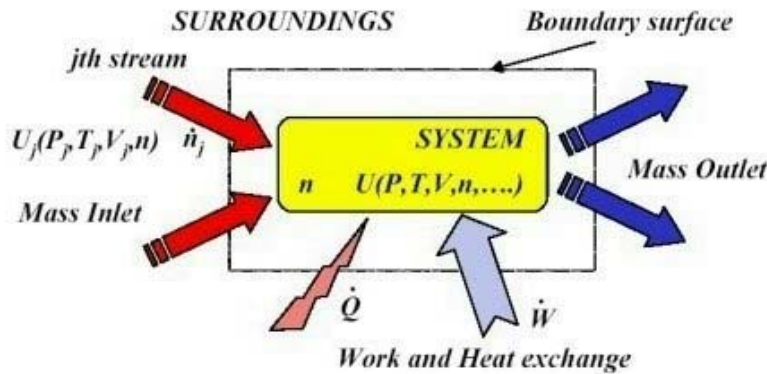


Figure 2. Sketch of a system open to exchange of work, heat, and mass through its boundaries

The particular condition where all the macroscopic properties of the system are known is defined as the “state of the system.” These macroscopic properties are defined through a series of measurable parameters or functions called “state functions” or “state variables.” Such functions can be defined as “extensive” or “intensive” ones. The extensive functions are additive, and among them the system volume V , its mass m , and the number of moles n_i of each species constituting the system can be mentioned. The intensive functions are not additive and their value can be different in any point of the system. Temperature T , pressure P , and the concentration C_i of the different species are significant examples. All the state functions here mentioned can be directly measured—the temperature through a thermometer, the pressure through a barometer, the composition through analytical methods, and the volume through the comparison with some linear lengths. Actually, the system geometry is characterized not only by the volume but also by its shape. However, most thermodynamic properties are largely independent from the shape, which becomes important only when the specific surface (i.e., surface per unit volume) is very large, such as in the dispersed systems.

For a given amount of the substance contained in the system, temperature, volume, and pressure are not independent one from the another. They are connected by a relationship of the general form:

$$\Phi(P, V, T) = 0 \quad (1)$$

which is called the “equation of state.” Generally, the form of the equation of state depends on the properties of the considered substance. Examples of equation of states are the ideal gas law, the Van der Waals equation for real gases and liquids, and all the other cubic-type equations, such as the Redlich–Kwang–Soave and the Peng–Robinson ones (see *Equilibrium in Multiphase Reacting Systems*). In any case, the main consequence is that any one of the three variables can be calculated as a function of the other two by solving Eq. (1) with respect to the given variable. Accordingly, the state of the system is determined completely by any two of the three state functions P , V , and T . Obviously, if multicomponent systems are examined, the concentrations of the different species are also part of the set of state functions needed for defining the system status.

Among all the possible states of a system, of particular importance are the “states of equilibrium.” These states have the property of remaining steady if the external conditions are unchanged. Furthermore, of particular interest are the transformations where the system evolves throughout a succession of states of equilibrium. These transformations are called “reversible.” Practically, a reversible transformation can be realized by modifying very slowly the external conditions to allow the system to gradually adjust itself to the altered conditions. Thus, these transformations can be regarded as infinitely slow ones.

A homogeneous part of the system is called a “phase.” A heterogeneous system is constituted by two or more phases. Furthermore, the passage through the interface among two phases leads to a discontinuous variation of one or more intensive functions, such as density or concentrations. Often thermodynamic systems are heterogeneous. In that case, each phase can be considered as an open system because through the interfaces both exchanges of mass and energy are possible.

Thermodynamics establishes suitable relationships between state functions in the framework of its three fundamental laws. These relationships can then be adopted to define the state of the system and its eventual transformations, as conceptually depicted in Figure 3.

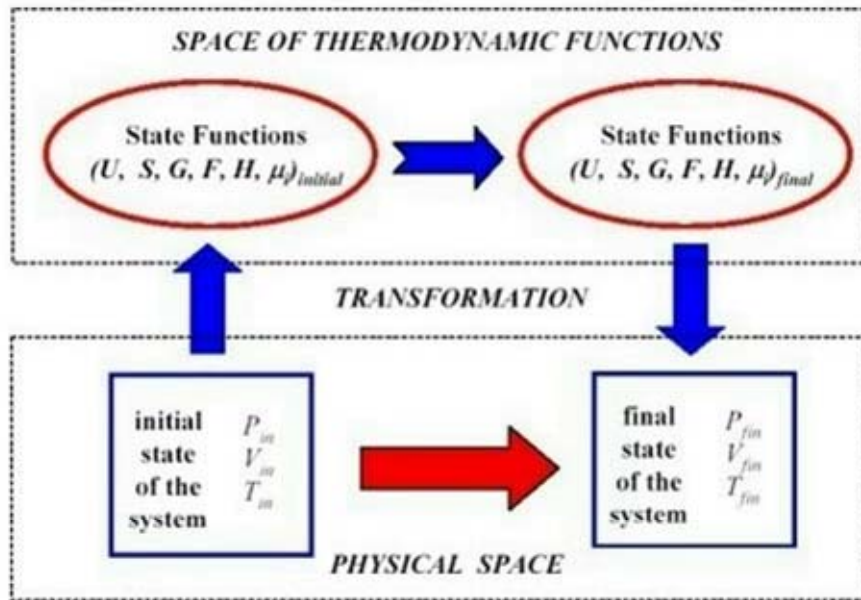


Figure 3. Conceptual sketch of classical thermodynamics framework. The transformations occurring to thermodynamic systems can be described in the space of thermodynamic functions by means of suitable relationships among state functions.

Because thermodynamics deals with the mutual transformations of heat and work, and their exchange between the system and the surroundings, it is necessary to define how such exchanges of energy can be related to the variation of some system properties. In particular, energy can be transferred to a system by altering some of its macroscopic physical properties, as, for example, its volume or surface. Such an exchange of energy is called work. Different forms of work can be identified in transformations of thermodynamic systems, and they can be always be expressed as the product of an intensive function by the differential of an extensive one, as illustrated in Table 2.

	Intensive function: X	Extensive function: y	Work: $\delta W = Xdy$
surface work	surface tension, σ	area, A	$\delta W = \sigma dA$
mechanical work	pressure, P	volume, V	$\delta W = -PdV$
electric work	electric potential, Ψ	electric charge, q	$\delta W = \Psi dq$

Table 2. Examples of different forms of work

In all the expressions summarized in Table 2 the work is assumed to be positive if entering into the system, in agreement with the sign convention illustrated in Figure 2. The main macroscopic difference between heat and work is that heat transfers energy directly into the atomic or molecular coordinates of the system without any macroscopic variation of the extensive functions: volume, surface, and electric charge.

3. Internal Energy and First Law of Thermodynamics

The internal energy U of a system represents the sum of the energy terms applicable to the motion and to the mutual interaction of the atoms or molecules constituting the system. As a type of energy, internal energy is also an extensive function, and then its value is proportional to the number of moles contained in the system through the specific value per unit mole:

$$U = n_t \cdot \tilde{U} \quad \text{mol} \cdot \frac{\text{J}}{\text{mol}} \quad (2)$$

To enhance the tutorial aspects of this contribution, in the equation above and in those that follow, the units and dimensions of the involved functions will also be indicated—on the right-hand side of the equation.

From a macroscopic point of view, the internal energy change can be measured in an adiabatic transformation (e.g., without any heat exchange) by measuring the mechanical work exchanged by the system with its surroundings. If a more general transformation of the system is considered, such as a transformation where both heat and work are exchanged by the system with its surroundings, the traditional formulation of the first law of thermodynamics can be obtained:

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = W + Q \quad (3)$$

where the symbol Δ is adopted to indicate the variation of a state function between the initial and the final state of the considered transformation. Eq. (3) represent the conservation of energy for a macroscopic system; closed to the exchange of mass, but open to the exchange of energy in any form. Here, only the contribution of internal energy to the overall system energy has been considered, because the contributions of kinetic and potential energies are usually negligible in thermodynamic systems. Furthermore, all the energy terms entering the system have been assumed conventionally with positive sign (see *Energy Balance of Reacting Systems*). In differential form (i.e., considering an infinitesimal transformation) Eq. (3) becomes:

$$dU = d^*Q + d^*W \quad (4)$$

Here a different notation has been adopted for exact and for not-exact differentials. The former type is indicated here with the symbol d , while the latter one is indicated with the symbol d^* . It is important to remark that the integration of an exact differential does not depend on the particular pathway followed, but only from the initial and final value of the considered function. On the contrary, the integration of not-exact differentials

depends on the particular path followed. If work can be exchanged only in term of the mechanical one (i.e., $d^*W = -PdV$), Eq. (4) can be written as:

$$dU = d^*Q - PdV \quad (5)$$

In the following, the first law will always be expressed by means of Eqs. (4) or (5).

Eq. (5) can also be adopted to define a new state function representative of the heat exchanged at constant pressure. Such a function is called enthalpy H and is defined as follows:

$$H = U + PV \quad (6)$$

Being a linear combination of two extensive functions, enthalpy is also an extensive function, and thus its value can always be expressed through the product of its specific value, as follows:

$$H = \tilde{H} \cdot n_t \quad mol \cdot \frac{J}{mol} \quad (6b)$$

Accordingly, by combining Eqs. (5) and (6) it is straightforward to demonstrate the assertion stated above:

$$d^*Q_p = dU + PdV = d_p(U + PV) = dH \quad (7)$$

where the subscript p indicates transformations at constant pressure. It is important to note that at constant pressure, the differential of heat becomes exact, being coincident with the variation of the state function enthalpy.

In a transformation at constant volume the heat exchanged corresponds directly to the system internal energy change:

$$d^*Q_v = dU \quad (8)$$

where the subscript v indicates transformations at constant volume. Again, the differential of heat becomes exact, being coincident with the variation of the state function internal energy.

The experimental measurement of the heat exchanged at constant pressure or volume is the field of calorimetry, where different instruments—known as calorimeters—are adopted to perform the desired measurements (see *Energy Balance in Reacting Systems*).

An additional important property of a system is its “thermal capacity,” that is, by definition the ratio between the infinitesimal amount of heat exchanged and the differential temperature change of the system during the transformation. Generally, the

thermal capacity is different depending if the system is heated at constant pressure or at constant volume, being the two thermal capacities indicated as C_p or C_v , respectively. Usually, these values are also referred to the specific amount of mass or moles contained in the system. The thermal capacity referred to the unit amount of mass is called “specific heat,” while “thermal capacity” usually indicates the molar quantity. Accordingly, by the above definition and by Eqs. (7) and (8):

$$\tilde{C}_v = \left(\frac{d\tilde{Q}}{dT} \right)_v = \left(\frac{d\tilde{U}}{dT} \right)_v = \left(\frac{\partial \tilde{U}}{\partial T} \right)_v \quad (9)$$

$$\tilde{C}_p = \left(\frac{d\tilde{Q}}{dT} \right)_p = \left(\frac{d\tilde{H}}{dT} \right)_p = \left(\frac{\partial \tilde{H}}{\partial T} \right)_p \quad (10)$$

where the superscript \sim is used to indicate the molar quantities. In the following, to keep a simpler notation no superscripts will be used. This choice does not alter the validity of the equations derived below; they remain valid and in the same form for both overall variables—molar and even mass ones.

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Biographical Sketch

Maurizio Masi, born in 1960, is Professor in Applied Physical Chemistry at the Department of Chimica, Materiali e Ingegneria Chimica of Politecnico di Milano, Italy. His activity is centered on reaction kinetics and chemical reaction engineering, on the study of production processes for advanced inorganic materials for microelectronics, optics and optoelectronics, and, generally, on the simulation of the chemical and physico-chemical processes and separation processes. In 1992 he was Visiting Scientist at the Massachusetts Institute of Technology, USA. He has co-authored about 100 scientific papers on the above topics.

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