2. THE POSTULATES OF EQUILIBRIUM THERMODYNAMICS

A thermodynamic system is characterized in terms of its extensive properties. In addition to the directly measurable extensive parameters such as the volume, \( V \), or the mole number, \( N \), complete characterization requires two additional extensive thermodynamic parameters, the internal energy, \( U \), and the entropy, \( S \). These are not measurable directly and are introduced through postulates. Three additional postulates complete the postulatory basis upon which the discussion of equilibrium thermodynamics in this text is based.

2.0 Chapter Contents

2.1 Existence of an Internal Energy – POSTULATE I
2.2 Additivity of the Internal Energy
2.3 Path Independence of the Internal Energy
2.4 Conservation of the Internal Energy – POSTULATE II
2.5 Transfer of Internal Energy: Work, Mass Action, and Heat
2.6 Heat as a Form of Energy Exchange—The First Law of Thermodynamics
2.7 Heat Exchanged with the Surroundings and Internally Generated Heat
2.8 Measurability of Changes in Internal Energy
2.9 Measurability of the Heat Flux
2.10 Measurability of the Mass Action
2.11 Infinitesimal Change in Work
2.12 Infinitesimal Change in Mass Action
2.13 Insufficiency of the Primitive Extensive Parameters
2.14 Existence of Entropy – POSTULATE III
2.15 Additivity of the Entropy
2.16 Path Independence of the Entropy
2.17 Non-Conservation of Entropy – POSTULATE IV
2.18 Dissipative Phenomena
2.19 Infinitesimal Change in Heat
2.20 Special Nature of Heat as a Form of Energy Exchange
2.21 Limit of Entropy – POSTULATE V — The Third Law of Thermodynamics
2.22 Monotonic Property of the Entropy
2.23 Significance of the Concept of Entropy

2.1 Existence of an Internal Energy – POSTULATE I

Postulate I asserts that:

"For any thermodynamic system there exists a continuous, differentiable, single-valued, first-order homogeneous function of the extensive parameters of the system, called the internal energy, \( U \), which is defined for all equilibrium states".

2.2 Additivity of the Internal Energy

Being a function of the extensive parameters of the system, the internal energy is itself extensive and is therefore additive over the subsystems of a composite system.
2.3 Path Independence of the Internal Energy

Being defined for all equilibrium states, the internal energy is a function of state or state function (§ 1.14). A change in internal energy therefore depends solely on the difference between the values of $U$ in the final and initial states and is independent of the path along which the system has been led between these states. A finite change, $\Delta U$, is thus given by

$$\Delta U = \int_{U_i}^{U_f} dU = U_f - U_i$$  (2.3)

where the subscripts $f$ and $i$ refer to the final and initial states, respectively. It further follows that $dU$, an infinitesimal change in $U$, is an exact differential (see Appendix 1).

2.4 Conservation of the Internal Energy – POSTULATE II

Postulate II claims that:

"In an isolated composite system the total change in internal energy over all subsystems involved in the change is zero."

Mathematically this is expressed by the relation

$$\Delta U_{\text{Total}} = 0.$$  (2.4)

Postulate II asserts the conservation of energy. According to this postulate, in an isolated system energy can neither be destroyed nor created. Clausius (1850) stated this in the words: 'Die Energie der Welt ist konstant' (The energy of the universe is constant).

2.5 Internal Energy Transfer: Work, Mass Action, and Heat

Equilibrium thermodynamics is concerned with the transfer, or exchange, of energy in quasistatic processes. In this text energy transferred to the system is positive, and energy transferred from the system is negative.

Work is the change in the internal energy of a non-reactive thermodynamic system resulting from the performance of physical work either on or by the system while it is isolated from its surroundings by adiabatic impermeable walls.

Mass action manifests itself in two distinct ways in a thermodynamic system. In an open system it is the change in internal energy resulting from a transfer of matter into or out of the system while it is enclosed by adiabatic rigid walls. In a closed system it is the change in internal energy resulting from a change in the composition of matter while the system is confined between adiabatic, rigid, and impermeable walls.

Heat is the change in the internal energy of a non-reactive thermodynamic system resulting from the transfer of energy to or from the system in a quasistatic process while the system is isolated from its surroundings by rigid impermeable walls.

Work, mass action, and heat are not functions of state. Because they are process functions (cf. § 1.14), elemental changes in these quantities are inexact differentials. We denote an inexact differential by $\delta$ instead of $d$ (see Appendix 1).
2. THE POSTULATES OF EQUILIBRIUM THERMODYNAMICS

2.6 Heat as a Form of Energy Exchange—The First Law of Thermodynamics

An increase in the internal energy, \( \Delta U \), of a system, not in motion, is equal to the energy transferred to it in the form of (physical) work, \( W \), mass action, \( M \), or heat, \( Q \). A finite change in \( U \) is therefore given by

\[
\Delta U = W + M + Q, \tag{2.6}_1
\]

while an elemental change becomes

\[
dU = \delta W + \delta M + \delta Q. \tag{2.6}_2
\]

Equations (2.6) represent the principle of the conservation of energy in thermodynamics. They extend the scope of the principle as formulated in mechanics to include heat as a form of energy transfer and are commonly considered to constitute mathematical expressions of the First Law of Thermodynamics (cf. §7.16).

The equations clarify the meaning of path in §2.3 and, hence, the meaning of the term process function and function of state (§1.14). The same change in internal energy will result if the change in any of the quantities \( W, M, Q, \) or \( \delta W, \delta M, \delta Q \), is exactly compensated by an equivalent change in either or both of the other two. Since the way in which this can be achieved is arbitrary, a final state can be reached from a given initial state along a variety of paths.

2.7 Heat Exchanged with the Surroundings and Internally Generated Heat

Apart from heat, \( Q \), that is imparted to, or is abstracted from, the system, i.e., the heat exchanged between the system and its surroundings, there is another form of heat, \( Q' \), that is not transferred into or out of the system but is generated in its interior as a result of the unavoidable energy dissipation in real physical, i.e., irreversible, processes.

Clausius (1850) who introduced the concept, called \( Q' \) the 'uncompensated heat' because it is not 'compensated' for in the surroundings of the system by a commensurate change in heat. It would more fittingly be called 'heat generated irreversibly in the interior of the system'. Since this expression is too unwieldy, we shall call it simply the internally generated heat. This heat is always produced at a finite rate and, hence, is not quasistatic. It is always positive and vanishes only in reversible processes (cf. Chapter 5). In the thermodynamics of irreversible processes an attempt is made to determine it quantitatively (cf. Part II). In equilibrium thermodynamics it plays only a subordinate qualitative role.

2.8 Measurability of Changes in Internal Energy

The internal energy, \( U \), cannot be measured directly. However, only changes in internal energy are of concern in thermodynamics and these changes can be measured by physical means. The measurability of changes in internal energy follows from Eq. (2.6)_1 and, hence, ultimately from Postulate II upon which the equation rests. For a non-reactive thermodynamic system of constant composition, enclosed by an adiabatic, impermeable wall, Eq. (2.6)_1 reduces to \( \Delta U = W \). Now, the physical work, \( W \), can be measured by physical means and, given two equilibrium states, \( A \) and \( B \), it is always possible to carry the system either from state \( A \) to state \( B \), or from state \( B \) to state \( A \), by some physical process while the system is enclosed by adiabatic impermeable walls (Joule 1847, 1849). Hence,
\( \Delta U \) can be determined by measuring the work, \( W \), done in the process under the stated conditions.

2.9 Measurability of the Heat Flux

By Eq. (2.6), in any process, the heat flux\(^1\) to or from a system enclosed by impermeable walls is equal to the change in internal energy diminished by any work done in the process. Since both \( \Delta U \) and \( W \) can be measured, so then can \( Q \). A device which measures heat fluxes is called a calorimeter. The heat evolved or absorbed in a system undergoing chemical reactions can also be determined calorimetrically (cf. § 21.6).

2.10 Measurability of the Mass Action

In a closed system mass action results from a change in composition within an isolated system. Since the system is isolated, \( \Delta U = 0 \), and, by Eq. (2.6), the mass action term becomes

\[
\mathcal{M} = -W - Q. \tag{2.10}
\]

If volume change is the only work, this can be determined, and the heat can be measured in a calorimeter. If volume change is not the only work, the mass action can still be measured in principle although it may be difficult to devise a suitable experimental arrangement.

The mass action representing the change in internal energy resulting from a flow of matter either to or from an open system is quite another matter. The flow of matter is an inherently irreversible process. Matter always transports with it a certain amount of energy. In isothermal diffusion in the steady state the energy transported per mole of matter, the so-called energy of transport, may be obtained, at least in principle, from measurements of the heat of transport if the molar enthalpy of the fluid is known. A fuller discussion of this topic must, however, be deferred until the concepts of the energy of transport and the heat of transport have been properly introduced in Part II. It will be taken up again in § 29.5.

2.11 Infinitesimal Change in Work

When only rigid barriers are lifted in a composite system, the infinitesimal change in internal energy equals the infinitesimal change in work and is given by

\[
dU = \delta W = \sum_k \left. \frac{\partial U}{\partial X_k} \right|_{X(\neq X_k)} dX_k \quad (k = 1, 2, \ldots, r) \tag{2.11}
\]

where the \( X_k \) are the extensive primitive (i.e., observable or measurable) parameters of the system excluding the mole numbers, and \( X \) denotes the totality of all extensive parameters.

\(^1\) The terms 'heat' and 'heat flux' may generally be used interchangeably.
2.12 Infinitesimal Change in Mass Action

When only impermeable barriers are lifted in a non-reactive composite system, the infinitesimal change in internal energy equals the infinitesimal change in mass action and is given by

$$dU = \delta M = \sum_k \left. \frac{\partial U}{\partial X_k} \right|_{X(\neq N_k)} dN_k$$  \hspace{1cm} (2.12)

where the $N_k$ are the $k$th mole numbers and $X$ is again the totality of all extensive parameters.

2.13 Insufficiency of the Primitive Extensive Parameters

The primitive, i.e., the directly measurable, extensive parameters, $X_k$, of a thermodynamic system are insufficient to determine the infinitesimal change in internal energy when an adiabatic constraint is lifted, because none of them is an extensive parameter of heat.

Temperature is the intensive parameter of heat. The recognition that energy can always be factored into the product of an extensive and an intensive parameter (cf. § 1.5) allows us to introduce the required extensive parameter of heat simply through a postulate.

2.14 Existence of Entropy – POSTULATE III

Postulate III states that:

"For any thermodynamic system there exists a continuous, differentiable, single-valued, first-order homogeneous function of the extensive parameters of the system, called the entropy, $S$, which is defined for all equilibrium states and which is the extensive parameter of heat."

2.15 Additivity of the Entropy

Being a function of the extensive parameters of the system, the entropy is itself extensive and is therefore additive over the subsystems of a composite system.

2.16 Path Independence of the Entropy

Being defined for all equilibrium states, the entropy is a state function. A change in entropy therefore depends solely on the difference between the values of $S$ in the final and initial states and is independent of the path along which the system has been led between these states. A finite change, $\Delta S$, is therefore given by

$$\Delta S = \int_{S_i}^{S_f} dS = S_f - S_i$$  \hspace{1cm} (2.16)

where the subscripts $f$ and $i$ again refer to the final and initial states. It follows further that $dS$, an infinitesimal change in $S$, is an exact differential (see Appendix 1).
2.17 Non-Conservation of Entropy – POSTULATE IV

In contrast to the internal energy, entropy is not conserved. Postulate IV asserts that:

"In a closed adiabatically isolated system the change in entropy over all subsystems involved in the change is positive semi-definite".

Mathematically this may be expressed by the relation

\[ \Delta S_{\text{Total}} \geq 0. \quad (2.17) \]

The change is zero only in a reversible process. In any real physical process (or spontaneous natural process) the change is positive. Equation (2.17) shows that while entropy, like internal energy, cannot be destroyed, unlike internal energy, it can be created and, in fact, always is created in any spontaneously occurring process. Clausius (1850) stated this in the words: 'Die Entropie der Welt strebt einem Maximum zu' (The entropy of the universe tends towards a maximum).

2.18 Dissipative Phenomena

Postulate IV is in accordance with the common experience that a real physical process is invariably accompanied by dissipative phenomena such as mechanical friction, turbulence, electrical resistance, viscosity, and others more. These dissipative phenomena (cf. § 7.3) manifest themselves as internally generated heat (cf. § 2.7), thus increasing the entropy of the system and decreasing the amount of energy available for work (cf. §§ 8.11, 8.14, and 8.17).

Production of entropy is the central problem of Part II of this text.

2.19 Infinitesimal Change in Heat

When only an adiabatic barrier is lifted in an isolated composite system, the infinitesimal change in internal energy in the subsystem under consideration equals the infinitesimal change in heat and is given by

\[ dU = \delta Q = \frac{\partial U}{\partial S} \bigg|_{X(\neq S)} \ dS. \quad (2.19) \]

2.20 Special Nature of Heat as a Form of Energy Exchange

Just like internal energy, entropy, the extensive parameter of heat, cannot be measured directly in the way in which the other extensive parameters, such as the volume and mole numbers, can be measured. This, together with the fact that entropy is not a conserved quantity in an isolated system, imparts a special status to heat as a form of energy exchange. This, indeed, is the reason for the existence of thermodynamics as a special branch of mechanics.
2. THE POSTULATES OF EQUILIBRIUM THERMODYNAMICS

2.21 Limit of Entropy – POSTULATE V — The Third Law of Thermodynamics

According to Postulate V:

"The entropy of any finite system is positive semi-definite in the state for which the partial derivative of the internal energy with respect to the entropy vanishes".

The state just referred to is characterized by the relation

$$\frac{\partial U}{\partial S} \bigg|_{S(\neq S)} = 0. \quad (2.21)$$

Postulate V embodies one form of the Third Law of Thermodynamics (see § 7.19 for other formulations of the Third Law).

2.22 Monotonic Property of the Entropy

It follows from Postulate V that

$$\frac{\partial S}{\partial U} \bigg|_{S(\neq U)} \geq 0, \quad (2.22)$$

i.e., the entropy is a monotone non-decreasing function of the internal energy.

2.23 Significance of the Concept of Entropy

The recognition that energy can always be factored into the product of an extensive and an intensive parameter lead to our introduction of the entropy as the extensive parameter of heat. The identification of the entropy as an extensive parameter of any thermodynamic system makes it possible to extend the theory of mechanical equilibrium to thermodynamic equilibrium involving thermal effects.