23. THE POSTULATES OF STEADY-STATE THERMODYNAMICS

Chapter 4 identified the problem of equilibrium as the central problem of the theory of equilibrium thermodynamics. The central problem of the thermodynamic theory of irreversible processes is the determination of the entropy produced as internally generated heat due to the various dissipative phenomena (cf. §§ 2.7, 2.18, 7.3 and 7.5) occurring in any natural spontaneous process. In the preceding chapter we have examined entropy production in chemical reactions. To determine the production of entropy in the general case is a rather difficult problem. No general theory of non-equilibrium thermodynamics is available. Much progress has been made, however, in the understanding of processes near equilibrium when the system is in a steady state, and when the steady state is characterized by linear relations between conjugate parameters. In most cases of practical interest the restriction to near equilibrium is not as stringent as it is in the case of chemical reactions. The remainder of this text is concerned primarily with the thermodynamics of the (linear) steady state.

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23.1 The Postulatory Basis of Steady-State Thermodynamics

Development of a comprehensive theory of steady-state thermodynamics requires the introduction of three new postulates in addition to those of equilibrium thermodynamics. The first of these is the postulate of the existence of local equilibrium. The second establishes relations between generalized thermodynamic driving forces and generalized thermodynamic fluxes. The third postulate imposes symmetry restrictions on these relations.

23.2 Local Equilibrium – POSTULATE VI

Postulate VI states that:

"Although a thermodynamic system as a whole may not be in equilibrium, small elements of its volume may be considered to be in thermodynamic equilibrium locally. Elements in local equilibrium can be characterized by the same state functions that characterize global equilibrium in equilibrium thermodynamics."
It is this postulate that permits us to place steady-state thermodynamics firmly onto the basis formed by the five postulates of equilibrium thermodynamics.

23.3 The Steady State

In view of Postulate VI we refine our earlier definition of the steady state (§ 1.12) as follows:

"A steady, or stationary, state of a thermodynamic system is a stable, time-invariant state, generally of an open system, which is characterized by local equilibrium of the thermodynamic variables."

The steady state is sustained by stable, time-invariant conditions at the system boundaries (see Appendix 7 for an example). These maintain a spontaneous, hence irreversible, process, resulting in the production of entropy.

23.4 Scalar Theory

In Chapter 22 we had already developed most of the basic concepts of the thermodynamics of the steady state when we considered chemical reactions as irreversible processes. We showed (cf. § 22.10) that in dynamic reaction equilibrium, i.e., in the steady state, the thermodynamic driving force, \( F = \frac{\Delta A}{T} \), and the thermodynamic flux, \( J = \nu \), could be related linearly through the phenomenological equation, \( J = LF \) in which \( L \) is the phenomenological coefficient. The equation contains only scalar quantities. The theory of chemical reactions viewed as irreversible processes is, therefore, a scalar theory. That scalar theory is, however, easily extended to a general theory of coupled linear steady-state processes by considering \( F \) to be a generalized thermodynamic scalar driving force (or generalized thermodynamic scalar affinity), and \( J \) to be a generalized thermodynamic scalar flux.

23.5 Vector Theory

In many steady-state processes of interest, the thermodynamic fluxes and the driving forces that give rise to them are vector quantities. The former are called generalized thermodynamic vector fluxes, flows, or currents, and will be represented by the symbols \( J \) or \( J_i \). These flow vectors are typically the fluxes (quantity per unit time per unit volume) of the extensive parameters of a system, such as the internal energy or the entropy. The generalized thermodynamic driving forces or generalized thermodynamic affinities that elicit them will be represented by the symbols \( F \) or \( F_i \). They are typically the gradients of a system's intensive parameters, exemplified by the temperature, pressure, or chemical potential. The fluxes and driving forces are conjugate quantities.

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22 Scalars are set in non-bold italics (S). Vectors and tensors will be represented in the indicial as well as in the symbolic notation. In the indicial notation vectors and tensors are set in non-bold italics as are scalars. The number of indices (zero, one, or two) identify the variable as a scalar, a vector, or a (second-rank) tensor. In the symbolic notation, vectors are set in bold italic serif type (\( \mathbf{F} \)) while second rank tensor are set in bold italic sans-serif type (\( \mathcal{F} \)). Thus, in the symbolic notation, vectors and tensors are in bold type but scalars are not. A single contraction, e.g., that of two vectors to a scalar, is indicated by a raised bold dot (\( \cdot \)). A double contraction, e.g., that of two second-rank tensors to a scalar, is indicated by a bold colon (\( : \)).
This text describes steady-state thermodynamics primarily in terms of the vector theory.

23.6 Tensor Theory

The generalized thermodynamic driving forces and fluxes may also be second-order tensors typified by, e.g., stress, strain, and rate of strain tensors. Such tensors would be represented by the symbols $F$ or $F_{ij}$, and $J$ or $J_{kl}$. The tensor theory encompasses the vector theory as a special case, while the vector theory comprises the scalar theory in similar fashion. However, the tensor theory is beyond the scope of this text and will therefore receive only an occasional mention (cf. e.g., §§ 23.7, 26.1, and 26.2). Extension to tensors of rank higher than the second does not seem to be required in the theory of steady-state thermodynamics.

23.7 The Curie Symmetry Principle

In the general case the generalized fluxes of whatever tensorial character are functions of all the generalized thermodynamic forces. In a system which is isotropic at equilibrium, symmetry considerations restrict these functional dependencies. According to P. Curie (1908):

"Quantities whose tensorial characters differ by an odd number of ranks cannot interact in an isotropic medium."

The principle can be understood as follows. If the thermodynamic forces and fluxes are tensors of the same rank, the elements of the matrix of phenomenological coefficients are scalars which depend on the local state of the medium but in an isotropic medium do not depend on the gradients of the intensive parameters. If they are tensors of different rank, the phenomenological coefficients are tensors of rank equal to the difference between the ranks of these tensors. A phenomenological coefficient which is a tensor of even rank can exist in an isotropic medium. One of odd rank would, however, cause the medium to be anisotropic and therefore cannot exist in an isotropic medium.

The Curie principle asserts the absence of cross-effects between scalar and vector phenomena in an isotropic medium. Second rank tensors can be separated into spherical and deviatoric tensors. The former can be treated as scalars. Cross-effects from the traceless deviatoric tensors appear to be weak or non-existent.

23.8 Phenomenological Equations—POSTULATE VII

The thermodynamic vector fluxes are linked to the driving forces through second-order tensors denoted by $L$ or $L_{ik}$. The latter are the generalized phenomenological coefficients, kinetic coefficients, or thermodynamic conductances or conductivities. The interrelations among these quantities are the phenomenological equations.

Postulate VII states that:

"The generalized thermodynamic vector fluxes depend on all the generalized thermodynamic driving forces through the phenomenological coefficients."
This is expressed succinctly by the equations

\[ J = L \cdot F \quad \text{or} \quad J_i = L_{ik} F_k \]  \hspace{1cm} (23.8)

where the \( J \) or \( J_i \) are the vector fluxes, the \( F \) or \( F_k \) are the driving forces, and the \( L \) or \( L_{ik} \) are the phenomenological coefficients linking them. We note that the fluxes and forces are related linearly. Invoking a mechanical analogy, Eqs. (23.8) are also called the *thermo-dynamic equations of motion*.

### 23.9 Reciprocity Relations – POSTULATE VIII

Postulate VIII asserts that:

"The phenomenological coefficients are related by the Onsager reciprocity relations, \( L_{ik} = L_{ki} \), if there are no forces determined by a vector product, and by \( L_{ik}(f) = L_{ki}(-f) \), the Onsager-Casimir reciprocity relations, if there are."

The Onsager-Casimir relations apply in the presence of Coriolis forces (in a rotating system) or of Lorentz forces (in a system subjected to centrifugal or magnetic fields). The field vector, \( f \), is thus either the angular velocity, \( \omega \), or the (external) magnetic field, \( B \).

The statistical mechanical analog of the reciprocity relations is the *principle of microscopic reversibility*. As formulated by Tolman (1938), it states:

"Under equilibrium conditions any molecular process and the reverse of that process will take place on the average at the same rate."

We had appealed to this principle earlier in § 22.10.

### 23.10 The Linear Steady State

The global equilibrium state is the limiting case of the steady state when the fluxes from the environment approach zero, i.e., when the system becomes isolated. If

- the phenomenological coefficients are *time-invariant* (Postulate VI),
- the phenomenological equations are *linear* (Postulate VII), and
- the matrix \( L_{ik} \) is *symmetrical* (Postulate VIII),

a steady state will be called a *linear steady state*. 