

# Chapter 2

## Thermodynamics

### 2.1 General

Thermodynamics is the theory of the interaction of heat and work and of their relationship to the physical properties and processes in material systems, dealt with at the macroscopic scale. One of its principal uses is therefore to provide constraints on the constitutive equations that describe the state of systems or the processes occurring in them. The foundation of thermodynamics consists of a minimal number of postulates or empirical laws drawn from experience. However, it has also been proposed that it can be regarded as being rooted in some universal and fundamental concepts of symmetry or invariance under transformation that apply to physical laws (Callen 1974). The scope of thermodynamics has traditionally been limited mainly to systems in equilibrium but has more recently been extended to deal also with non-equilibrium situations. We shall give here a brief summary of the principal results of these two branches of the theory.

### 2.2 Equilibrium Thermodynamics

We first recall the elements of classical equilibrium thermodynamics (or thermostatics). We take the concepts of heat  $Q$  and work  $W$  to be understood from classical physics or physical experience. However, because of path dependences, these quantities are inadequate for the proper description of the state of a physical system at any instant, for which further concepts are required (for general texts, see Callen 1960; Denbigh 1971; Guggenheim 1985; Callen 1985; for general texts, see Pippard 1957).

Thermodynamics therefore begins with the introduction of the macroscopic concept of the energy of a system, which is defined in terms of its conservation, through the First Law, as function of state called the *internal energy*  $U$ .

Only changes in the energy of a system can be measured and these changes derive from work done on the system or from heat or substance added to the system. The internal energy is thus an extensive variable of fundamental importance in describing the state of the system. Other extensive or additive variables of similar importance are the amount of substance in the system and the dimensions of the system, if mechanical work is involved, or analogous parameters associated with other forms of work (electrical, etc.). For simplicity in exposition we shall here only consider systems having as the other extensive variables the volume  $V$  and the amounts of substance (moles)  $n_i$  of each of  $i$  components ( $n_i = N_i/L$  where  $N_i$  is the number of molecules or entities of substance  $i$  and  $L$  is the Avogadro number). The state of such a system is then completely specified by  $U$ ,  $V$  and  $n_i$  if it is at equilibrium.

However, we also wish to consider systems in which changes of state (transitions or processes) are occurring and to establish criteria of equilibria. Further, it is well known that real physical processes are irreversible or dissipative in some fundamental sense and we need a criterion for determining the direction of change. In order to deal with these aspects, another extensive variable and function of state called the *entropy*  $S$  is introduced through the Second Law, according to which, in an isolated system, entropy is unchanged ( $\Delta S = 0$ ) in a reversible process and increases ( $\Delta S > 0$ ) in an irreversible process. This law can be restated to give a criterion of equilibrium, namely, that in an isolated system the entropy is a maximum at equilibrium.

Some insight into the nature of entropy can be obtained from the molecular point of view of statistical mechanics, in which entropy is given by  $S = k \ln g$  where  $k$  is the Boltzmann constant and  $g$  is the number of quantum states accessible to the system and assumed to be equally probable (Kittel and Kroener 1980, Chap. 2), that is, the number of different microscopic possibilities or configurations under which the given thermodynamic state can be realized. Macroscopically, it can only be stated that the entropy is a function of the other extensive variables,

$$S = S(U, V, n_i) \quad (2.1)$$

This relation serves as a *fundamental relation* from which all other properties of the thermodynamic system in equilibrium can be derived, since the specification of the extensive variables fully characterizes the state of the system. From consideration of the differential of  $S$  in the case of the reversible addition of an amount of heat  $\Delta Q$  to the system at constant  $V$  and  $n_i$  it follows that  $\Delta S = \Delta Q/T$ , or  $S = \int \Delta Q/T$  where the integration path is a reversible path; in the irreversible case,  $\Delta S > \Delta Q/T$  but no other statement can in general be made, that is, we cannot in general define an entropy exactly in a system out of equilibrium unless some restrictive statements are made about the nature of the system.

The fundamental relation in the “entropic form” (2.1) can be rewritten in the “energetic form”

$$U = U(S, V, n_i) \quad (2.2)$$

From the differential of  $U$  the following (energetic) intensive variables are defined:

$$\begin{aligned}
 \text{absolute temperature} \quad T &\equiv \left( \frac{\partial U}{\partial S} \right)_{V, n_i} \\
 \text{pressure} \quad p &\equiv - \left( \frac{\partial U}{\partial V} \right)_{S, n_i} \\
 \text{(electro) chemical potential} \\
 \text{of the } i\text{th component} \quad \mu_i &\equiv \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}}
 \end{aligned}$$

The intensive variables enable one to deal with the coupling of the system to its environment. Using them the relation (2.2) can be rewritten in the Gibbs form

$$dU = TdS - pdV + \sum_i \mu_i dn_i \quad (2.3a)$$

or in the Euler form

$$U = TS - pV + \sum_i \mu_i n_i \quad (2.3b)$$

It follows from (2.3) that the above criterion of equilibrium can be restated in terms of minimizing the internal energy at constant  $S$ ,  $V$ ,  $n_i$ .

In practice it is often convenient to use one or both the intensive variables  $T$ ,  $p$  as independent variables instead of the respective conjugate extensive variables  $S$ ,  $V$  used in writing (2.2). Such transformation leads to the definition of the additional functions,

$$\begin{aligned}
 \text{Helmholtz (free) energy} \quad A &\equiv A(T, V, n_i) = U - TS \\
 \text{enthalpy} \quad H &\equiv H(S, p, n_i) = U + pV \\
 \text{Gibbs (free) energy} \quad G &\equiv G(T, p, n_i) = U + pV - TS,
 \end{aligned}$$

to equivalent forms of the fundamental relations (2.3),

$$dA = -SdT - pdV + \sum_i \mu_i dn_i \quad (2.4)$$

$$dH = TdS + Vdp + \sum_i \mu_i dn_i \quad (2.5)$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \quad (2.6)$$

and to corresponding extremum conditions for equilibrium under constraint of the specified independent variables (for example, the Gibbs energy  $G$  is a minimum at equilibrium when  $T$ ,  $p$  and  $n_i$  are the independent variables). There are many mathematical relations between the various parameters or functions of state so far

introduced and others derivable from them, which constitute much of the useful content of thermodynamic theory and are summarized in textbooks (for example Callen 1960, Chaps. 3 and 7; Denbigh 1971, pp. 89–98). One such relation of particular importance is the Gibbs–Duhem relation expressing an interdependence among the intensive variables,

$$SdT - Vdp + \sum n_i d\mu_i = 0 \quad (2.7)$$

In the application of the thermodynamic principles to a real physical situation, it is necessary to know the explicit form of the fundamental relation, in any of its equivalent versions (2.1)–(2.6), in order to fully express the physics of the situation, although the search for this explicit form is not strictly part of thermodynamics itself. The physics of the situation can alternatively be introduced in the form of equations of state, which are explicit relations between the independent extensive variables and the intensive variables, such as the ideal gas laws  $V = nRT/p$  and  $U = 3nRT/2$  ( $R = Lk$ ).

Since systems at equilibrium are homogeneous within regions free from internal walls it is sufficient to discuss the total amounts  $S$ ,  $U$ ,  $V$ ,  $n_i$ ,  $G$ , . . . . . of the extensive properties within the homogeneous regions. However, in chemical thermodynamics, it is often useful to normalize the extensive properties to the total amount of substance  $n$  ( $= \sum n_i$ ) in the system to give, respectively, the molar quantities  $S_m$ ,  $U_m$ ,  $V_m$ ,  $x_i$ ,  $G_m$ , . . . . . (where  $S_m = S/n$  . . . and  $x_i$  = mole fraction of the  $i$ 'th component); further, the molar quantities may be partitioned among the components of substance as the partial molar quantities, noting that the partial molar Gibbs energy is identical to the chemical potential.

## 2.3 Non-Equilibrium Thermodynamics

We now turn to systems out of equilibrium. Here, the thermodynamic treatment rests on less well-defined foundations than does classical equilibrium thermodynamics. There exist, in fact, a number of distinct approaches of diverse aims, but two major branches of theory can be distinguished, characterized by Germain (1974) as the “ambitious attitude” and the “cautious attitude”. The former, variously labeled as rational thermodynamics or continuum thermodynamics, claims to attempt the broadest possible analysis. It aims not to depend on generalization from classical equilibrium thermodynamics but to deal *ab initio* with processes (described by constitutive relations) rather than with states. The physical specification of the system at any instant involves not only the values of the measurable parameters at that instant but also their histories at all previous instants, expressed as functionals such as hereditary integrals (Malvern 1969, pp. 256, 319). The concepts of temperature and entropy are introduced as primitive quantities. No attempt will be made to expound this approach here (see Coleman 1964; Day 1972; Noll 1974; Truesdell 1984).

The alternative and more conservative approach is to retain the concept of local state in giving the physical specification of a system at any instant. The postulate that a local state exists is often taken as being equivalent to assuming some form of local equilibrium (Glansdorff and Prigogine 1971, p. 14) but it can have a wider meaning (Lavenda 1978, p. 77). Attempts to justify this postulate usually point to the relaxation time for fluctuations at the atomic scale being short compared with the timescale of the macroscopic processes to which the theory is applied. Where the local state cannot be fully specified in terms of measurable macroscopic variables it is assumed that there exist additional internal or hidden variables (for example, dislocation density) which complete the description of the local state. The importance of the postulate of a local state is that it enables many concepts to be carried over from classical equilibrium thermodynamics, such as the concepts of entropy and energy as scalar potentials and the Gibbs–Duhem and the Gibbs relations (2.3a) and (2.7). The production of entropy envisaged by the Second Law for irreversible processes is then discussed with a view to placing constraints on the laws governing these processes, especially in relation to their stability. The applications have commonly been confined to processes in systems not very far from equilibrium, the theory for which is termed the *linear* thermodynamics of irreversible processes. The theoretical situation for more general applications is less well developed, and still to a considerable extent the subject of research. Thus there have been attempts to develop the theory of the nonlinear thermodynamics of irreversible processes applicable to systems far from equilibrium; see for example, Glansdorff and Prigogine (1971), who introduce the concept of dissipative structures; also Lavenda (1978). Other applications have been to processes such as friction or ideal plasticity where dissipation is equally important no matter how slowly the process proceeds, for example, Kestin (1966) and Nemat-Nasser (1974). The remainder of these notes will concern linear thermodynamic theory under the assumption of the existence of a local state, as expounded by Denbigh (1951), Meixner and Reik (1959), de Groot and Mazur (1962), Katchalsky and Curran (1965), Prigogine (1967), Fisher and Lasaga (1981), Kuiken (1994), Martyushev and Seleznev (2006), Holyst (2009), Kleidon (2009), and others.

The starting point for the *linear thermodynamics of irreversible processes* is the Second Law and the concept of entropy production in an irreversible process. In any irreversible change in a system, the rate of change in entropy is made up of a part due to entropy flow from the surroundings and a part due to changes within the system. The latter part is known as the rate of entropy production, or simply the entropy production, and designated  $\sigma$  per unit volume; according to the Second Law it must be positive. In the energy representation of the evolution of the system, the corresponding quantity is  $T\sigma$ , which is sometimes called a dissipation function or potential since it represents the rate at which irrecoverable energy or work must be supplied or done to maintain the process. The dissipation function can be written in the form

$$T\sigma \equiv \sum_{\alpha} J_{\alpha} X_{\alpha} > 0 \quad \alpha = 1, 2, 3, \dots \quad (2.7)$$

where  $J_\alpha$  are the rates of change of local extensive parameters and  $X_\alpha$  are conjugate intensive parameters, the summation being over all the component processes contributing to the entropy production. There can be some ambiguity in the factoring of the terms of (2.7) into the  $J_\alpha$  and  $X_\alpha$  but no serious confusion arises if consistent rules are followed (Miller 1974).

Where heat flow, diffusion, and chemical reactions are to be taken into account, the dissipation function can be expressed in the following terms (Katchalsky and Curran 1965, Chap. 7)

$$T\sigma = J_Q \cdot T \text{grad} \frac{1}{T} + J_i \cdot T \text{grad} \left( -\frac{\mu_i}{T} \right) + \frac{d\xi}{dt} A \quad (2.8a)$$

or

$$T\sigma = J_S \cdot \text{grad}(-T) + J_i \cdot \text{grad}(-\mu_i) + \frac{d\xi}{dt} A \quad (2.8b)$$

where  $J_Q$ ,  $J_S$  and  $J_i$  are vectors representing the currents or rates of flow of heat, entropy, and substance  $i$ , respectively,  $d\xi/dt$  is a scalar representing the rate of advancement of the chemical reaction ( $\xi$  is the extent of chemical reaction), and  $A = -\sum v_i \mu_i$  is the chemical affinity driving the reaction ( $v_i$  are the stoichiometric coefficients for the reaction). In cases involving viscous flow, electric and magnetic effects, or other dissipative processes, further terms can be added. The factors  $J_Q$ ,  $J_S$ ,  $J_i$  and  $d\xi/dt$  in (2.8a) can be clearly identified as the extensive parameters  $J_\alpha$  in (2.7) and their multiplying factors are then the respective conjugate intensive parameters  $X_\alpha$ . The seeming ambiguity regarding the intensive parameter conjugate to  $J_i$  arises from the different ways in which the total dissipation is partitioned between the different terms in (2.8a) and (2.8b). The form (2.8a) is appropriate where flow of heat and diffusion of substance are being individually and simultaneously measured in the presence of a temperature gradient, in which case it is evident that the intensive parameter driving the diffusion is to be taken to be  $T \text{grad}(\mu_i/T)$ . The form (2.8b) is appropriate when the entropy changes associated with the movement in the temperature gradient of the measurable heat and of the substance (through its heat content) are brought together in the factor  $J_S$ ; although the latter quantity is not directly measurable, the form (2.8b) is useful in indicating that, in the absence of a temperature gradient, the intensive parameter driving the isothermal diffusion can be taken to be  $\text{grad}(-\mu_i)$ .

In the entropy representation, the interest centers on  $\sigma$ , the rate of entropy production itself, instead of on  $T\sigma$ . Again  $\sigma$  is written as a sum of terms that are the products of extensive and intensive parameters and, somewhat confusingly, the same symbols are often used as were used in (2.7) for  $T\sigma$ ; further,  $\sigma$  or  $\sigma/2$  is often taken as a dissipation function or potential. In both representations, the  $J_\alpha$  factors are commonly termed “fluxes” or “flows”, although these terms are scarcely appropriate for quantities such as  $d\xi/dt$ , and the  $X_\alpha$  are variously termed the “thermodynamic forces” or “affinities”, regardless of whether being in energy or entropy representation and in spite of the  $1/T$  factor subsumed in the  $X_\alpha$  in the

latter case. The applications of the linear thermodynamics of irreversible processes now follow from consideration of the quantities in the terms of  $T\sigma$  and of the inequality expressed in (2.7).

The physics of the processes is expressed in the relationships between the forces and fluxes,  $X_\alpha$ ,  $J_\alpha$ , known as the phenomenological, constitutive, or kinetic relations or as the thermodynamic equations of motion; their role is in many respects analogous to that of the equations of state relating extensive and intensive quantities in equilibrium thermodynamics. One of the main activities of thermodynamic theory has been to place constraints on the relations between the thermodynamic variables and to discuss criteria for stability and stationary states. However, whereas the constraints governing the quantities entering the equilibrium equations of state can generally be stated independently of the particular nature of these equations, it is very difficult to establish laws of general validity governing the quantities entering the phenomenological equations for an arbitrary non-equilibrium situation. Substantial progress has only been made for certain classes of situations, chiefly for those close to equilibrium. We therefore restrict considerations to the latter and in particular to the situations in which the relationships between forces and fluxes can be written in the linear form

$$J_\alpha = \sum_{\beta} L_{\alpha\beta} X_\beta \quad \beta = 1, 2, 3, \dots \quad (2.9)$$

where  $L_{\alpha\beta}$  are constants, often called the phenomenological or kinetic coefficients. In writing the phenomenological relations in the form (2.9), the quantities  $X_\beta$ ,  $J_\alpha$  are treated as scalars but in practice they can represent scalar quantities or the Cartesian components of vector or tensor quantities. The relations (2.9) take into account the possibility of coupling effects between non-conjugate forces and fluxes, for example, coupling between heat flow and diffusion or between the diffusion of different species. It is now possible, using (2.9), to write (2.7) in the form

$$T\sigma = \sum_{\alpha, \beta} L_{\alpha\beta} J_\alpha J_\beta \geq 0 \quad (2.10)$$

which has important consequences.

The principal initial success of the linear thermodynamics of irreversible processes lies in the enunciation of the Onsager (1931a) reciprocal relations

$$L_{\alpha\beta} = L_{\beta\alpha} \quad (2.11)$$

which express a symmetry between coupling effects. Note that some elaboration of (2.11) is needed when magnetic fields or rotational effects are present or the forces or fluxes are mixed in respect of being odd or even in tensorial character; see Casimir (1945) and Meixner and Reik (1959). Much has been written concerning the statistical mechanical derivation of (2.11) using a fundamental principle of microscopic reversibility; for critical discussion and references, see Lavenda (1978, Chap. 2); also Callen (1960). However, (2.11) can also be treated as an empirical axiom of

macroscopic theory adequately supported by experimental observation (Miller 1974). Curie's principle concerning the symmetry relationships between cause and effect (Curie 1894; Paterson and Weiss 1961) is also often invoked to constrain further the possible values of  $L_{\alpha\beta}$ , this principle being paraphrased to state that no direct coupling occurs between processes described respectively by quantities of odd and even tensorial character, for example, between chemical reaction (scalar) and diffusion (vector). Then, we can put  $L_{\alpha\beta} = 0$  where  $\alpha, \beta$  ( $\alpha \neq \beta$ ) refer to two such processes, although this does not prevent indirect interference occurring (Prigogine 1967, p. 89). Other possible constraints on the  $L_{\alpha\beta}$  are discussed by Fisher and Lasaga 1981.

One can expect non-equilibrium thermodynamics to be concerned also with the likely paths to be followed by processes, with the nature of stationary states, and with questions of stability, in analogy with topics in equilibrium thermodynamics such as the criteria of equilibrium and conditions governing phase transitions. Actually, when not ignored, these non-equilibrium topics appear to be the subject of considerable debate and research, and only a few general remarks are appropriate here (for a summary on stability considerations, see Prigogine 1980). It seems that a general principle of fundamental and far-reaching importance is the principle of least dissipation of energy (Lavenda 1978, Chap. 6; Onsager 1931a, b). In the particular case of linear phenomenological laws, it follows that a system will evolve in the direction of diminishing rate of entropy production, towards a state characterized by a minimum rate of entropy production (Prigogine 1967). However, in a completely unconstrained situation this minimum rate will be zero, reached when all irreversible processes have stopped and equilibrium is attained. In order to maintain a stationary or steady non-equilibrium state, that is, one that no longer evolves with time, it is therefore necessary to constrain at least one term in the dissipation function  $T\sigma$  to be nonzero, that is, to hold at least one of the thermodynamic forces  $X_\alpha$  at a constant, nonzero value. It follows that in the stationary state all unconstrained parameters  $X_\alpha$ ,  $J_\alpha$  will become zero. Thus the stationary state in any system in which linear processes are occurring is that in which the rate of entropy production is a minimum under certain auxiliary conditions such as specified nonzero values for at least one of the  $X_\alpha$  or  $J_\alpha$ , and this state will be stable.

For corresponding considerations in nonlinear and far from-equilibrium situations, including the occurrence of stable "dissipative" structures, see (Glandsdorff and Prigogine 1971; Lavenda 1978; Prigogine 1980; Fisher and Lasaga 1981 and Ross 2008).

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