

Chap. 5 Free Energy and the Criterion of Equilibrium

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5.1 Importance of the Gibbs Free Energy

The objective of this brief chapter is to introduce two properties that have until played virtually no part in the applications of thermodynamics. Of the two, F , the Helmholtz free energy and G , the Gibbs free energy, the latter is our focus. The reason is the unique importance of G as a criterion of equilibrium when the restraints on a system are constant pressure and temperature.

The function of G as an arbiter of equilibrium is analogous to that of the entropy in determining the equilibrium state of isolated systems (see Chap. 1, bottom of p. 22). If volume and internal energy are fixed, the entropy is a maximum at equilibrium. This criterion is succinctly described by:

$$dS_{U,V} = 0 \quad \text{at equilibrium of an isolated system} \quad (5.1)$$

where the subscripts denote the constraints on the system and the vanishing of dS indicates a maximum entropy at equilibrium. If an isolated system is off equilibrium, its entropy must increase as it spontaneously moves towards equilibrium:

$$dS_{U,V} > 0 \quad \text{disequilibrium of an isolated system} \quad (5.1a)$$

The equilibrium condition of Eq(5.1) is of minimal practical consequence because the constraints of constant U and V are rarely imposed on real systems. Instead, the usual properties that are specified during a process are total pressure and temperature. With these constraints, the equilibrium criterion is no longer the entropy maximum of Eq (5.1) but the minimization of the Gibbs free energy. This criterion, which is derived below, forms the foundation of the thermodynamics of multiphase and multicomponent as well as equilibrium in chemically reacting systems.

5.2 The Fundamental Differentials

Associated with each of the energy-like properties U , H , F , and G are their differentials, which are expressed in terms of the state functions S , V , p , and T . These differentials constitute the basis for important relations between properties and for the development of criteria of equilibrium other than Eq (5.1). The differentials of U and H were obtained in Sect. 3.5 by combining the First and Second laws. For an arbitrary quantity of material in the system, upper-case notation for extensive properties is used, and the first two fundamental differentials are:

$$dU = TdS - pdV \quad (5.2)$$

$$dH = TdS + Vdp \quad (5.3)$$

The Helmholtz free energy is defined by:

$$F = U - TS \quad (5.4)$$

Taking the differential gives $dF = dU - TdS - SdT$. Eliminating dU using Eq(5.2) yields:

$$dF = -SdT - pdV \quad (5.5)$$

Similarly, the Gibbs free energy is defined by:

$$G = H - TS \quad (5.6)$$

The differential is $dG = dH - TdS - SdT$. When combined with Eq (5.3), the result is:

$$dG = -SdT + Vdp \quad (5.7)$$

Equations (5.2), (5.3), (5.5) and (5.7) are the *fundamental differentials* of thermodynamics of single-component substances. In multicomponent systems, additional terms are needed to account for the effect of composition changes on the differentials (Chap. 8). The fundamental differentials also require that the only form of work is pV expansion work.

5.3 Maximum external work and the Gibbs free energy

The limitation to expansion work in the fundamental differentials is contained in the pdV term in Eq (5.2). However, systems can perform other types of work, including chemical, electrical, and shaft work. In order to include these contributions, which are generically labeled external work, Eq (5.2) is modified to read:

$$dU = TdS - pdV - \delta W_{\text{ext}} \quad (5.8)$$

The consequence of including external work on dG is determined as follows: Substituting the definition $H = U + pV$ into Eq (5.6) and taking the differential of the result gives $dG = dU + pdV + Vdp - TdS - SdT$. Eliminating dU using Eq (5.8) yields:

$$dG = -SdT + Vdp - \delta W_{\text{ext}} \quad (5.9)$$

For the practically important case of constant T and p , Eq (5.9) reduces to:

$$\delta W_{\text{ext}} = -dG_{T,p} \quad (5.10)$$

where the subscript T,p indicates that these two properties are held constant during any change in the system. With this constraint, the Gibbs free energy decreases as the system performs work (other than expansion work) on its surroundings. In its integrated form, Eq (5.10) is useful in determining the maximum work that can be extracted from devices

such as a fuel cell that operate at constant pressure and temperature. However, the most important application of this equation is what it implies about systems that are in a state in which external work *cannot* be produced.

5.4 Equilibrium and the Gibbs free energy

A useful definition of a system in equilibrium is one that cannot perform useful (non-expansion) work. Applying this notion to Eq(5.10), the criterion of equilibrium for closed systems constrained by fixed T and p is:

$$dG_{T,p} = 0 \quad (\text{at equilibrium}) \quad (5.11)$$

This equation is useful chiefly for systems with more than one phase or more than one component. For a single-phase, single-component system, fixing any two properties determines the others, and Eq (5.11) is a trivial example of this fact. However, for heterogeneous (multiphase) systems or homogeneous (single-phase) systems containing chemically reacting species, Eq (5.10) provides the essential starting point for determining the state of equilibrium.

Equation (5.11) states that G is an extremum at equilibrium under the constraint of fixed T and p. However, it does not indicate whether the extremum is a maximum or a minimum. Equation (5.10) clarifies this point: if a system could perform useful work, its Gibbs free energy would necessarily decrease, or

$$dG_{T,p} < 0 \quad (\text{disequilibrium}) \quad (5.11a)$$

The appropriate interpretation of Eq(5.11a) is that a system at constant T and p will spontaneously seek to minimize its Gibbs free energy. This process occurs whether or not the system performs external work in moving towards its equilibrium state.

Equations (5.11) and (5.11a) give conditions on G for equilibrium and spontaneous change, respectively, that are analogous to Eqs (5.1) and (5.1a) for S. Figure 5.1 compares the two equilibrium criteria. At equilibrium in an isolated system, the entropy is maximized; if pressure and temperature are fixed, the Gibbs free energy is minimized. Of the two criteria, the latter is by far the most important by virtue of the constant p-T restriction, which is much more practical than the constant U-V condition required of the maximum-entropy criterion. Even less utilized equilibrium criteria are based on the other two energy-like properties, H and F. Problem 5.1 deals with the restraints that cause the Helmholtz free energy to be minimized at equilibrium.

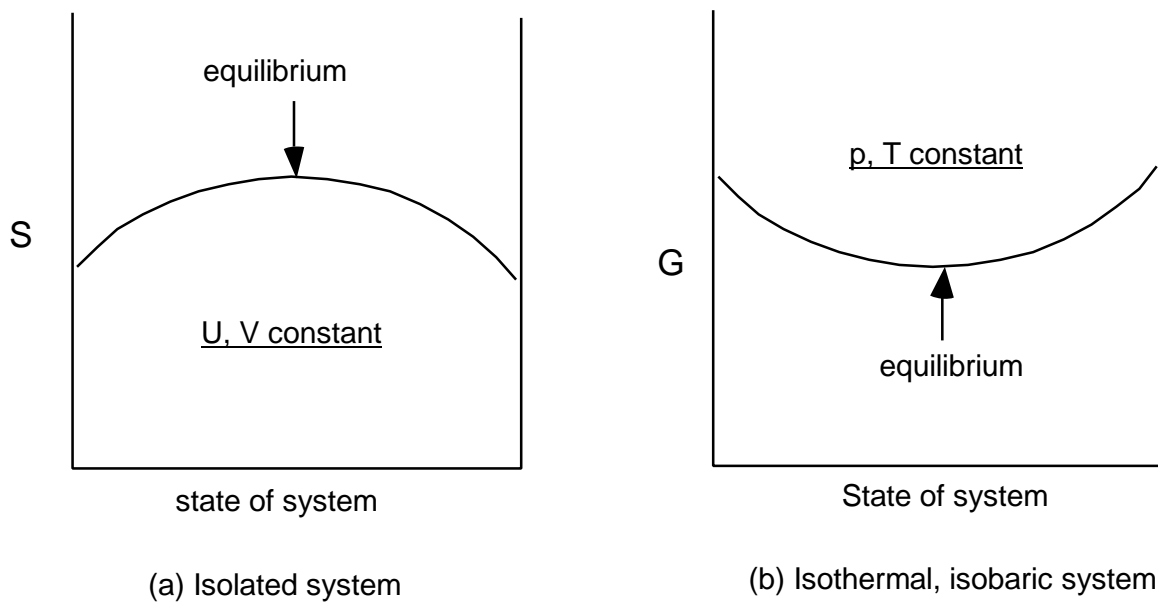


Fig. 5.1 Two equilibrium conditions