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ABSTRACT

We discuss relations among properties of systems that consist of any amounts of constituents (including one particle), that have volume as the only parameter, and that are in thermodynamic equilibrium or stable equilibrium states. For large amounts of constituents, we introduce the concept of a simple system, and derive additional relations among properties.

1. INTRODUCTION

Gibbs[1] devoted more than five pages of somewhat convoluted discussion to justify the validity of the Euler relation

$$U - TS + pV - \sum_{i=1}^{r} \mu_i n_i = 0 \qquad (1)$$

All subsequent expositions of thermodynamics of which we are aware have overlooked the serious concern addressed by Gibbs in those pages.

An essential prerequisite of the derivation of Equation 1 is that the stable-equilibrium-state energy relation $U = U(S, V, \boldsymbol{n})$ be a homogeneous function of degree one of each of its variables, entropy S, volume V, amounts of constituents $\boldsymbol{n} = \{n_1, n_2, \ldots, n_r\}$. This prerequisite is either postulated[2,3] or presented in a few lines as an almost obvious consequence of the fact that each of the quantities U, S, V, and n_i is additive[4,5]. The former is not always warranted, and the latter is faulty and, perhaps, the reason for Gibbs' five-page discussion.

The logic of the usual but faulty derivation is as follows. Two different systems are considered. One is a system A with no internal partitions and a stable-equilibrium-state energy relation $U = U^A(S, V, \boldsymbol{n})$. Of this system, two different states are considered. The first is a stable equilibrium state A_1 with entropy S_1, volume V_1, and amount $(n_i)_1$ of constituent i, for $i = 1, 2, \ldots, r$. By the energy relation, state A_1 has energy $U_1 = U^A(S_1, V_1, (\boldsymbol{n})_1)$. The second is a stable equilibrium state A_k with entropy $S_k = kS_1$, volume $V_k = kV_1$, and amount $(n_i)_k = k(n_i)_1$, for $i = 1, 2, \ldots, r$. By the energy relation, state A_k has energy $U_k = U^A(kS_1, kV_1, k(\boldsymbol{n})_1)$.

The second system is a composite system K consisting of k identical replicas of system A, each in a stable equilibrium state identical to A_1. By the additivity of energy, entropy, volume, and amounts of constituents, system K has energy $U_K = kU_1$, entropy $S_K = kS_1$, volume $V_K = kV_1$, and amount $(n_i)_K = k(n_i)_1$ for $i = 1, 2, \ldots, r$.

Now, the fact that system K consists of k separate subsystems, each with constituents confined in a partition of volume V_1 of the entire volume kV_1, is overlooked. It is stated—and here is the fault—that $U_K = U_k$. It then follows that $U^A(kS_1, kV_1, k(\boldsymbol{n})_1) = U_k = U_K = kU_1 = kU^A(S_1, V_1, (\boldsymbol{n})_1)$, namely, that the function $U = U^A(S, V, \boldsymbol{n})$ is a homogeneous function of degree one. But the conclusion is based on the faulty assumption that the stable-equilibrium-state energy relation $U = U^K(S, V, \boldsymbol{n})$ of system K (with internal partitions) is the same as that of system A (without internal partitions), that is, $U^K(S, V, \boldsymbol{n}) = U^A(S, V, \boldsymbol{n})$.

In this paper, we recognize and emphasize that in general $U^K(S, V, \boldsymbol{n}) = U^A(S, V, \boldsymbol{n})$ except under a condition specified by the definition of a simple system introduced in Ref.6 (Chapter 17). The condition turns out to be valid in the limit of relatively large values of the amounts of constituents, and is the reason why certain results, including the Euler relation, are valid only for macroscopic systems. Though expressed in a different language, the condition captures the essence of the concerns discussed by Gibbs[1].

2. SYSTEMS WITH VOLUME AS THE ONLY PARAMETER

2.1 Definition

In any physical study, we always focus attention on an identifiable collection of constituents that may be subjected to a nest of forces. When the constituents and the nest of forces

are well-defined, we call such a collection a system. For definiteness we briefly review the requirements for constituents and nest of forces to be well-defined, that is, the requirements for the definition of a system.

The forces required to define a system are of two kinds, internal and external. Internal forces describe the influences that hold the molecular structure of a constituent together, such as the forces between the nuclei and the electrons of H_2O, the influences between constituents, such as the forces between H_2O molecules, and the forces that promote or inhibit reaction schemes by which some constituents may combine or dissociate to give rise to other constituents. All are part of the specification of the system, and may differ from study to study of the same constituents. For example, in some studies of H_2 and O_2, the forces involved in the formation of water out of hydrogen and oxygen, the chemical reaction mechanism $2\,H_2 + O_2 = 2\,H_2O$, may be neglected as unimportant, whereas in other studies, these forces may be included as important. Each internal force on a given constituent depends on the coordinates of that constituent and on the coordinates of one or more of the other constituents of the system, but not on any coordinates of constituents of bodies in the environment.

Each external force describes a well-defined influence on the constituents by bodies not included in the collection under study, such as the influence of applied gravity, electric charges, magnets, and the solid walls of the container that confines the constituents within a region of space. Each external force on a given constituent depends on the coordinates of that constituent and one or more external parameters or, simply, parameters that describe the overall effect of the bodies in the environment, but not on the coordinates of any other constituent, either of the system or of bodies in the environment. For example, the effects of gravity on the water molecules in a small container depend on the elevations of these molecules above sea level, and on the intensity of gravity, but not on the coordinates of the substances of the earth. The gravitational potential γ is the parameter associated with this external gravitational force, where $\gamma = gz$, g is the constant gravitational acceleration, and z the elevation above sea level. Again, the effects of the walls of an airtight container on an enclosed gas depend on the positions of the gas molecules relative to the internal surface of the container, but not on the coordinates of the molecules of the materials of the walls. For a wide variety of applications, the effects of the walls are completely described by the volume of the container, i.e., volume is the only parameter needed to characterize such effects. For other applications, we may need a more detailed geometrical description of the shape of the enclosure in which the consituents are confined. For example, if the enclosure is a parallelepiped, the lengths L_1, L_2, and L_3 of its sides may be required as parameters to describe the confining external forces.

For certain systems, the characterization of the external forces may require two or more parameters. For example, in a system consisting of a fixed amount of hydrogen, half of which is confined in a volume V', and the other half in a volume V'', we need the two parameters V' and V'', and their respective ranges, for the characterization of the effects of the confining walls.

Because external forces are independent of coordinates of constituents in the environment, a system is also said to be separable from the environment or, simply, separable. This distinction is not trivial. If the forces exerted by a body not included in the object of study depend explicitly on the coordinates of the constituents of that body, then the object of study is not separable, and cannot be a system. To proceed in this case, we must redefine the collection of constituents so as to include the body in question. Thus, the troublesome forces become internal, and a system may be defined. For example, this situation arises when we wish to study the oxygen atom in a molecule of water. Such an atom cannot be defined as a system because it experiences forces that depend explicitly on the coordinates of the two hydrogen atoms in the water molecule. However, by including the two hydrogen atoms in the object of study, these forces become internal, and the oxygen and hydrogen atoms bound together in a water molecule can be well-defined as a system.

We emphasize that whenever we use the term system, such as in the statements of the laws of thermodynamics, we imply that the system is well-defined according to all the specifications and restrictions summarized in the present section, and discussed thoroughly in Ref.6.

2.2 Stable Equilibrium States

We restrict our study to the stable equilibrium states of a system that: (1) is confined in a region of space of variable volume; and (2) has volume as the only parameter. Such a system has no internal partitions and is not influenced by external forces resulting from gravity, electricity, magnetism, shear deformation, capillarity and other surface effects, because each of these effects requires one or more parameters in addition to volume.

The fundamental stable-equilibrium-state relation of the system is written as

$$S = S(U, V, \boldsymbol{n}) \tag{2}$$

where the explicit form of the function $S(U, V, \boldsymbol{n})$ is determined by the structure of the system, the constituents, and the internal and external forces. Moreover, Equation 2 can be solved for U to obtain the energy relation

$$U = U(S, V, \boldsymbol{n}) \tag{3}$$

where again the explicit form of the function $U(S, V, \boldsymbol{n})$ depends on the system.

For any system, large or small, we can use the energy relation to evaluate the temperature, pressure, and chemical potentials at each stable equilibrium state by means of the relations

$$T(S, V, \boldsymbol{n}) = \left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} \tag{4}$$

$$p(S, V, \boldsymbol{n}) = -\left(\frac{\partial U}{\partial V}\right)_{S,\boldsymbol{n}} \tag{5}$$

$$\mu_i(S, V, \boldsymbol{n}) = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,\boldsymbol{n}} \qquad \text{for } i = 1, 2, \ldots, r \tag{6}$$

In terms of these properties, we can express dU as a total differential of Equation 3, that is,

$$dU = T\,dS - p\,dV + \mu_1\,dn_1 + \mu_2\,dn_2 + \cdots + \mu_r\,dn_r \tag{7}$$

where in writing this differential we use the definitions of T, p,

$\mu_1, \mu_2, \ldots, \mu_r$ (Equations 4 to 6). This differential is known as the Gibbs relation.

We can also use Equations 3 to 6 to define other properties such as the enthalpy $H = U + pV$, the Helmholtz free energy $A = U - TS$, and the Gibbs free energy $G = U - TS + pV$. Moreover, from the independence of the order of differentiation of each of the characteristic functions $U = U(S, V, \boldsymbol{n})$, $H = H(S, p, \boldsymbol{n})$, $A = A(T, V, \boldsymbol{n})$, and $G = G(T, p, \boldsymbol{n})$ with respect to any two of its variables, we obtain the Maxwell relations

$$\left(\frac{\partial T}{\partial V}\right)_{S,\boldsymbol{n}} = -\left(\frac{\partial p}{\partial S}\right)_{V,\boldsymbol{n}} \tag{8}$$

$$\left(\frac{\partial \mu_i}{\partial S}\right)_{V,\boldsymbol{n}} = \left(\frac{\partial T}{\partial n_i}\right)_{S,V,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{9}$$

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{S,\boldsymbol{n}} = -\left(\frac{\partial p}{\partial n_i}\right)_{S,V,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{10}$$

$$\left(\frac{\partial T}{\partial p}\right)_{S,\boldsymbol{n}} = \left(\frac{\partial V}{\partial S}\right)_{p,\boldsymbol{n}} \tag{11}$$

$$\left(\frac{\partial \mu_i}{\partial S}\right)_{p,\boldsymbol{n}} = \left(\frac{\partial T}{\partial n_i}\right)_{S,p,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{12}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{S,\boldsymbol{n}} = \left(\frac{\partial V}{\partial n_i}\right)_{S,p,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{13}$$

$$\left(\frac{\partial S}{\partial V}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial p}{\partial T}\right)_{V,\boldsymbol{n}} \tag{14}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{V,\boldsymbol{n}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,V,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{15}$$

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,\boldsymbol{n}} = -\left(\frac{\partial p}{\partial n_i}\right)_{T,V,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{16}$$

$$\left(\frac{\partial S}{\partial p}\right)_{T,\boldsymbol{n}} = -\left(\frac{\partial V}{\partial T}\right)_{p,\boldsymbol{n}} \tag{17}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{18}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,\boldsymbol{n}} \quad \text{for } i = 1, 2, \ldots, r \tag{19}$$

We reiterate that all these results are valid for any amounts of constituents, including a single particle with only one translational degree of freedom in any of its stable equilibrium states. There are other results, however, which obtain only for systems with large values of the amounts of constituents.

3. SIMPLE SYSTEMS

3.1 Definition

We define a system as simple if it has volume as the only parameter, and if it satisfies the following two additional requirements.

(a) If in any of its stable equilibrium states it is partitioned into a set of contiguous subsystems in mutual stable equilibrium, the system is such that the effects of the partitions are negligible.

(b) In any of its stable equilibrium states, the instantaneous "switching on or off" of one or more internal reaction mechanisms causes negligible instantaneous changes in the values of the energy, entropy, volume, and amounts of constituents.

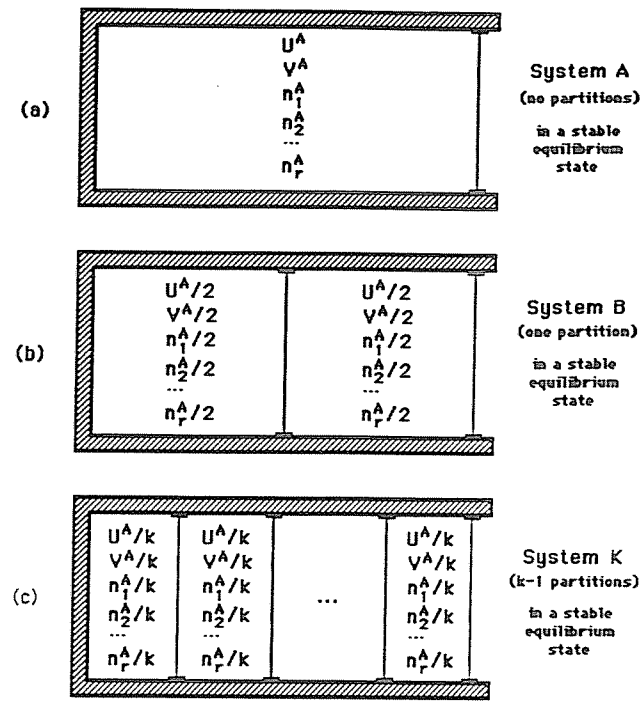

Figure 1.

In general, when Conditions (a) and (b) are satisfied, we find that results obtained for stable equilibrium states of a simple system with one set of values of the amounts of constituents and the volume can be readily extended to other sets of values, and that certain properties and variables are explicitly interrelated.

In this paper, we explore the implications of the validity of Condition (a). The discussion of the implications of both Conditions (a) and (b) is given in Ref.6, Chapter 30.

3.2 Implications of Partitioning

We consider systems A and B shown schematically in Figures 1a and 1b. System A is in a stable equilibrium state with energy U^A, volume V^A, and amounts of constituents n_1^A, n_2^A, ..., n_r^A. System B consists of two subsystems, each identical to system A but in a stable equilibrium state with energy $U^A/2$, volume $V^A/2$, and amounts of constituents $n_1^A/2$, $n_2^A/2$, ..., $n_r^A/2$. Being in identical stable equilibrium states, the two subsystems have identical values of temperature T, pressure p, and chemical potentials $\mu_1, \mu_2, \ldots, \mu_r$, that is, they are in mutual stable equilibrium and, therefore, system B is in a stable equilibrium state. It is noteworthy that system B is not identical to system A because it requires two parameters, that is, a volume for each of the two subsystems, rather than just one volume.

By virtue of the fundamental relation for systems with volume as the only parameter (Equation 2), and the additivity of entropy, systems A and B have entropies

$$S^A = S^A(U^A, V^A, \boldsymbol{n}^A) \tag{20}$$

and

$$S^B = 2\,S^A(U^A/2, V^A/2, \boldsymbol{n}^A/2) \tag{21}$$

In general, S^A is not equal to S^B because of the presence of the partition that separates the two subsystems of system B. For example, if each of the two subsystems of B contains only one particle, then it can be shown with the tools of quantum theory that the particle is not uniformly distributed in the available space, it is more rarefied near the confining walls and, therefore, the wall partitioning system B into the two subsystems imposes a significant difference between the properties of systems A and B.

However, it can also be shown with the tools of quantum theory that such differences become less and less important, and negligible for all practical purposes, as the values of the amounts of constituents in each subsystem increase beyond a relatively small number[7.8]. Hence, if the amounts of constituents are large, we can neglect the effects of the partition, write $S^B = S^A$ without appreciable error, neglect the differences between systems A and B, and conclude that the stable equilibrium state of A is the same as the state of B, and that the temperature, pressure, and chemical potentials of A have the same values as the respective properties of each subsystem of B.

We can repeat the preceding reasoning for the systems A and K shown in Figures 1a and 1c. System K consists of a large number k of subsystems, each in a stable equilibrium state with energy U^A/k, volume V^A/k, and amounts of constituents n_1^A/k, n_2^A/k, ..., n_r^A/k. For large amounts of constituents, we conclude again that the effects of the partitions can be neglected, and that

$$S^K = k\,S^A(U^A/k, V^A/k, n_1^A/k, n_2^A/k, \ldots, n_r^A/k) \approx S^A \quad (22)$$

Of course, we reiterate that the influence of partitions is not negligible if the number of particles in any of the subsystems is very small. Hence, the results just cited cannot hold for arbitrarily large values of k. However, because we are usually concerned with amounts of constituents that correspond to very large numbers of particles, the effect of partitions is negligible up to a very large number of subdivisions, so that each subsystem resulting from such a subdivision can be considered for all practical purposes infinitesimal as compared to the overall system.

Subject to the restriction just cited, we can write the relation between the entropies of A and each subsystem of K in Figure 1 in the form

$$S(U, V, \boldsymbol{n}) = k\,S(U/k, V/k, \boldsymbol{n}/k) \quad (23)$$

where we drop the superscript "A" for simplicity.

Using Equation 3, we write $U^A = U^A(S^A, V^A, \boldsymbol{n}^A)$. Because each of the subsystems of K is in a stable equilibrium state with entropy S^A/k, volume V^A/k, and amounts of constituents $\boldsymbol{n}^A/k$, its energy must be $U^A(S^A/k, V^A/k, \boldsymbol{n}^A/k)$. Because the effects of the partitions are negligible and energy is additive, $U^A = U^K$ and, therefore,

$$U(S, V, \boldsymbol{n}) = k\,U(S/k, V/k, \boldsymbol{n}/k) \quad (24)$$

where again we drop the superscript "A" for simplicity.

From Equations 23 and 24, we conclude that each of the functions $S = S(U, V, \boldsymbol{n})$ and $U = U(S, V, \boldsymbol{n})$ is homogeneous of degree one with respect to each of its variables. Moreover, if the homogeneity holds for any integer number k, it holds also for any real number k because such k can always be approximated by a sequence of ratios of integers k_1/k_2 that tend to k.

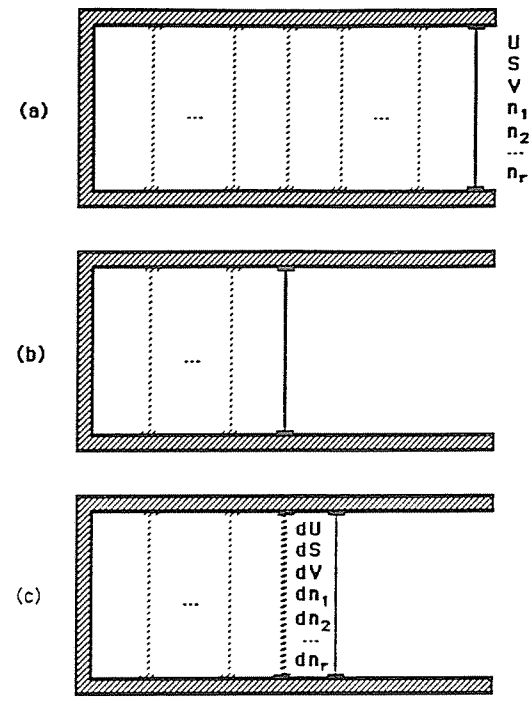

Figure 2.

The homogeneities of degree one of the fundamental relation $S = S(U, V, \boldsymbol{n})$ and the energy relation $U = U(S, V, \boldsymbol{n})$ are the main consequences of Condition (a) in the definition of a simple system. From these consequences follow many results that simplify the study of the stable equilibrium states of any substance. For example, experimental values of properties of a simple system corresponding to given values U, V, $\boldsymbol{n}$ can be readily extended to any other larger or smaller values of these variables. We discuss this result in more detail in Sections 3.5 and 3.6.

From Equation 24 we see that the stable equilibrium properties of a simple system with entropy S, volume V, and amounts of constituents $\boldsymbol{n}$ are identical to those of a composite of k subsystems each of which is identical to the overall system but in a stable equilibrium state with entropy, volume, and amounts of constituents k times smaller. Being identical and in identical states, all such subsystems have the same temperature, pressure, and chemical potentials, and these are also the temperature, pressure and chemical potentials of the overall system. Because the number k can be chosen very large, a simple system in a stable equilibrium state can always be viewed as a composite of a contiguous collection of infinitesimal simple subsystems, all in mutual stable equilibrium.

3.3 Euler and Gibbs-Duhem Relations

We consider a simple system (Figure 2a) in a stable equilibrium state having entropy S, volume V, amounts of constituents $\boldsymbol{n}$, energy $U(S, V, \boldsymbol{n})$, temperature T, pressure p, and chemical potentials μ_1, μ_2, ..., μ_r. We subdivide this system into a contiguous collection of infinitesimal subsystems, each

having the same temperature T, pressure p, and chemical potentials μ_1, μ_2, ..., μ_r as the system itself, and entropy dS, volume dV, amounts of constituents dn_1, dn_2, ..., dn_r, and energy dU.

Alternatively, the differential dU may be regarded as the difference in energy between two neighboring stable equilibrium states (Figures 2b and 2c) differing in entropy by dS, in volume by dV, and in amounts of constituents by dn_1, dn_2, ..., dn_r. As such, it is given by Equation 7, the Gibbs relation. This relation imposes a restriction on the differences dU, dS, dV, and dn_i for $i = 1, 2, \ldots, r$ between two neighboring stable equilibrium states and the values of T, p, and μ_i for $i = 1, 2, \ldots, r$ of one of these states.

The additive properties energy U and entropy S, the additive volume V, and the additive amounts n_1, n_2, ..., n_r of the simple system can each be viewed as the sum or integral of the energies, entropies, volumes, and amounts, respectively, of all the infinitesimal subsystems in a given partition of the spatial extension of the simple system.

Thus, for given values of T, p, μ_1, μ_2, ..., μ_r, we can think of the simple system in Figure 2a as resulting from successive additions of infinitesimal parts which build up the value of each of U, S, V, n_1, n_2, ..., n_r from zero to the value of the simple system, while maintaining each of the properties T, p, μ_1, μ_2, ..., μ_r unchanged throughout all the additions. At each step (Figures 2b and 2c) the increments dU, dS, dV, dn_1, dn_2, ..., dn_r are related by the Gibbs relation. Hence, upon integration of Equation 7 at constant T, p, μ_1, μ_2, ..., μ_r, we find the Euler relation, that is,

$$U = TS - pV + \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_r n_r \qquad (25)$$

Clearly, Equation 25 is valid for any set of values T, p, μ_1, μ_2, ..., μ_r consistent with the values of S, V, n_1, n_2, ..., n_r and, therefore, it is valid for all such values.

The Euler relation can be derived also by a different procedure, based directly on the homogeneity of degree one of the energy relation. Indeed, we define the variables $S' = S/k$, $V' = V/k$, and $\boldsymbol{n}' = \boldsymbol{n}/k$, so that Equation 24 becomes $U(S, V, \boldsymbol{n}) = k\,U(S', V', \boldsymbol{n}')$. Differentiating this equation with respect to k at constant S', V', $\boldsymbol{n}'$, we find

$$\left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} S' + \left(\frac{\partial U}{\partial V}\right)_{S,\boldsymbol{n}} V' + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V,\boldsymbol{n}} n_i' = U(S', V', \boldsymbol{n}') \qquad (26)$$

This equation holds for all values of k, including $k = 1$. But then $S' = S$, $V' = V$, $n' = n$ and, recalling the definitions of T, p, and μ_i for $i = 1, 2, \ldots, r$, we obtain Equation 25.

Upon writing the differential of Equation 25 in the form

$$dU = T\,dS + S\,dT - p\,dV - V\,dp + \mu_1\,dn_1 + n_1\,d\mu_1 + \mu_2\,dn_2 + n_2\,d\mu_2 + \cdots + \mu_r\,dn_r + n_r\,d\mu_r \qquad (27)$$

and substituting dU from Equation 7, we find another important and useful result, the Gibbs-Duhem relation

$$S\,dT - V\,dp + n_1\,d\mu_1 + n_2\,d\mu_2 + \cdots + n_r\,d\mu_r = 0 \qquad (28)$$

This relation imposes a restriction on the differences dT, dp, and $d\mu_i$ for $i = 1, 2, \ldots, r$ between two neighboring stable equilibrium states, and the values of S, V, and n_i for $i = 1, 2, \ldots, r$ of one of these states.

3.4 Extensive and Intensive Properties

For a simple system in a stable equilibrium state, and for any number k, the temperature $T(S, V, \boldsymbol{n}) = (\partial U/\partial S)_{V,\boldsymbol{n}}$, pressure $p(S, V, \boldsymbol{n}) = -(\partial U/\partial V)_{S,\boldsymbol{n}}$, and chemical potentials $\mu_i(S, V, \boldsymbol{n}) = (\partial U/\partial n_i)_{S,V,\boldsymbol{n}}$, for $i = 1, 2, \ldots, r$, satisfy the relations

$$T(S, V, \boldsymbol{n}) = T(S/k, V/k, \boldsymbol{n}/k) \qquad (29)$$

$$p(S, V, \boldsymbol{n}) = p(S/k, V/k, \boldsymbol{n}/k) \qquad (30)$$

$$\mu_i(S, V, \boldsymbol{n}) = \mu_i(S/k, V/k, \boldsymbol{n}/k) \quad \text{for } i = 1, 2, \ldots, r \qquad (31)$$

namely, if each of the values of the additive variables S, V, n_1, n_2, ..., n_r is altered by a factor k, the values of the temperature T, the pressure p, and the chemical potentials μ_1, μ_2, ..., μ_r remain unaltered.

To provide a proof, we define the variables $S' = S/k$, $V' = V/k$ and $\boldsymbol{n}' = \boldsymbol{n}/k$ so that Equation 24 becomes $U(S, V, \boldsymbol{n}) = k\,U(S', V', \boldsymbol{n}')$. Differentiating this equation with respect to S at constant V, $\boldsymbol{n}$ and k, we find

$$T(S, V, \boldsymbol{n}) = \left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}} = k\left(\frac{\partial U}{\partial S'}\right)_{V',\boldsymbol{n}'} \frac{1}{k} = T(S', V', \boldsymbol{n}') \qquad (32)$$

that is, Equation 29. Similarly, by differentiating $U(S, V, \boldsymbol{n})$ with respect to V at constant S, $\boldsymbol{n}$ and k, we obtain Equation 30 and by differentiating $U(S, V, \boldsymbol{n})$ with respect to n_i at constant S, V, k and the remaining n's, we obtain Equation 31.

In contrast to T, p, and μ_i, other properties of a stable equilibrium state change by a factor of k if each of the additive variables S, V, $\boldsymbol{n}$ changes by the same factor. For example, energy behaves in this manner (Equation 24). Again, the enthalpy $H(S, p, \boldsymbol{n})$, the Helmholtz free energy $A(T, V, \boldsymbol{n})$, and the Gibbs free energy $G(T, p, \boldsymbol{n})$ exhibit the same behavior because they satisfy the relations

$$H(S, p, \boldsymbol{n}) = k\,H(S/k, p, \boldsymbol{n}/k) \qquad (33)$$

$$A(T, V, \boldsymbol{n}) = k\,A(T, V/k, \boldsymbol{n}/k) \qquad (34)$$

$$G(T, p, \boldsymbol{n}) = k\,G(T, p, \boldsymbol{n}/k) \qquad (35)$$

Indeed, consider the simple system as a composite of k identical simple subsystems all in mutual stable equilibrium with temperature T, pressure p, chemical potentials μ_i, for $i = 1, 2, \ldots, r$, entropy S/k, volume V/k, and amounts n_i/k for $i = 1, 2, \ldots, r$. By Equations 23 and 29 to 31, the overall simple system with entropy S, volume V, and amounts n_i, for $i = 1, 2, \ldots, r$, has energy $U(S, V, \boldsymbol{n})$, temperature T, pressure p, and chemical potentials μ_i, for $i = 1, 2, \ldots, r$. Therefore, the enthalpy of the overall system is given by $H(S, p, \boldsymbol{n}) = U(S, V, \boldsymbol{n}) + pV = k[U(S/k, V/k, \boldsymbol{n}/k) + pV/k] = k\,H(S/k, p, \boldsymbol{n}/k)$ (Equation 33). Similar proofs yield Equations 34 and 35 for the Helmholtz free energy and the Gibbs free energy, respectively.

It is noteworthy that the enthalpy, the Helmholtz free energy, and the Gibbs free energy are defined only for stable equilibrium

states. For example, if a system is composed of two subsystems each in a stable equilibrium state but not in mutual stable equilibrium, then the enthalpy, the Helmholtz free energy, and the Gibbs free energy are defined for each subsystem but not for the overall system.

We call extensive any property of a stable equilibrium state which remains unchanged if each of the additive variables S, V, and $\boldsymbol{n}$ changes by a factor k. For example, the energy and the enthalpy of a simple system are extensive properties because of Equations 24 and 33, respectively.

We suggest that the concept of extensiveness should be used exclusively for stable equilibrium states of simple systems and not synonymously with the concept of additivity.

Every additive property is also extensive, but an extensive property is additive only if restricted to systems in mutual equilibrium and not for all systems in all states. For example, energy is both extensive and additive, but enthalpy is only extensive and not additive because, in general, the sum of the enthalpies of two systems in stable equilibrium states does not represent an enthalpy of the composite of the two systems unless they are in mutual stable equilibrium.

We call intensive any property of a stable equilibrium state of a simple system which remains unchanged if each of the additive variables S, V, and $\boldsymbol{n}$ changes by a factor k. Mathematically, a function of many variables which remains unchanged if some of the variables change by a factor k is called homogeneous of degree zero with respect to these variables. For example, temperature, pressure, and chemical potentials are all intensive properties of stable equilibrium states of any simple system because of Equations 29 to 31. Again, any partial derivative of an extensive property with respect to another extensive property is intensive according to our definition because both the numerator and the denominator of the partial derivative change by the same factor as the common factor that denotes the change in S, V, and $\boldsymbol{n}$.

Other properties of stable equilibrium states of simple systems that are intensive are all the ratios of any two extensive quantities such as U, S, V, n_1, n_2, ..., n_r, H, A, G, or ratios of any linear combination of these quantities such as U and either the total amount of constituents $n = n_1 + n_2 + \cdots + n_r$ or the mass m. Indeed, if each of S, V, $\boldsymbol{n}$ changes by a factor k, each extensive quantity changes by the same factor and, therefore, the ratio of any two extensive quantities remains unchanged. A ratio of two extensive quantities or properties is also called a specific property.

Extensive and intensive properties are not all inclusive. Some properties fail to conform to either definition. For example, the square of the energy is a property that is neither extensive nor intensive. No special name is provided for such properties because they are not encountered very often in practice.

3.5 Dependences of Intensive Properties

In general, a property of a stable equilibrium state of a simple system with r constituents depends on $r + 2$ independent variables such as S, V, n_1, n_2, ..., n_r. In contrast, each intensive property depends at most on $r + 1$ independent variables because each such property is independent of the total amount of constituents.

We can verify the last assertion by considering any intensive property. For example, if in Equation 29 for temperature we assume that $k = n$, where n is the total amount of constituents, $n = n_1 + n_2 + \cdots + n_r$, then we find

$$T(S, V, n_1, n_2, \ldots, n_r) = T(s, v, y_1, y_2, \ldots, y_r) \qquad (36)$$

where $s = S/n$, $v = V/n$, $y_1 = n_1/n$, $y_2 = n_2/n$, ..., $y_r = n_r/n$. The function $T(s, v, y_1, y_2, \ldots, y_r)$ depends at most on $r + 1$ independent intensive variables because we can use the relation $y_1 + y_2 + \cdots + y_r = 1$ to eliminate one of the fractions y_i. The same conclusion can be reached for the pressure and the chemical potentials, by examining Equations 30 and 31.

A consequence of these results is that the $r+2$ intensive properties T, p, μ_1, μ_2, ..., μ_r cannot all be varied independently because they depend at most on $r + 1$ independent variables. We reach the same conclusion by recognizing that the Gibbs-Duhem relation (Equation 28) imposes a general restriction on the possible changes in these properties.

Another illustration of the reduced number of independent variables necessary to describe intensive properties is provided by the dependences of ratios of extensive properties. Using the Gibbs-Duhem relation, and evaluating it for different combinations of differentials, we find

$$\frac{S}{V} = \left(\frac{\partial p}{\partial T}\right)_{\mu} \quad \frac{S}{n_i} = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\mu} \quad \frac{V}{n_i} = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\mu} \qquad (37)$$

where subscript "μ" stands for all the μ_j's being kept fixed except for the one that appears in the partial derivative. We see that each of the ratios of the extensive quantities S, V, n_1, n_2, ..., n_r is determined by a partial derivative, and that each function that is being differentiated depends at most on $r + 1$ independent variables. For example, S/V depends on T, μ_1, μ_2, ..., μ_r.

3.6 Dependences of Extensive Properties

For simple systems, another important aspect of the reduced dependences of intensive and specific properties is that they are independent of the amount n. To verify this assertion, we consider the specific internal energy u defined by the relation

$$\begin{aligned} u &= U(S, V, n_1, n_2, \ldots, n_r)/n \\ &= U(ns, nv, ny_1, ny_2, \ldots, ny_r)/n \end{aligned} \qquad (38)$$

Upon differentiating this relation, we find

$$\begin{aligned} du &= \frac{1}{n}\,dU - \frac{U}{n^2}\,dn \\ &= \frac{1}{n}\left[\left(\frac{\partial U}{\partial S}\right)_{V,\boldsymbol{n}}(n\,ds + s\,dn) + \left(\frac{\partial U}{\partial V}\right)_{S,\boldsymbol{n}}(n\,dv + v\,dn) \right. \\ &\qquad \left. + \sum_{i=1}^{r}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,\boldsymbol{n}}(n\,dy_i + y_i\,dn)\right] - \frac{U}{n^2}\,dn \\ &= T\,ds - p\,dv + \sum_{i=1}^{r}\mu_i\,dy_i \\ &\qquad - \frac{1}{n^2}\left(U - TS + pV - \sum_{i=1}^{r}\mu_i n_i\right)dn \end{aligned} \qquad (39)$$

Each of the coefficients of the $r+3$ differentials in the right-hand

side of the third of Equations 39 represents a partial derivative with respect to the variable in the corresponding differential. In particular, the coefficient of dn equals $(\partial u/\partial n)_{s,v,\boldsymbol{y}}$, where the subscript "$\boldsymbol{y}$" denotes that all mole fractions are kept fixed. But $U-TS+pV-\sum_{i=1}^{r}\mu_i n_i = 0$ because of the Euler relation (Equation 25), and therefore $(\partial u/\partial n)_{s,v,\boldsymbol{y}} = 0$,

$$du = T\,ds - p\,dv + \sum_{i=1}^{r}\mu_i\,dy_i \tag{40}$$

and

$$u = u(s, v, y_1, y_2, \ldots, y_r) \tag{41}$$

subject to the relation $y_1 + y_2 + \cdots + y_r = 1$.

A similar procedure can be used to show that the specific Gibbs free energy $g = G/n$ is a function of T, p, and $\boldsymbol{y}$ only, i.e., $g = g(T, p, y_1, y_2, \ldots, y_r)$. Indeed, upon differentiating the relation $g = G(T, p, \boldsymbol{n})/n$ we find

$$\begin{aligned} dg &= -s\,dT + v\,dp + \sum_{i=1}^{r}\mu_i\,dy_i - \frac{1}{n^2}\left(G - \sum_{i=1}^{r}\mu_i n_i\right)dn \\ &= -s\,dT + v\,dp + \sum_{i=1}^{r}\mu_i\,dy_i \\ &\quad - \frac{1}{n^2}\left(U - TS + pV - \sum_{i=1}^{r}\mu_i n_i\right)dn \\ &= -s\,dT + v\,dp + \sum_{i=1}^{r}\mu_i\,dy_i \end{aligned} \tag{42}$$

where the second of Equations 42 results from the relation $G = U - TS + pV$, and the third from the Euler relation. Thus, we verify that g is a function of T, p, and $\boldsymbol{y}$ only, independent of n.

In particular, for a single-constituent simple system it also follows that $G = \mu n$ and, therefore,

$$\mu = \frac{G}{n} = g(T, p) = u + pv - Ts = h - Ts \tag{43}$$

i.e., the chemical potential is equal to the specific Gibbs free energy, and can be expressed in terms of the specific enthalpy h and the specific entropy s. Moreover, because for such a system $y = 1$ and $dy = 0$, Equations 40 and 42 become

$$du = T\,ds - p\,dv \tag{44}$$

$$d\mu = -s\,dT + v\,dp \tag{45}$$

where in writing Equation 46 we use the result $\mu = g$ (Equation 43). The last equation is the Gibbs-Duhem relation of the single-constituent simple system in terms of its specific entropy and specific volume.

Equations 38 and 41 imply that in order to evaluate the energy relation $U = U(S, V, n_1, n_2, \ldots, n_r)$ for a simple system it suffices to determine the relation $u = u(s, v, y_1, y_2, \ldots, y_r)$ and then multiply by the total amount n, i.e.,

$$U(S, V, \boldsymbol{n}) = n\,u(s, v, \boldsymbol{y}) \tag{46}$$

and therefore the number of independent variables is reduced by one. In practice this result allows to obtain the values of properties of an arbitrary amount of a pure substance ($r = 1$) or a mixture with given proportions ($r > 1$) from data on the properties of a unit amount, say, one mole. This result is so useful and so powerful that it is often given for granted in most expositions of thermodynamics. In this paper we emphasize that it follows from the Euler relation, and therefore from the homogeneity of degree one of the fundamental relation which in turn is valid only when Condition (a) in our definition of a simple system is satisfied.

CONCLUSIONS

If a phenomenon can be modeled as occurring in a simple system in stable equilibrium states, a host of practical and powerful results obtain. A prerequisite for such modeling is that the system consist of relatively large amounts of constituents.

However, not all consequences of thermodynamics are subject to the restriction of large magnitudes of the amounts of constituents. For example, all the results summarized in Section 2 are valid regardless of the magnitudes of the amounts of constituents, including microsystems.

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