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The Consequences of Extensivity

Every mathematician knows it is impossible to understand an elementary course in thermodynamics.

V. I. Arnold, Soviet and Russian mathematician, 1937–2010

In this chapter we return to the thermodynamic postulates and consider the consequences of extensivity. As defined in Section 9.7.1, the entropy is extensive if

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \quad (13.1)$$

for any positive value of the parameter λ . The postulate of extensivity means that S , U , V , and N are all proportional to the size of the system.

The properties of additivity and extensivity are often confused. However, they are not the same. As long as the molecular interactions are short-ranged, the entropy of the macroscopic system will be additive, that is, the total entropy of systems A and B is given by the sum of the individual entropies,

$$S_{A,B}(U_A, V_A, N_A; U_B, V_B, N_B) = S_A(U_A, V_A, N_A) + S_B(U_B, V_B, N_B). \quad (13.2)$$

It is common for books on thermodynamics to assume from the beginning that all systems are homogeneous. If a system is homogeneous, then additivity automatically implies extensivity. This is the source of the confusion.

Most real systems are not extensive. A simple example is given by a container of gas that can adsorb molecules on its walls. As the size of the container is varied, the surface-to-volume ratio varies, and the fraction of the molecules adsorbed on the walls also varies. The properties of the system will depend on the surface-to-volume ratio, and eq. (13.1) will not be satisfied.

Even crystals or liquids with free boundary conditions will have contributions to the energy and free energies from surfaces and interfaces. It is important to be able to treat such systems, so that surface properties can be unambiguously defined and studied.

On the other hand, we are often interested in the bulk properties of a material and would like to be able to investigate its thermodynamic behavior without concerning ourselves with surfaces or interfaces. In these circumstances it is reasonable to consider

a homogeneous and extensive system consisting entirely of the material of interest. Such a system would satisfy the postulate of extensivity.

13.1 The Euler Equation

If a system is extensive its energy is a homogeneous first-order function, and satisfies eq. (13.1), $\lambda U(S, V, N) = U(\lambda S, \lambda V, \lambda N)$, for any value of λ .

If we differentiate eq. (13.1) with respect to λ , we find

$$\begin{aligned} U(S, V, N) &= \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial (\lambda S)} \frac{\partial (\lambda S)}{\partial \lambda} \\ &\quad + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial (\lambda V)} \frac{\partial (\lambda V)}{\partial \lambda} \\ &\quad + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial (\lambda N)} \frac{\partial (\lambda N)}{\partial \lambda}. \end{aligned} \quad (13.3)$$

Setting $\lambda = 1$, this becomes

$$U(S, V, N) = \frac{\partial U(S, V, N)}{\partial S} S + \frac{\partial U(S, V, N)}{\partial V} V + \frac{\partial U(S, V, N)}{\partial N} N. \quad (13.4)$$

If we now substitute for the partial derivatives, we find

$$U = TS - PV + \mu N \quad (13.5)$$

which is known as the Euler equation.

Note that the Euler equation is trivial to remember if you have memorized eq. (10.27), which states: $dU = TdS - PdV + \mu dN$.

The Euler equation can also be expressed in terms of the entropy,

$$S = \left(\frac{1}{T}\right)U + \left(\frac{P}{T}\right)V - \left(\frac{\mu}{T}\right)N. \quad (13.6)$$

or, using \tilde{S} from Section 12.6,

$$\tilde{S} = \beta U + (\beta P) V - (\beta \mu) N. \quad (13.7)$$

This equation can be found directly from the homogeneous first-order property of the entropy given in eq. (13.1), or more simply by rewriting eq. (13.5).

The most important consequence of extensivity is the Euler equation. It can be extremely useful, but it must be kept in mind that it is valid only for extensive systems.

13.2 The Gibbs–Duhem Relation

If a system is extensive, the three intensive parameters, T , P , and μ are not independent. The Gibbs–Duhem relation, which can be derived from the Euler equation, makes explicit the connection between changes in these parameters.

First, we can write the complete differential form of eq. (13.5),

$$dU = TdS - PdV + \mu dN + SdT - VdP + Nd\mu. \quad (13.8)$$

Comparing eq. (13.8) to the differential form of the First Law, eq. (10.27),

$$dU = TdS - PdV + \mu dN \quad (13.9)$$

and subtracting the one from the other, we find the Gibbs–Duhem relation:

$$0 = SdT - VdP + Nd\mu. \quad (13.10)$$

Another way of writing this is to exhibit the change in μ as a function of the changes in T and P

$$d\mu = -\left(\frac{S}{N}\right)dT + \left(\frac{V}{N}\right)dP. \quad (13.11)$$

This form of the Gibbs–Duhem relation involves the entropy per particle and the volume per particle, which might not be the most convenient quantities to work with. If we carry out the same derivation starting with the fundamental relation in the entropy representation, $S = S(U, V, N)$, we find an alternative formulation of the Gibbs–Duhem relation:

$$d\left(\frac{\mu}{T}\right) = \left(\frac{U}{N}\right)d\left(\frac{1}{T}\right) + \left(\frac{V}{N}\right)d\left(\frac{P}{T}\right). \quad (13.12)$$

Using \tilde{S} and β , this becomes

$$d(\beta\mu) = \left(\frac{U}{N}\right)d\beta + \left(\frac{V}{N}\right)d(\beta P). \quad (13.13)$$

For our simple example of a one-component system, we can see that only two parameters are free. For any changes in the temperature or pressure, the change in the chemical potential is fixed by eq. (13.11). The number of free parameters needed

to specify a thermodynamic system is called the number of *thermodynamic degrees of freedom* for the system. A simple, homogeneous, one-component system has two degrees of freedom.

The Euler equation and the Gibbs–Duhem relation can both be generalized to r components by including a chemical potential term $\mu_j dN_j$ for each component j in the differential form of the fundamental relation

$$dU = TdS - PdV + \sum_{j=1}^r \mu_j dN_j. \quad (13.14)$$

The Gibbs–Duhem relation becomes

$$0 = SdT - VdP + \sum_{j=1}^r N_j d\mu_j. \quad (13.15)$$

A direct consequence is that if we have an extensive system with r components, it will have $r+1$ thermodynamic degrees of freedom.

13.3 Reconstructing the Fundamental Relation

We have seen in Section 8 that although an equation of state contains thermodynamic information, the information is not complete. For a general system we can only reconstruct the fundamental relation and obtain complete information if we know all three equations of state for a one-component system, or all $r+2$ equations of state for a system with r components.

An important consequence of the Gibbs–Duhem relation is that for extensive systems we only need $r+1$ equations of state for an r -component system to recover the fundamental relation and with it access to all thermodynamic information.

As an example, consider the classical, one-component ideal gas. Suppose we were to know only two of the three equations of state,

$$PV = Nk_B T \quad (13.16)$$

and

$$U = \frac{3}{2} Nk_B T. \quad (13.17)$$

If we can calculate the third equation of state, we can substitute it into the Euler equation to find the fundamental relation.

To carry out this project, it is convenient to introduce the volume per particle $v = V/N$ and the energy per particle $u = U/N$. The ideal gas law in the form

$$\frac{P}{T} = k_B v^{-1} \quad (13.18)$$

gives us

$$d\left(\frac{P}{T}\right) = -k_B v^{-2} dv \quad (13.19)$$

and the energy equation

$$\frac{1}{T} = \frac{3}{2} k_B u^{-1} \quad (13.20)$$

gives us

$$d\left(\frac{1}{T}\right) = -\frac{3}{2} k_B u^{-2} du. \quad (13.21)$$

Inserting eqs. (13.19) and (13.21) into the Gibbs–Duhem relation, eq. (13.12),

$$d\left(\frac{\mu}{T}\right) = u d\left(\frac{1}{T}\right) + v d\left(\frac{P}{T}\right), \quad (13.22)$$

we find

$$d\left(\frac{\mu}{T}\right) = -u \frac{3}{2} k_B u^{-2} du - v k_B v^{-2} dv = -\frac{3}{2} k_B u^{-1} du - k_B v^{-1} dv. \quad (13.23)$$

Integrating eq. (13.23) we obtain the third equation of state,

$$\frac{\mu}{T} = -\frac{3}{2} k_B \ln(u) - k_B \ln(v) + X. \quad (13.24)$$

An arbitrary constant of integration, X , is included in this equation, which reflects the arbitrary constant in classical expressions for the entropy. Putting these results together to find a fundamental relation is left as an exercise.

13.4 Thermodynamic Potentials

The Euler equation (13.5) puts strong restrictions on thermodynamic potentials introduced in Chapter 12 for extensive systems in the form of alternative expressions. For

the thermodynamic potentials F , H , and G , we have the following identities for extensive systems:

$$F = U - TS = -PV + \mu N \quad (13.25)$$

$$H = U + PV = TS + \mu N \quad (13.26)$$

$$G = U - TS + PV = \mu N. \quad (13.27)$$

Note that eq. (13.27) expresses the chemical potential as the Gibbs free energy per particle for extensive systems

$$\mu = \frac{G}{N}. \quad (13.28)$$

The thermodynamic potential $U[T, P, \mu]$ vanishes for extensive systems,

$$U[T, P, \mu] = U - TS + PV - \mu N = 0. \quad (13.29)$$

For this reason, $U[T, P, \mu]$ is often omitted in books on thermodynamics that restrict the discussion to extensive systems. However, $U[T, P, \mu]$ does not vanish for general thermodynamic systems, and it is sensitive to surface and interface properties.