

Basic interfacial thermodynamics and related mathematical background

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Abstract This study is intended to give the reader a brief overview of the mathematical background to the thermodynamic theory of surfaces and interfaces. Some general aspects of the thermodynamics of systems with interfaces are discussed, and a concise treatment of interfaces within the framework of classical thermodynamics is provided. First, to introduce the reader to the topic, a reasonably simple thermodynamic treatment of interfaces, together with a brief description of the models widely used in the literature, is presented, the characteristics of the Gibbs “dividing plane” model and the Guggenheim “interphase” model are outlined, and a derivation of the Gibbs adsorption equation is given. In the subsequent sections, several important mathematical concepts (e.g., theory of homogeneous functions and partly homogeneous functions, Euler’s theorem and the Gibbs–Duhem equation, Legendre transformation) and various functional relationships of the thermodynamics of surfaces and interfaces are summarized, with particular attention to some alternative formulations. Some of the mathematical principles and methods are explained using illustrative examples.

Keywords Interfacial thermodynamics · Gibbs model · Guggenheim model · Homogeneous functions · Partly homogeneous functions · Euler’s theorem · Legendre transformation · Gibbs–Duhem equation

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Introduction

Despite the advent of surface-sensitive techniques, thermodynamic measurements remain a valuable tool for the investigation of surfaces and interfaces.

Many (heterogeneous) systems of practical importance can only be described by complex thermodynamic models including interface(s). For instance, electrodes are, in fact, capillary systems, because the interactions between the different phases take place via the surface region. Thus, the understanding of the thermodynamics of these interfaces is of importance to all surface scientists and electrochemists.

The aim of the present study is to give a brief overview of the mathematical background, some important mathematical concepts, and various functional relationships underlying the thermodynamic theory of interfaces (theory of homogeneous functions and partly homogeneous functions, Euler’s theorem and the Gibbs–Duhem equation, Legendre transformation). The mathematical principles are explained and illustrated with some typical examples.

First, to introduce the reader to the topic, a reasonably simple thermodynamic treatment of interfaces, together with a brief description of the models widely used in the literature, is presented (more detailed discussions can be found in several reviews and research papers [1–16]).

Basic concepts and notions related to the thermodynamics of interfaces

Models of the interfacial region

Interfacial thermodynamics is the study of the application of thermodynamics to interfacial phenomena, addressing topics, including adsorption, interfacial energies, interfacial

tion, and superficial charge, and about relations among them [see e.g., 1–18]. Adsorption of one or more of the components, at one or more of the phase boundaries of a multicomponent, multiphase system, is said to occur if the concentrations in the interfacial layers are different from those in the adjoining bulk phases. Consequently, the overall stoichiometry of the system deviates from that corresponding to a reference system of (hypothetical) homogeneous bulk phases whose volumes and/or amounts are defined by suitably chosen dividing surfaces, or by a suitable algebraic method (see later).

The classic work is that of Gibbs [19]; a paper by Guggenheim and Adam [20] discusses the physical interpretation of surface excesses, and Guggenheim [21] has given a good summary of interfacial thermodynamics emphasizing a viewpoint somewhat different from that of Gibbs.

In many studies, the plane ideally marking the boundary between two phases is called the interface. Although interfaces are always dealt with from a thermodynamic point of view, if attention is actually focused on only one of the two phases, the plane marking the boundary between the phase and the environment is often called the surface of the phase (see e.g., [22]). The two words (i.e., “interface” and “surface”) are often used synonymously, although interface is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly, e.g., the solid/gas interface [23].

The region between two phases where the properties vary between those in the bulk is the “interfacial” or “interface” region, and sometimes it is called the “interphase.”

An interface or interphase does not exist in isolation, and valid thermodynamic conclusions can only be drawn by considering the system, namely the interface and the two bordering regions, as a whole. Provided that the radius of curvature is large, the interface/interphase may be regarded as a plane and its energy then differs from that of a bulk phase by a term expressing the contribution of changes of energy due to a change of the area of contact. Edge effects can be eliminated by considering a section of an interface in a larger system. There is no clear boundary between the interfacial region and the bulk of the phases, so that the thickness of the interphase depends on the model chosen to describe this region. The geometric area is represented by the product of the length and breadth of a rectangle enclosing part of a surface. Many properties of a system, for example, concentration of a particular species, vary as a function of the distance perpendicular to the surface, as shown in Fig. 1.

The classical Gibbs approach is based on a model in which a real interface layer is replaced by a dividing

surface [19]. Gibbs found it mathematically convenient to consider an idealized system depicted in Fig. 1b, with properties identical with those of the whole real system. The “surface of discontinuity” or “dividing surface” in the idealized system is a two-dimensional region whose position is determined by the requirements that the property under consideration should maintain a uniform value in each bulk phase right up to the dividing surface. This corresponds to equating the two shaded areas in Fig. 1b. A disadvantage of this approach is that the position of the dividing surface alters according to the property considered.

In the Guggenheim model, two dividing surfaces, one at each boundary, are employed (Fig. 1c). It is assumed that there is a “surface” or “interfacial” layer of finite thickness (τ) bounded by two appropriately chosen surfaces parallel to the phase boundary, one in each of the adjacent homogeneous bulk phases. A layer of this kind is sometimes called a Guggenheim layer or “interphase.” A disadvantage is that terms dependent on surface volume are present in the equations, but it is difficult to assign values to these terms. (It should be noted that for very highly curved surfaces, i.e., when the radius of curvature is of the same magnitude as τ , the notion of a surface layer may lose its usefulness.)

Given a system, subsystems consisting of a segment of the interface and finite volumes of the adjacent phases can be selected. In principle, these subsystems should not be geometrically regular in shape; however, the rectangular parallelepiped-shaped domain is usually the most expedient selection. In two dimensions, the macroscopic subsystem selected for investigation is represented by the ABCD rectangle (Fig. 1).

Usually, the thickness of the interface or local values of physical quantities (parameters) cannot be measured. That is the reason why integrated quantities (which are accessible experimentally, or can be calculated from experimental data) are used for the thermodynamic characterization of interfaces. Generally, these quantities are given by the expression:

$$\Psi^\sigma = \int_{\alpha\alpha}^{\beta\beta} Y(\xi) d\xi, \quad (1)$$

where ξ is the coordinate perpendicular to the plane of the interface, Y is the function of ξ , Ψ^σ is the integrated physical quantity, and $\alpha\alpha$ and $\beta\beta$ are the two adjacent (homogeneous) phases.

Let the area of the surface or interface in the system defined according to the above concepts be denoted by A , and the internal energy by U . The volume V of the system is the sum of the volumes of the two phases $\alpha\alpha$ and $\beta\beta$, and the volume of the inhomogeneous region is as follows:

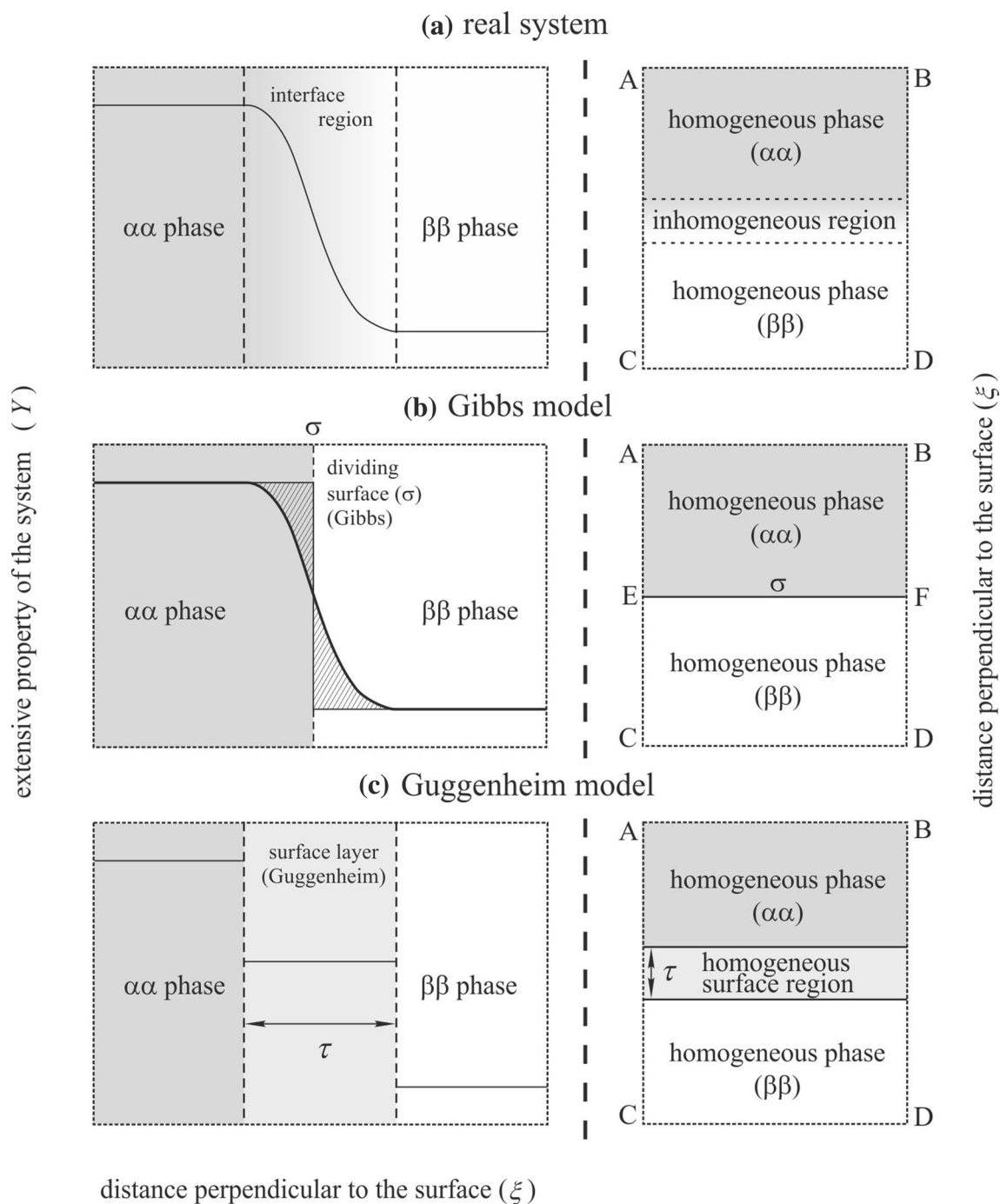


Fig. 1 A schematic representation of the interfacial region, the Gibbs “dividing surface” (“surface of discontinuity” or “mathematical plane”) and the “interfacial layer” concept (“interphase”) proposed by Guggenheim. **a** The real system, **b** the Gibbs model of the

interface, and **c** the Guggenheim model of the interface. On the *right-hand side*: the macroscopic subsystems selected for investigation are represented by the ABCD rectangles

$$V = V^{\alpha\alpha} + V^{\beta\beta} + V^{\text{inh}}. \quad (2)$$

The internal energy can be given as

$$U = U^{\alpha\alpha} + U^{\beta\beta} + U^{\text{inh}}. \quad (3)$$

Of course, this division is completely arbitrary, since the values on the right-hand sides of Eqs. (2) and (3) depend on

the (arbitrary) choice of the dividing surface(s). In the Guggenheim model, the volume V^σ of the interfacial layer is $V^\sigma = \tau A$. (4)

The Gibbs dividing surface (or Gibbs surface) is a geometrical surface chosen parallel to the interface and used to define the volumes of the bulk phases. That is

$$V = V^{\alpha\alpha} + V^{\beta\beta}. \quad (5)$$

This means that the volume of the “surface phase is” $V^\sigma \equiv 0$.

Adsorption

As already discussed above, the Gibbs interface is a two-dimensional homogeneous phase without thickness (i.e., the interface is regarded as a mathematical dividing surface). In Guggenheim’s approach, the interface is considered to be a surface phase with finite thickness and volume treated in a way analogous to bulk phases, except that the thermodynamic equations contain terms related to the contributions of changes of energy due to changes of area and electrical state of the interface.

The two apparently different approaches can be essentially characterized by the following procedure:

- There is an idealized surface or surface phase separating two homogeneous bulk phases (see Fig. 1). The bulk phases are in equilibrium with the surface phase.
- Two separated reference systems α and β thought to be noninteracting homogeneous bulk phases have to be chosen (see Fig. 2), the conditions of temperature, pressure, and composition being identical to those in the adsorption equilibrium. Both reference phases consist of suitably defined amounts of the components. Each of the chosen reference amounts is characterized by its respective molar or specific properties.
- Any extensive property of the reference systems is simply the sum of the contributions from the reference amounts, without any contributions from interactions with the interfacial layer in the real system.

The surface excess quantities are then the respective differences between the real system and the chosen reference systems (or reference phases). As explained above, this can be done, e.g., in the Gibbs sense of the total extensive quantity minus its amount residing in hypothetical bulk phases that are uniform up to a mathematical dividing surface, or in the Guggenheim sense of excesses over the average bulk amount in a boundary zone (“surface phase”) of finite but small thickness. Obviously, if the Gibbs model is used for the definition of surface excesses, the reference amounts in the two reference phases are thought to be contained in and making up the volume of the actual real system, but can equally well be thought to be quite independent and spatially apart one from the other. On the other hand, however, the volume of the chosen

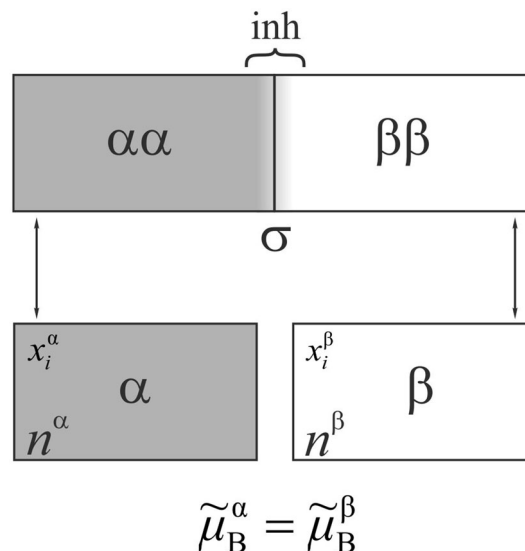


Fig. 2 Scheme of the “real system” with the inhomogeneous “interfacial region” (inh) and the “model system.” In the Gibbsian model, there is a hypothetical “dividing surface” (σ) (in the Guggenheim model a hypothetical, three-dimensional surface phase, see Fig. 1) which is separating two homogeneous bulk phases $\alpha\alpha$ and $\beta\beta$ (that are in equilibrium with the surface region). The two reference systems are α and β

reference amounts is not necessarily equal to the volume of the real system. It is even not necessary that the corresponding phases are effectively present in their chosen reference states within the real system. In principle, this is why the Gibbs and the Guggenheim approaches can be considered as equivalent. Nevertheless, there is an important restriction in the Guggenheim approach replacing the condition of equivalent volumes in the Gibbs method: the reference systems must be chosen in such a manner that the remaining “surface phase” has a constant thickness. Thus, this restriction essentially affects the choice of the geometrical shape of the reference systems. However, since the reference systems are homogeneous bulk phases, their thermodynamic properties are independent of the shape. For this reason, a set of appropriate reference systems can be always selected without loss of generality. This consideration determines implicitly the selection of thermodynamic systems “with cylindrical shape” [24], a “parallelepiped” [25], or simply as a “section” of the interface cut out by perpendicular planes [26–28].

The surface excess amount or Gibbs adsorption of component i is n_i^σ , which may be positive or negative, and is defined as the excess of the amount of this component actually present in the system over that present in a reference system of the same volume as the real system and in which the bulk concentrations in the two phases remain uniform up to the Gibbs dividing surface.

$$\begin{aligned} n_i^\sigma &= n_i - n_i^\alpha - n_i^\beta = n_i - n^\alpha x_i^\alpha - n^\beta x_i^\beta \\ &= n_i - n^\alpha x_i^{\alpha\alpha} - n^\beta x_i^{\beta\beta}, \end{aligned} \quad (6)$$

where n_i is the total amount of component i in the “real” system, x_i^α and x_i^β are the mole fractions in phases α and β , respectively, and n^α and n^β are the total amounts of the components (“total number of moles”) in the reference systems. It is clear from Eq. (6) that the surface excess amount is well defined only when n^α and n^β are fixed. It can be also seen that with different n^α and n^β values we have different values for n_i^σ .

According to the above considerations, the surface excess X^σ of any extensive property X is calculated as

$$X^\sigma = X - X^\alpha - X^\beta, \quad (7)$$

where X denotes the value of the extensive property for the whole system and X^α and X^β are the values for the reference systems.

The relation that gives the internal energy U as a function of the extensive parameters is a fundamental relation. If the fundamental relation of a particular system is known, all conceivable thermodynamic information about this system can be ascertained [29]. The internal energies of the reference phases are given by

$$U^\alpha = U^\alpha(S^\alpha, V^\alpha, n_1^\alpha \dots n_m^\alpha) \quad (8)$$

and

$$U^\beta = U^\beta(S^\beta, V^\beta, n_1^\beta \dots n_m^\beta). \quad (9)$$

The internal energy (U) of the system depends on the entropy (S), volume (V), amounts $n_1 \dots n_m$ of the components 1, ... m , and the surface area (A):

$$U = U(S, V, A, n_1 \dots n_m). \quad (10)$$

The excess of the internal energy is given by

$$U^\sigma = U - U^\alpha - U^\beta, \quad (11)$$

and the excess of the entropy is

$$S^\sigma = S - S^\alpha - S^\beta. \quad (12)$$

The excess internal energy function

$$U^\sigma = U^\sigma(S^\sigma, V^\sigma, A, n_1^\sigma \dots n_m^\sigma) \quad (13)$$

is a homogeneous function of degree one with respect to all variables (see “[Homogeneous functions](#)” section, especially Examples #1 and #4), if $V^\sigma \equiv 0$ (Gibbs model), or $V^\sigma = A\tau$ (Guggenheim model), since it is evident that

$$U^\sigma(kS^\sigma, kV^\sigma, kA, kn_i^\sigma \dots kn_m^\sigma) = kU^\sigma(S^\sigma, V^\sigma, A, n_i^\sigma \dots n_m^\sigma) \quad (14)$$

for all $k > 0$ real numbers.

Therefore, according to Euler’s theorem (see “[Homogeneous functions](#)” section and Example #4), and in the framework of the Gibbs model

$$U^\sigma = T^\sigma S^\sigma + \gamma A + \sum_i \mu_i^\sigma n_i^\sigma, \quad (15)$$

where γ is the intensive (interfacial) parameter conjugate to the extensive variable A .

Due to the thermodynamic equilibrium

$$T^\sigma = T^\alpha = T^\beta = T^{\alpha\alpha} = T^{\beta\beta} = T, \quad (16)$$

and

$$\mu_i^\sigma = \mu_i^\alpha = \mu_i^\beta = \mu_i^{\alpha\alpha} = \mu_i^{\beta\beta} = \mu_i. \quad (17)$$

According to the equations like the two above, it is not necessary to use superscripts to distinguish T , $\mu_1 \dots \mu_m$, in the different equilibrium phases because these must have uniform values throughout α , β , $\alpha\alpha$, $\beta\beta$, and σ (due to the equilibrium assumptions).

In the two reference phases, the following relationships are valid:

$$U^\alpha = TS^\alpha - pV^\alpha + \sum_i \mu_i n_i^\alpha, \quad (18)$$

and

$$U^\beta = TS^\beta - pV^\beta + \sum_i \mu_i n_i^\beta. \quad (19)$$

According to Eq. (15), the intensive parameter (γ) is defined by

$$\gamma = \left(\frac{\partial U^\sigma}{\partial A} \right)_{S^\sigma, n_1^\sigma \dots n_m^\sigma}. \quad (20)$$

Although this expression is mathematically correct, it is not really useful for practical purposes. Equation (15) expresses the dependence of the energy U on the basis of independent variables S^σ , A , $n_1^\sigma \dots n_m^\sigma$. This set of independent variables is not by any means the most convenient. It is usually preferable to use T as an independent variable instead of S . If the experiment is such that the external conditions are constant temperature and constant pressure, the most convenient potential function to use is the Gibbs free energy function, $G(T, p, n_1 \dots n_m)$, obtained from $U(S, V, n_1 \dots n_m)$ by two subsequent Legendre transformations (see “[Adsorption](#)” section and especially Example #12):

$$G^\alpha = U^\alpha + pV^\alpha - TS^\alpha \quad (21)$$

and

$$G^\beta = U^\beta + pV^\beta - TS^\beta. \quad (22)$$

Consequently

$$G^\alpha = \sum_i \mu_i n_i^\alpha \quad (23)$$

and

$$G^\beta = \sum_i \mu_i n_i^\beta. \quad (24)$$

The excess Gibbs free energy function is given as

$$G^\sigma = \gamma A + \sum_i \mu_i n_i^\sigma, \quad (25)$$

and γ is defined by

$$\gamma = \left(\frac{\partial G^\sigma}{\partial A} \right)_{T, n_1^\sigma, \dots, n_m^\sigma}. \quad (26)$$

Unfortunately, this definition of γ is still not appropriate for experimental studies or to confirm experimental results since $G^\sigma(T, A, n_1^\sigma \dots n_m^\sigma)$ remains ill-defined and arbitrary (because $n_1^\sigma \dots n_m^\sigma$ clearly depend on the selection of the reference systems). The Gibbs free energy function for the whole system can be expressed as

$$\begin{aligned} G &= \gamma A + \sum_i \mu_i n_i^\alpha + \sum_i \mu_i n_i^\beta + \sum_i \mu_i n_i^\sigma \\ &= \gamma A + \sum_i \mu_i (n_i^\alpha + n_i^\beta + n_i^\sigma). \end{aligned} \quad (27)$$

This means that γ can also be defined in terms of the Gibbs free energy function of the whole system as

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T, p, n_1, \dots, n_m}, \quad (28)$$

or in terms of the Helmholtz (free) energy function as

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T, V, n_1, \dots, n_m}, \quad (29)$$

when the Helmholtz energy or “free energy” function is defined as the Legendre transform of the internal energy function ($F = U - T \cdot S$). On the other hand—still remaining in the framework of the Gibbs model—it should be noted that since no volume term appears in Eq. (15), there is no distinction between the surface Helmholtz and Gibbs free energies.

According to the above discussions, G^σ is a partly homogeneous function of degree one (see “[The Gibbs–Duhem equation](#)” section) in the variables A and $n_1^\sigma \dots n_m^\sigma$. The expression for the total differential of G^σ is

$$\begin{aligned} dG^\sigma &= \left(\frac{\partial G^\sigma}{\partial T} \right)_{A, n_1^\sigma, \dots, n_m^\sigma} dT + \left(\frac{\partial G^\sigma}{\partial A} \right)_{T, n_1^\sigma, \dots, n_m^\sigma} dA \\ &\quad + \sum_i \left(\frac{\partial G^\sigma}{\partial A} \right)_{T, A, n_{j \neq i}^\sigma} dn_i^\sigma. \end{aligned} \quad (30)$$

Taking into account that $\left(\frac{\partial G^\sigma}{\partial T} \right)_{A, n_1^\sigma, \dots, n_m^\sigma} = -S^\sigma$, $\left(\frac{\partial G^\sigma}{\partial A} \right)_{T, n_1^\sigma, \dots, n_m^\sigma} = \gamma$, and $\left(\frac{\partial G^\sigma}{\partial A} \right)_{T, A, n_{j \neq i}^\sigma} = \mu_i$, Equation (30) can be written as

$$dG^\sigma = -S^\sigma dT + \gamma dA + \sum_i \mu_i dn_i^\sigma. \quad (31)$$

The differential of Eq. (25) is

$$dG^\sigma = \gamma dA + A d\gamma + \sum_i \mu_i dn_i^\sigma + \sum_i n_i^\sigma d\mu_i. \quad (32)$$

There are thus two (general) expressions for dG^σ (Eqs. 31 and 32), both of which are correct. This can only be the case if

$$S^\sigma dT + A d\gamma + \sum_i n_i^\sigma d\mu_i = 0. \quad (33)$$

Equation (33) is the so-called Gibbs–Duhem equation for interfaces (see “[The Gibbs–Duhem equation](#)” section). At constant temperature

$$-A d\gamma = \sum_i n_i^\sigma d\mu_i. \quad (34)$$

Dividing both sides of Eq. (33) by A yields

$$-d\gamma = \sum_i \frac{n_i^\sigma}{A} d\mu_i = \sum_i \Gamma_i d\mu_i, \quad (35)$$

where Γ_i is the surface excess concentration of species i . Equation (35) is commonly called the Gibbs adsorption equation.

In the case of liquid/liquid interfaces, the interfacial intensive parameter (γ) can be identified with the interfacial tension. (Note that in case of solid/liquid interfaces there is some controversy in the literature concerning the correct name of γ , e.g., it is sometimes called “specific surface energy” or “surface stress” [1, 16, 26, 30, 31]).

There are two important points that should be addressed here:

1. In the case of ionic components (charged species), “electrochemical potentials” ($\tilde{\mu}_i$) may be used instead of “chemical potentials” in the corresponding equations.
2. It follows from Eq. (6) (which is the definition equation of the surface excess amounts) that the Γ_i values are uncertain, since they depend on the arbitrary selection of n^α and n^β .

Nevertheless, for the analysis of the experimental data we need measurable physical quantities that do not depend on the size of the reference phases.

The following procedure can be used for this purpose. At constant T and p , the Gibbs–Duhem relationships for the two reference bulk phases are

$$\sum_i x_i^\alpha d\mu_i = 0 \quad (36)$$

and

$$\sum_i x_i^\beta d\mu_i = 0. \quad (37)$$

Using the above two relationships, it is possible to express $d\mu_1$ and $d\mu_2$ (i.e., the differential changes of the chemical potentials of two selected components) as a function of the other $d\mu_i$ values and the mole fractions at constant temperature and pressure:

$$d\mu_1 = -\frac{x_2^\alpha}{x_1^\alpha} d\mu_2 - \sum_{i \neq 1,2} \frac{x_i^\alpha}{x_1^\alpha} d\mu_i, \quad (38)$$

and

$$d\mu_2 = -\frac{x_1^\beta}{x_2^\beta} d\mu_1 - \sum_{i \neq 1,2} \frac{x_i^\beta}{x_2^\beta} d\mu_i. \quad (39)$$

Combining Eq. (35) with Eqs. (38) and (39), we obtain

$$-d\gamma = \frac{1}{A} \sum_{i \neq 1,2} \left(n_i^\sigma + \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} n_1^\sigma + \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} n_2^\sigma \right) d\mu_i \quad (40)$$

or

$$-d\gamma = \sum_{i \neq 1,2} \left(\Gamma_i + \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} \Gamma_1 + \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} \Gamma_2 \right) d\mu_i. \quad (41)$$

By taking into account that

$$\Gamma_i = \frac{1}{A} \left(n_i - n^\alpha x_i^\alpha - n^\beta x_i^\beta \right), \quad (42)$$

we have

$$-d\gamma = \frac{1}{A} \sum_{i \neq 1,2} \left(n_i + n_1 \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} + n_2 \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} \right) d\mu_i \quad (43)$$

or

$$-d\gamma = \sum_{i \neq 1,2} \left(\Gamma_i + \Gamma_1 \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} + \Gamma_2 \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} \right) d\mu_i. \quad (44)$$

Equation (44) can be written in the simpler form:

$$-d\gamma = \sum_{i \neq 1,2} \Gamma_i' d\mu_i, \quad (45)$$

where Γ_i' denotes the (relative) surface excess of component i with respect to the two selected components, and

$$\Gamma_i' = \Gamma_i + \Gamma_1 \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} + \Gamma_2 \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta}. \quad (46)$$

It is clear that the Γ_i' values do not depend on the selection of the reference systems (that is, on the selection of n^α and n^β).

Therefore, the Γ_i' values can be determined as

$$\Gamma_i' = - \left(\frac{\partial \gamma}{\partial \mu_i} \right)_{T,p,\mu_j \neq i} = - \frac{1}{RT} \left(\frac{\partial \gamma}{\partial a_i} \right)_{T,p,a_j \neq i} \quad (47)$$

(or more exactly $\Gamma_i' = - \left(\frac{\partial \gamma}{\partial a_{i(i \neq 1,2)}^{\mu_{i \neq 1,2}}} \right)_{T,p,a_j \neq i}$), where a_i denotes the relative activity of component i .

Equation (45) (*Gibbs adsorption isotherm* also called the *Gibbs adsorption equation*) is one of the most important results from interfacial thermodynamics, and it is used all the time in physical chemistry and surface science.

In the following sections, we will briefly review the relevant mathematical background necessary for some of the derivations presented above.

The mathematical background of interfacial thermodynamics

Homogeneous functions

Definition

Let $f(x_1, x_2, \dots, x_m)$ be a real function of variables x_1, x_2, \dots, x_m . The function f is a homogeneous function if for all values of the factor $k > 0$

$$f(kx_1, kx_2, \dots, kx_m) = s(k)f(x_1, x_2, \dots, x_m), \quad (\text{M.1})$$

where the function $s(k)$ is usually called the scaling function, and is given by $s(k) = k^n$.

In other words, a homogeneous function is a function of one or several variables that satisfies the following condition: when all independent variables of a function are simultaneously multiplied by the same (arbitrary) factor, the value of the function is multiplied by some power of this factor. That is, if

$$f(kx_1, kx_2, \dots, kx_m) = k^n f(x_1, x_2, \dots, x_m) \quad (\text{M.2})$$

for all $k > 0$, then f is said to be a *homogeneous function of degree n* . The degree n can take on any value (positive, negative, or zero). A function f is linearly homogeneous if it is homogeneous of degree 1.

If for a function f the equation

$$f(kx_1, \dots, kx_m, y_1, \dots, y_w) = k^n f(x_1, \dots, x_m, y_1, \dots, y_w) \quad (\text{M.3})$$

is true, then we say that this function is homogeneous of degree n in the variables x_1, x_2, \dots, x_m . Such functions are called partly (or partially) homogeneous functions [1]. (It should be noted that it is possible for functions to be homogeneous of different degree in different variables, but

here we restrict our attention to functions for which Eq. (M.2) or Eq. (M.3) holds.

Some remarks to the definition of homogeneous functions

Remark #1 A homogeneous function of degree n gives rise to a set of derivative functions that are homogeneous in the same set of variables and of degree $n - 1$, that is, partial derivatives of a homogeneous function of degree n are homogeneous functions of degree $n - 1$.

Proof Differentiating both sides of Eq. (M.2) with respect to x_i (for $i = 1, \dots, m$), we get

$$k \frac{\partial f(kx_1, \dots, kx_m)}{\partial kx_i} = k^n \frac{\partial f(x_1, \dots, x_m)}{\partial x_i}, \quad (\text{M.4})$$

and then dividing both sides of Eq. (M.4) by k we obtain

$$\frac{\partial f(kx_1, \dots, kx_m)}{\partial kx_i} = k^{n-1} \frac{\partial f(x_1, \dots, x_m)}{\partial x_i}. \quad (\text{M.5})$$

Hence the derivatives of f are homogeneous of degree $n - 1$.

For example, in case of a homogeneous function of the first degree $f(kx_1, kx_2, \dots, kx_m) = kf(x_1, x_2, \dots, x_m)$ the partial derivative with respect to x_i is $\frac{\partial f(kx_1, \dots, kx_m)}{\partial kx_i} \frac{\partial kx_i}{\partial x_i} = k \frac{\partial f(x_1, \dots, x_m)}{\partial x_i}$, and therefore $\frac{\partial f(kx_1, \dots, kx_m)}{\partial kx_i} = \frac{\partial f(x_1, \dots, x_m)}{\partial x_i}$.

Remark #2 Suppose that the domain of definition of the function f lies in the first quadrant, $x_1 > 0, \dots, x_m > 0$, and contains the whole ray (kx_1, \dots, kx_m) , $k > 0$, whenever it contains (x_1, \dots, x_m) , i.e., it is assumed that for every point (x_1, \dots, x_m) in the domain of f , the point (kx_1, \dots, kx_m) also belongs to this domain for any $k > 0$. Then f is homogeneous of degree n if and only if there exists a function g of $m-1$ variables defined on the set of points of the form $(x_2/x_1, \dots, x_m/x_1)$ such that for all (x_1, \dots, x_m) in the domain of definition [see for example refs. 32, 33]:

$$f(x_1, \dots, x_m) = x_1^n g(x_2/x_1, \dots, x_m/x_1). \quad (\text{M.6})$$

Proof Let $f(x_1, x_2, \dots, x_m)$ be a homogeneous function of degree n of variables x_1, x_2, \dots, x_m such that for all $k > 0$

$$f(kx_1, \dots, kx_m) = k^n f(x_1, \dots, x_m). \quad (\text{M.7})$$

Obviously

$$f(x_1, x_2, \dots, x_m) = f\left(x_1, \frac{x_2}{x_1}x_1, \dots, \frac{x_m}{x_1}x_1\right). \quad (\text{M.8})$$

If we set $k = 1/x_1$, we have

$$f(x_1, x_2, \dots, x_m) = x_1^n f\left(1, \frac{x_2}{x_1}, \dots, \frac{x_m}{x_1}\right). \quad (\text{M.9})$$

This means that f is represented by

$$f = x_1^n g\left(\frac{x_2}{x_1}, \dots, \frac{x_m}{x_1}\right) \quad (\text{M.10})$$

with some function g . Since, conversely, every function f formed by means of an appropriate function g of $m - 1$ variables satisfies the condition of homogeneity, the expression (M.10) represents the totality of homogeneous functions of degree n .

Euler's theorem

Euler's Theorem states that the differentiable function f of m variables is homogeneous of degree n , then the following identity holds:

$$nf(x_1, x_2, \dots, x_m) = \sum_{i=1}^m x_i \frac{\partial f}{\partial x_i}. \quad (\text{M.11})$$

Proof Let f be a homogeneous function of degree n such that

$$f(\kappa \hat{x}_1, \kappa \hat{x}_2, \dots, \kappa \hat{x}_m) = \kappa^n f(\hat{x}_1, \hat{x}_2, \dots, \hat{x}_m), \quad (\text{M.12})$$

and $k \neq 0$, $\frac{1}{k} = \kappa$, $x_i = \frac{1}{k} \hat{x}_i = \kappa \hat{x}_i$, $kx_i = \hat{x}_i$.

Evidently

$$\begin{aligned} f(\kappa \hat{x}_1, \kappa \hat{x}_2, \dots, \kappa \hat{x}_m) &= f(x_1, x_2, \dots, x_m) \\ &= \left(\frac{1}{k}\right)^n f(kx_1, kx_2, \dots, kx_m), \end{aligned} \quad (\text{M.13})$$

and

$$\begin{aligned} k^n f(x_1, x_2, \dots, x_m) &= f(kx_1, kx_2, \dots, kx_m) \\ &= f(\hat{x}_1, \hat{x}_2, \dots, \hat{x}_m), \end{aligned} \quad (\text{M.14})$$

i.e., $f(x_1, x_2, \dots, x_m)$ is also a homogeneous function of degree n .

Differentiating each side of formula (M.12) with respect to κ , we have the following relationship:

$$\begin{aligned} \frac{\partial f(\kappa \hat{x}_1, \kappa \hat{x}_2, \dots, \kappa \hat{x}_m)}{\partial \kappa \hat{x}_1} \hat{x}_1 + \frac{\partial f(\kappa \hat{x}_1, \kappa \hat{x}_2, \dots, \kappa \hat{x}_m)}{\partial \kappa \hat{x}_2} \hat{x}_2 + \dots \\ + \frac{\partial f(\kappa \hat{x}_1, \kappa \hat{x}_2, \dots, \kappa \hat{x}_m)}{\partial \kappa \hat{x}_m} \hat{x}_m = n \kappa^{n-1} f(\hat{x}_1, \hat{x}_2, \dots, \hat{x}_m). \end{aligned} \quad (\text{M.15})$$

Introducing $\kappa = \frac{1}{k}$, $x_i = \kappa \hat{x}_i$, $\hat{x}_i = kx_i$, Eq. (M.15) combined with Eq. (M.14) can be rewritten as

$$\begin{aligned} \frac{\partial f(x_1, x_2, \dots, x_m)}{\partial x_1} kx_1 + \frac{\partial f(x_1, x_2, \dots, x_m)}{\partial x_2} kx_2 + \dots \\ + \frac{\partial f(x_1, x_2, \dots, x_m)}{\partial x_m} kx_m = n \left(\frac{1}{k}\right)^{n-1} k^n f(kx_1, kx_2, \dots, kx_m). \end{aligned} \quad (\text{M.16})$$

This means that

$$\sum_{i=1}^m \frac{\partial f(x_1, x_2, \dots, x_m)}{\partial x_i} x_i = nf(x_1, x_2, \dots, x_m), \quad (\text{M.17})$$

or obviously

$$\sum_{i=1}^m \frac{\partial f(\hat{x}_1, \hat{x}_2, \dots, \hat{x}_m)}{\partial \hat{x}_i} \hat{x}_i = nf(\hat{x}_1, \hat{x}_2, \dots, \hat{x}_m), \quad (\text{M.18})$$

which is exactly *Euler's theorem*.

(Alternatively, by differentiating Eq. (M.2) with respect to k we get

$$\frac{\partial}{\partial k} f(kx_1, kx_2, \dots, kx_m) = \frac{\partial}{\partial k} k^n f(x_1, x_2, \dots, x_m) \quad (\text{M.19})$$

and thus

$$\sum_{i=1}^m \frac{\partial f(kx_1, kx_2, \dots, kx_m)}{\partial kx_i} x_i = nk^{n-1} f(x_1, x_2, \dots, x_m). \quad (\text{M.20})$$

Then, setting $k = 1$

$$\sum_{i=1}^m x_i \frac{\partial f(x_1, x_2, \dots, x_m)}{\partial x_i} = nf(x_1, x_2, \dots, x_m) \quad (\text{M.21})$$

which was to be proved).

We can show that the *converse theorem* also holds, that is if the function f of the real variables x_1, x_2, \dots, x_m satisfies the identity (M.11), then the function f is homogeneous of degree n .

Let us fix (x_1, x_2, \dots, x_m) and define the function g of a single variable t as

$$g(t) = t^{-n} f(tx_1, \dots, tx_m) - f(x_1, \dots, x_m). \quad (\text{M.22})$$

Differentiating each side of this equation with respect to t , we get

$$\frac{dg(t)}{dt} = -nt^{-n-1} f(tx_1, \dots, tx_m) + t^{-n} \sum_{i=1}^m x_i \frac{df(tx_1, \dots, tx_m)}{dtx_i}. \quad (\text{M.23})$$

By Euler's theorem, we have

$$\sum_{i=1}^m \frac{\partial f(tx_1, \dots, tx_m)}{\partial tx_i} tx_i = nf(tx_1, \dots, tx_m), \quad (\text{M.24})$$

so that

$$\begin{aligned} \frac{\partial g(t)}{\partial t} &= -nt^{-n-1} f(tx_1, \dots, tx_m) + t^{-n} \frac{1}{t} nf(tx_1, \dots, tx_m) \\ &= 0. \end{aligned} \quad (\text{M.25})$$

Thus $g(t)$ is constant for all t . It is clear that $g(1) = 0$, and therefore $g(t) = 0$ for all t , and with Eq. (M.22) we get

$$t^{-n} f(tx_1, \dots, tx_m) - f(x_1, \dots, x_m) = 0, \quad (\text{M.26})$$

and so

$$f(tx_1, \dots, tx_m) = t^n f(x_1, \dots, x_m) \quad (\text{M.27})$$

for all $t > 0$, which means that f is homogeneous of degree n .

(Alternative proof: Let $g(t) = f(tx_1, \dots, tx_m)$. After differentiation with respect to t and by taking into account Eq. (M.11), we see that

$$\begin{aligned} \frac{\partial g(t)}{\partial t} &= x_1 \frac{\partial f(tx_1, tx_2, \dots, tx_m)}{\partial tx_1} + x_2 \frac{\partial f(tx_1, tx_2, \dots, tx_m)}{\partial tx_2} \\ &\quad + \dots + x_m \frac{\partial f(tx_1, tx_2, \dots, tx_m)}{\partial tx_m} \\ &= \frac{1}{t} \left[tx_1 \frac{\partial f(tx_1, tx_2, \dots, tx_m)}{\partial tx_1} + tx_2 \frac{\partial f(tx_1, tx_2, \dots, tx_m)}{\partial tx_2} \right. \\ &\quad \left. + \dots + tx_m \frac{\partial f(tx_1, tx_2, \dots, tx_m)}{\partial tx_m} \right] \\ &= \frac{n}{t} f(tx_1, tx_2, \dots, tx_m) = \frac{n}{t} g(t) \end{aligned} \quad (\text{M.28})$$

This means that

$$\frac{dg(t)}{dt} = \frac{n}{t} g(t). \quad (\text{M.29})$$

After integration, we obtain for any $t > 0$

$$\ln|g(t)| = n \ln t + c, \quad (\text{M.30})$$

where c is an integration constant, which is independent on t . This means that

$$g(t) = e^c t^n. \quad (\text{M.31})$$

Choosing $t = 1$, we see that $g(1) = e^c$ and consequently $g(t) = g(1)t^n$, i.e., Eq. (M.27) holds).

Some remarks to Euler's theorem

Extensive variables in thermodynamics are those that depend linearly on the size of the system. This means that if a system is composed of several subsystems, the value of the extensive variable ("extensive quantity") for the composite system is calculated by summing over the subsystems. As a consequence, extensive thermodynamic functions are homogeneous functions of degree $n = 1$ (homogeneous linear functions) with respect to their extensive arguments, i.e.,

$$f(kx_1, \dots, kx_m) = kf(x_1, \dots, x_m), \quad (\text{M.32})$$

and so

$$\sum_{i=1}^m \frac{\partial f}{\partial x_i} x_i = f(x_1, \dots, x_m). \quad (\text{M.33})$$

According to Eq. (M.5), partial derivatives of a homogeneous linear function are homogeneous functions of degree $n = 0$ (homogeneous function of 0th degree), i.e.,

$$f(kx_1, \dots, kx_m) = f(x_1, \dots, x_m) \tag{M.34}$$

and

$$\sum_{i=1}^m \frac{\partial f}{\partial x_i} x_i = 0. \tag{M.35}$$

Example #1 Let us consider the following function:

$$f(x, y, z) = -\frac{x^3}{yz}. \tag{E.1.1}$$

Since

$$f(kx, ky, kz) = -\frac{(kx)^3}{(ky)(kz)} = k \left(-\frac{x^3}{yz} \right) = kf(x, y, z), \tag{E.1.2}$$

the function $f(x, y, z)$ is homogeneous of the first degree in the variables $x, y,$ and z . The partial derivatives are $\frac{\partial f}{\partial x} = -\frac{3x^2}{yz}, \frac{\partial f}{\partial y} = \frac{x^3}{y^2z},$ and $\frac{\partial f}{\partial z} = \frac{x^3}{yz^2}.$

Thus, applying Euler's theorem

$$\begin{aligned} f(x, y, z) &= \frac{\partial f}{\partial x} \cdot x + \frac{\partial f}{\partial y} \cdot y + \frac{\partial f}{\partial z} \cdot z \\ &= \left(-\frac{3x^2}{yz} \right) x + \left(\frac{x^3}{y^2z} \right) y + \left(\frac{x^3}{yz^2} \right) z = -\frac{x^3}{yz}. \end{aligned} \tag{E.1.3}$$

Example #2 We know that partial derivatives of a homogeneous function of degree n are homogeneous functions of degree $n - 1$.

The partial derivative of the function f (which is a homogeneous function of degree 1, as defined by Eq. (E.1.1)) with respect to x is

$$f_x = \frac{\partial f}{\partial x} = -\frac{3x^2}{yz}. \tag{E.2.1}$$

The function f_x is a homogeneous function of degree 0 in the variables $x, y,$ and $z,$ since

$$f_x(kx, ky, kz) = -\frac{3(kx)^2}{(ky)(kz)} = -\frac{3x^2}{yz} = f_x(x, y, z). \tag{E.2.2}$$

The partial derivatives are $\frac{\partial f_x}{\partial x} = -\frac{6x}{yz}, \frac{\partial f_x}{\partial y} = \frac{3x^2}{y^2z},$ and $\frac{\partial f_x}{\partial z} = \frac{3x^2}{yz^2},$ that is

$$\left(-\frac{6x}{yz} \right) x + \left(\frac{3x^2}{y^2z} \right) y + \left(\frac{3x^2}{yz^2} \right) z = 0 \tag{E.2.3}$$

in accordance with Euler's theorem.

The Gibbs–Duhem Equation

If the function $f(x_1, x_2, \dots, x_m)$ is homogeneous of degree $n = 1$ with respect to the variables $x_1, x_2, \dots, x_m,$ then one has the identity (M.2):

$$f(kx_1, kx_2, \dots, kx_m) = kf(x_1, x_2, \dots, x_m).$$

Let us set $\frac{\partial f}{\partial x_1} = p_1, \dots, \frac{\partial f}{\partial x_m} = p_m,$ etc., and apply Euler's theorem to the function $f.$

We will obtain

$$f = x_1 p_1 + x_2 p_2 + \dots + x_m p_m. \tag{M.36}$$

It results from this formula that the functions p_1, p_2, \dots, p_m are quantities (functions) of the same type as the quotient of energy or work by charge, mass, etc., and hence these are quantities (functions) of the same type as a potential, e.g., in thermodynamics, if f is the internal energy function ($U,$ see “Models of the interfacial region” and “Adsorption” sections), and the x_i -s are the amounts of substances, we can call them *partial molar internal energies of the constituents* 1, ..., m in the system (thermodynamic or chemical potentials).

According to the considerations outlined above, the functions p_1, p_2, \dots, p_m are homogeneous functions of degree zero in the variables $x_1, x_2, \dots, x_m.$ To each of these functions, we can apply Euler's theorem, and we will find the identities

$$\begin{aligned} x_1 \frac{\partial p_1}{\partial x_1} + x_2 \frac{\partial p_1}{\partial x_2} + \dots + x_m \frac{\partial p_1}{\partial x_m} &= 0 \\ &\vdots \end{aligned} \tag{M.37}$$

$$x_1 \frac{\partial p_m}{\partial x_1} + x_2 \frac{\partial p_m}{\partial x_2} + \dots + x_m \frac{\partial p_m}{\partial x_m} = 0.$$

The identities

$$\frac{\partial p_i}{\partial x_j} = \frac{\partial p_j}{\partial x_i}, \tag{M.38}$$

which result from the definition of the functions (the mixed second partial derivatives are equal), permit the substitution of equations

$$\begin{aligned} x_1 \frac{\partial p_1}{\partial x_1} + x_2 \frac{\partial p_2}{\partial x_1} + \dots + x_m \frac{\partial p_m}{\partial x_1} &= 0 \\ &\vdots \end{aligned} \tag{M.39}$$

$$x_1 \frac{\partial p_1}{\partial x_m} + x_2 \frac{\partial p_2}{\partial x_m} + \dots + x_m \frac{\partial p_m}{\partial x_m} = 0,$$

and therefore

$$x_1 dp_1 + x_2 dp_2 + \dots + x_m dp_m = 0. \tag{M.40}$$

This relation is known as *Gibbs–Duhem equation* or *Gibbs–Duhem relation.*

Historical outlook Duhem was a great admirer of Gibbs, and extended a number of Gibbs' ideas. According to Miller [34] most probably Duhem was the first to use Euler's theorem explicitly to prove the Gibbs–Duhem equation. The first references appear in his book “Le Potentiel Thermodynamique” which was published in 1886 [35]. It is altogether fitting that his name be appended to the Gibbs–Duhem equation.

(An alternative derivation of the Gibbs–Duhem equation: consider an arbitrary function of

$$x_1, x_2, \dots, x_m : f(x_1, x_2, \dots, x_m). \quad (\text{M.41})$$

The total derivative (full derivative) of $f(x_1, x_2, \dots, x_m)$ with respect to x_1 is

$$\begin{aligned} \frac{df}{dx_1} &= \frac{\partial f}{\partial x_1} + \frac{\partial f}{\partial x_2} \frac{dx_2}{dx_1} + \dots + \frac{\partial f}{\partial x_m} \frac{dx_m}{dx_1} \\ &= p_1 + p_2 \frac{dx_2}{dx_1} + \dots + p_m \frac{dx_m}{dx_1}, \end{aligned} \quad (\text{M.42})$$

where $p_1 = \frac{\partial f}{\partial x_1}$, $p_2 = \frac{\partial f}{\partial x_2}$, $p_m = \frac{\partial f}{\partial x_m}$, etc.

Multiplying both sides of the equation by the differential dx_1 :

$$\begin{aligned} df &= \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots + \frac{\partial f}{\partial x_m} dx_m \\ &= p_1 dx_1 + p_2 dx_2 + \dots + p_m dx_m. \end{aligned} \quad (\text{M.43})$$

The result will be the differential change df in the function f . The differential of the form

$$df = \sum_{i=1}^m p_i(x_1, x_2, \dots, x_m) dx_i \quad (\text{M.44})$$

is called the *total differential* or the *exact differential* of the function f .

According to Eq. (M.33)

$$\sum_{i=1}^m p_i x_i = f(x_1, \dots, x_m). \quad (\text{M.45})$$

In order to get an expression for df/dx_1 from (M.45) comparable with that in (M.42), we must differentiate (M.45) “generally,” that is

$$\begin{aligned} \frac{df}{dx_1} &= p_1 + x_1 \frac{\partial p_1}{\partial x_1} + p_2 \frac{\partial x_2}{\partial x_1} + x_2 \frac{\partial p_2}{\partial x_1} + \dots + p_m \frac{\partial x_m}{\partial x_1} \\ &\quad + x_m \frac{\partial p_m}{\partial x_1}. \end{aligned} \quad (\text{M.46})$$

There are thus two (general) expressions for df/dx_1 , both of which are correct. This can only be the case if

$$x_1 \frac{\partial p_1}{\partial x_1} + x_2 \frac{\partial p_2}{\partial x_1} + \dots + x_m \frac{\partial p_m}{\partial x_1} = 0 \quad (\text{M.47})$$

or

$$x_1 dp_1 + x_2 dp_2 + \dots + x_m dp_m = \sum_i^m x_i dp_i = 0, \quad (\text{M.48})$$

which is the Gibbs–Duhem equation).

Example #3 Consider the function

$$f(x, y, z) = -\frac{x^3}{yz}, \quad (\text{E.3.1})$$

which is homogeneous of degree 1 (see Example #1).

The partial derivatives with respect to x , y , and z are

$$f'_x = \frac{\partial f}{\partial x} = -\frac{3x^2}{yz}, \quad f'_y = \frac{\partial f}{\partial y} = \frac{x^3}{y^2z}, \quad \text{and } f'_z = \frac{\partial f}{\partial z} = \frac{x^3}{yz^2}.$$

The partial derivatives of f'_x , f'_y , and f'_z with respect to x can be given as

$$\frac{\partial f'_x}{\partial x} = -\frac{6x}{yz}, \quad \frac{\partial f'_y}{\partial x} = \frac{3x^2}{y^2z} \quad \text{and} \quad \frac{\partial f'_z}{\partial x} = \frac{3x^2}{yz^2}$$

In accordance with Eq. (M.39)

$$x \frac{-6x}{yz} + y \frac{3x^2}{y^2z} + z \frac{3x^2}{yz^2} = \frac{-6x^2 + 3x^2 + 3x^2}{yz} = 0. \quad (\text{E.3.2})$$

Alternatively, we can formally write

$$df'_x = \frac{-6xyz \cdot dx + 3x^2z \cdot dy + 3x^2y \cdot dz}{y^2z^2} \quad (\text{E.3.3})$$

$$df'_y = \frac{3x^2y^2z \cdot dx - 2x^3yz \cdot dy - x^3y^2 \cdot dz}{y^4z^2} \quad (\text{E.3.4})$$

and

$$df'_z = \frac{3x^2yz^2 \cdot dx - x^3z^2 \cdot dy - 2x^3yz \cdot dz}{y^2z^4}. \quad (\text{E.3.5})$$

Thus,

$$\begin{aligned} xdf'_x + ydf'_y + zdf'_z &= \frac{-6x^2y^2z^2 \cdot dx + 3x^3yz^2 \cdot dy + 3x^3y^2z \cdot dz}{z^3y^3} \\ &\quad + \frac{3x^2y^2z^2 \cdot dx - 2x^3yz^2 \cdot dy - x^3y^2z \cdot dz}{z^3y^3} \\ &\quad + \frac{3x^2y^2z^2 \cdot dx - x^3yz^2 \cdot dy - 2x^3y^2z \cdot dz}{z^3y^3} = 0 \end{aligned} \quad (\text{E.3.6})$$

in accordance with the *Gibbs–Duhem equation* (M.40).

Example #4 Consider the internal energy function U defined by

$$U = U(S, V, n_1, \dots, n_m), \quad (\text{E.4.1})$$

where S is the entropy, V is the volume, and n_i ($i = 1, \dots, m$) is the chemical amount of component i . Since U is a homogeneous function of degree 1 with respect to all of its variables

$$U(kS, kV, kn_1, \dots, kn_m) = kU(S, V, n_1, \dots, n_m), \quad (\text{E.4.2})$$

The temperature (T), pressure (p), and the chemical potentials μ_i ($i = 1, \dots, m$) of the components are $T = \left(\frac{\partial U}{\partial S}\right)_{V, n_1, \dots, n_m}$, $p = -\left(\frac{\partial U}{\partial V}\right)_{S, n_1, \dots, n_m}$, $\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{i \neq m}}$ respectively. (In the above equations, n_i denotes the set $[n_1, \dots, n_m]$ ($i = 1, \dots, m$) and $n_{j \neq i}$ denotes all the elements (variables) in $[n_1, \dots, n_m]$ except for the i th.) According to Euler's theorem

$$U = TS + (-pV) + \sum_i \mu_i n_i. \quad (\text{E.4.3})$$

The Gibbs–Duhem relation is written as

$$-SdT + Vdp + n_1 d\mu_1 + \dots + n_m d\mu_m = 0. \quad (\text{E.4.4})$$

It follows that T , p , and μ_i cannot be independently variable, i.e., the intensive variables are not independent. If we know $m - 1$ of them, the value of the m th can be determined from the Gibbs–Duhem equation. It is particularly useful in its application to changes at constant temperature and pressure, and it may be written as

$$\sum_{i=1}^m n_i d\mu_i = 0. \quad (\text{E.4.5})$$

Partly homogeneous functions of degree 1

A function f is called “partly homogeneous” of degree 1 in terms of m among $m + w$ variables if

$$f(kx_1, \dots, kx_m, y_1, \dots, y_w) = kf(x_1, \dots, x_m, y_1, \dots, y_w) \quad (k > 0), \quad (\text{M.49})$$

i.e., the function f is homogeneous with respect to certain variables (x_1, x_2, \dots, x_m), but not homogeneous with respect to all of the variables. These functions are important as they are frequently encountered in thermodynamics [36].

Let us introduce new variables

$$z_i = x_1 \cdot y_i \quad (\text{M.50})$$

and the function \hat{f} as

$$\hat{f}(x_1, \dots, x_m, z_1, \dots, z_w) = f\left(x_1, \dots, x_m, \frac{z_1}{x_1}, \dots, \frac{z_w}{x_1}\right). \quad (\text{M.51})$$

We can prove that \hat{f} is homogeneous of the first order with respect to all of its variables. According to Eq. (M.51)

$$\begin{aligned} \hat{f}(kx_1, \dots, kx_m, kz_1, \dots, kz_w) &= f\left(kx_1, \dots, kx_m, \frac{kz_1}{kx_1}, \dots, \frac{kz_w}{kx_1}\right) \\ &= f\left(kx_1, \dots, kx_m, \frac{z_1}{x_1}, \dots, \frac{z_w}{x_1}\right). \end{aligned} \quad (\text{M.52})$$

On the other hand, f is a homogeneous linear function with respect to (x_1, x_2, \dots, x_m) . Thus

$$f\left(kx_1, \dots, kx_m, \frac{z_1}{x_1}, \dots, \frac{z_w}{x_1}\right) = kf\left(x_1, \dots, x_m, \frac{z_1}{x_1}, \dots, \frac{z_w}{x_1}\right). \quad (\text{M.53})$$

By taking into account the definition of \hat{f} ,

$$\hat{f}(kx_1, \dots, kx_m, kz_1, \dots, kz_w) = k\hat{f}(x_1, \dots, x_m, z_1, \dots, z_w) \quad (\text{M.54})$$

which was to be proved.

The partial derivatives of f and \hat{f} with respect to x_i , y_i , and z_i are, respectively, given by

$$\begin{aligned} f_i^x &= \left(\frac{\partial f}{\partial x_i}\right)_{x_{j \neq i}, y_j}, & f_i^y &= \left(\frac{\partial f}{\partial y_i}\right)_{x_j, y_{j \neq i}}, & \hat{f}_i^x &= \left(\frac{\partial \hat{f}}{\partial x_i}\right)_{x_{j \neq i}, z_j}, \\ \hat{f}_i^z &= \left(\frac{\partial \hat{f}}{\partial z_i}\right)_{x_j, z_{j \neq i}} \end{aligned} \quad (\text{M.55})$$

For $i = 1, \dots, m$, the partial derivatives of \hat{f} are given as

$$\hat{f}_i^x = \frac{\partial \hat{f}}{\partial x_i} = \frac{\partial f}{\partial x_i} = f_i^x \quad (\text{M.56})$$

and for $j = 1, \dots, w$

$$\hat{f}_j^z = \frac{\partial \hat{f}}{\partial z_j} = \frac{\partial f}{\partial y_j} \cdot \frac{1}{x_1} = f_j^y \cdot \frac{1}{x_1}. \quad (\text{M.57})$$

Thus, the total derivative of \hat{f} is

$$\begin{aligned} \frac{\partial \hat{f}}{\partial x_1} &= \frac{\partial f}{\partial x_1} + \frac{\partial f}{\partial y_1} \cdot \left(\frac{-z_1}{x_1^2}\right) + \frac{\partial f}{\partial y_2} \cdot \left(\frac{-z_2}{x_1^2}\right) + \dots + \frac{\partial f}{\partial y_w} \\ &\quad \cdot \left(\frac{-z_w}{x_1^2}\right). \end{aligned} \quad (\text{M.58})$$

Using Eqs. (M.50) and (M.55, M.56), Eq. (M.58) can be rewritten in the form

$$\hat{f}_1^x = f_1^x + f_1^y \cdot \left(\frac{-y_1}{x_1}\right) + f_2^y \cdot \left(\frac{-y_2}{x_1}\right) + \dots + f_w^y \cdot \left(\frac{-y_w}{x_1}\right) \quad (\text{M.59})$$

and with Eq. (M.57)

$$\hat{f}_1^x = f_1^x - \sum_{i=1}^w \hat{f}_i^z y_i. \quad (\text{M.60})$$

Since \hat{f} is homogeneous of the first degree with respect to all of its variables, and its partial derivatives are homogeneous of degree zero, we can apply Euler's theorem. Hence

$$\hat{f} = \sum_{i=1}^m x_i \hat{f}_i^x + \sum_{j=1}^w z_j \hat{f}_j^z \quad (\text{M.61})$$

and

$$0 = \sum_{i=1}^m x_i df_i^x + \sum_{j=1}^w z_j df_j^z. \quad (\text{M.62})$$

With Eqs. (M.51) and (M.56–M.62), we have

$$f = x_1 \left(f_1^x - \sum_{j=1}^w \frac{f_j^y}{x_1} y_j \right) + \sum_{i=2}^m x_i f_i^x + \sum_{j=1}^w x_1 y_j \frac{f_j^y}{x_1}, \quad (\text{M.63})$$

and

$$0 = x_1 d \left(f_1^x - \sum_{j=1}^w \frac{f_j^y}{x_1} y_j \right) + \sum_{i=2}^m x_i df_i^x + \sum_{j=1}^w x_1 y_j d \frac{f_j^y}{x_1}. \quad (\text{M.64})$$

Consequently

$$f = \sum_{i=1}^m x_i f_i^x = \sum_{i=1}^m x_i \left(\frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}, y_j} \quad (\text{M.65})$$

and

$$0 = \sum_{i=1}^m x_i df_i^x - \sum_{j=1}^w f_j^y dy_j. \quad (\text{M.66})$$

The latter relation is the Gibbs–Duhem equation for “partly homogeneous functions.”

Example #5 The function

$$f = -\frac{x^2}{y} w + u^5 x \quad (\text{E.5.1})$$

is not fully homogeneous, since

$$f(kx, ky, ku, kw) \neq k^n f(x, y, u, w). \quad (\text{E.5.2})$$

(If the powers of x , y , u , and w are added, the first term on the right-hand side of the expression yields 2, and the second term 6.)

However, if u and w are constant, the sum of the powers of x and y for each term is 1. Therefore, the function is partly homogeneous (with respect to x and y), so that

$$f(kx, ky, u, w) = kf(x, y, u, w). \quad (\text{E.5.3})$$

The partial derivatives with respect to x and y are

$$f'_x = \frac{\partial f}{\partial x} = -\frac{2xw}{y} + u^5 \quad (\text{E.5.4})$$

and

$$f'_y = \frac{\partial f}{\partial y} = \frac{x^2 w}{y^2}. \quad (\text{E.5.5})$$

Thus, applying Euler's theorem

$$f(x, y, u, w) = \left(-\frac{2xw}{y} + u^5 \right) x + \left(\frac{x^2 w}{y^2} \right) y = -\frac{x^2 w}{y} + u^5 x. \quad (\text{E.5.6})$$

The partial derivatives with respect to u and w are

$$f'_u = \frac{\partial f}{\partial u} = 5u^4 x \quad (\text{E.5.7})$$

and

$$f'_w = \frac{\partial f}{\partial w} = -\frac{x^2}{y}. \quad (\text{E.5.8})$$

We can formally write

$$x \cdot df'_x = \frac{-2wyx \cdot dx - 2x^2 y \cdot dw + 2x^2 w \cdot dy}{y^2} + 5u^4 x \cdot du, \quad (\text{E.5.9})$$

and

$$y \cdot df'_y = \frac{2xwy^2 \cdot dx + x^2 y^2 \cdot dw - 2x^2 wy \cdot dy}{y^3}. \quad (\text{E.5.10})$$

Similarly

$$f'_u \cdot du = 5u^4 x \cdot du, \quad (\text{E.5.11})$$

$$f'_w \cdot dw = -\frac{x^2}{y} \cdot dw. \quad (\text{E.5.12})$$

Thus,

$$\begin{aligned} xdf'_x + ydf'_y - f'_u du - f'_w dw &= \frac{-2wyx \cdot dx - 2x^2 y \cdot dw + 2x^2 w \cdot dy}{y^2} + 5u^4 x \cdot du \\ &+ \frac{2xwy^2 \cdot dx + x^2 y^2 \cdot dw - 2x^2 wy \cdot dy}{y^3} \\ &- 5u^4 x \cdot du - \left(-\frac{x^2}{y} \cdot dw \right) = 0 \end{aligned} \quad (\text{E.5.13})$$

in accordance with the Gibbs–Duhem equation for “partly homogeneous functions” (Eq. M.66).

Example #6 The function

$$f = -\frac{x^2}{y} w + u^3 x \quad (\text{E.6.1})$$

is not fully homogeneous, since $f(kx, ky, ku, kw) \neq k^n f(x, y, u, w)$.

Let us introduce new variables $\alpha = x \cdot u$ and $\beta = x \cdot w$, i.e., $u = \alpha / x$ and $w = \beta / x$, and the function \hat{f} as

$$\hat{f} = -\frac{x^2 \beta}{y x} + \left(\frac{\alpha}{x}\right)^3 = -\frac{x \beta}{y} + \frac{\alpha^3}{x^2}. \quad (\text{E.6.2})$$

Since

$$\begin{aligned} \hat{f}(kx, ky, k\alpha, k\beta) &= -\frac{kx \cdot k\beta}{ky} + \frac{(k\alpha)^3}{(kx)^2} = k \left(-\frac{x \cdot \beta}{y} + \frac{\alpha^3}{x^2} \right) \\ &= k \hat{f}(x, y, \alpha, \beta), \end{aligned} \quad (\text{E.6.3})$$

it is obvious that \hat{f} is a homogeneous function of degree 1 with respect to all of its variables (x, y, α, β).

Example #7 Let us consider the Gibbs free energy function G defined by

$$G = G(T, p, n_1, n_2, \dots, n_m), \quad (\text{E.7.1})$$

where T is the temperature, p is the pressure, and n_i ($i = 1, \dots, m$) is the chemical amount of component i . At given (constant) T and p , the function G is partly homogeneous of degree one in terms of the variables n_1, \dots, n_m . We thus have

$$G(T, p, kn_1, \dots, kn_m) = kG(T, p, n_1, \dots, n_m). \quad (\text{E.7.2})$$

The total differential of G is given as

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p, n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T, n_i} dp + \sum_{i=1}^m \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_j \neq i} dn_i. \quad (\text{E.7.3})$$

The entropy (S), volume (V), and the chemical potentials μ_i ($i = 1, \dots, m$) of the components are $S = -\left(\frac{\partial G}{\partial T}\right)_{p, n_i}$, $V = \left(\frac{\partial G}{\partial p}\right)_{T, n_i}$, and $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, p, n_j \neq i}$, respectively. Thus, Eq. (E.7.3) can be rewritten as

$$dG = -SdT + Vdp + \sum_{i=1}^m \mu_i dn_i. \quad (\text{E.7.4})$$

According to Euler's theorem

$$G = \sum_i \mu_i n_i. \quad (\text{E.7.5})$$

In order to obtain an expression for dG from (E.7.5) comparable with that in (E.7.3), we must differentiate (E.7.5). This gives

$$dG = \sum_{i=1}^m \mu_i dn_i + \sum_{i=1}^m n_i d\mu_i, \quad (\text{E.7.6})$$

and by comparing Eq. (E.7.6) with Eq. (E.7.4) we obtain the following important relation (i.e., the Gibbs–Duhem equation):

$$SdT - Vdp + \sum_i n_i d\mu_i = 0. \quad (\text{E.7.7})$$

Legendre transformation

(The transform is named after the French mathematician Adrien-Marie Legendre (1752–1833).)

Let $f(x_1, x_2, \dots, x_m)$ be an arbitrary analytic function of variables x_1, x_2, \dots, x_m . The differential of f is

$$\begin{aligned} df &= \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots + \frac{\partial f}{\partial x_m} dx_m \\ &= p_1 dx_1 + p_2 dx_2 + \dots + p_m dx_m. \end{aligned} \quad (\text{M.67})$$

Consider a new function g of the variables p_1 and x_2, x_3, \dots, x_m :

$$g(p_1, x_2, \dots, x_m) = f(x_1(p_1), x_2, \dots, x_m) - p_1 x_1(p_1), \quad (\text{M.68})$$

where $p_1 = \frac{\partial f}{\partial x_1}$. A necessary condition is the existence of a one-to-one relation between p_1 and x_1 , that is, the function $p_1(x_1, x_2, \dots, x_m)$ can be inverted to give $x_1(p_1)$ (This means that p_1 is bijective).

The new function $g(p_1, x_2, \dots, x_m)$ is called the *Legendre transform* of the function $f(x_1, x_2, \dots, x_m)$. A Legendre transform converts from a function of one set of variables to another function of a “conjugate” set of variables. In general, this is a special transformation that allows us to replace variables in a function in a consistent manner.

The differential of $g(p_1, x_2, \dots, x_m)$ is

$$dg = df - x_1(p_1) dp_1 - p_1(x_1, x_2, \dots, x_m) dx_1. \quad (\text{M.69})$$

With Eq. (M.67)

$$dg = -x_1(p_1) dp_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots + \frac{\partial f}{\partial x_m} dx_m. \quad (\text{M.70})$$

Formally, the total differential of g is

$$dg = \frac{\partial g}{\partial p_1} dp_1 + \frac{\partial g}{\partial x_2} dx_2 + \dots + \frac{\partial g}{\partial x_m} dx_m. \quad (\text{M.71})$$

Comparing Eqs. (M.70) and (M.71) $x_1 = -\frac{\partial g}{\partial p_1}$, $\frac{\partial f}{\partial x_2} = \frac{\partial g}{\partial x_2}$, $\frac{\partial f}{\partial x_3} = \frac{\partial g}{\partial x_3}$, etc. Let us take a look at some simple examples to see how this works.

Example #8 One-dimensional Legendre transformation

Consider an arbitrary function of x : $f(x)$. We know that locally the slope of this curve is precisely its derivative with respect to x , so the change in the function $f(x)$ at the point x for a small change in the argument dx is

$$df = \frac{\partial f}{\partial x} dx \equiv p(x) dx, \quad (\text{E.8.1})$$

where $p = \frac{\partial f(x)}{\partial x} = f'(x)$, as usual. Now suppose that we want to find a function that reverses the roles of the slope and infinitesimal, i.e., a function $g(p)$ such that

$dg = x dp$ (where we now view x as a function of p defined by the inverse of $p = f'(x)$). We can see that the function

$$g = f(p) - px(p) \quad (\text{E.8.2})$$

(the Legendre transform) has the desired property:

$$dg = df - xdp - pdx = -xdp. \quad (\text{E.8.3})$$

Notice that since $g(p)$ is a function of p only, we must have

$$\frac{dg(p)}{dp} = -x. \quad (\text{E.8.4})$$

Consequently, we have a pair of functions $f(x)$ and $g(p)$ related in the following way:

$$f(x) \rightarrow g(p) = f(x(p)) - x(p)p \quad \dots \quad x(p) : \frac{df(x)}{dx} = p,$$

$$g(p) \rightarrow f(x) = g(p(x)) - p(x)x \quad \dots \quad p(x) : \frac{dg(p)}{dp} = -x, \quad (\text{E.8.5})$$

where $f(x)$ and $g(p)$ are Legendre transforms of each other. There is a certain symmetry here, and the same transformation takes us back and forth.

Consider the function $f(x) = ax^2$. In this case $p = \frac{df(x)}{dx} = 2ax$, and $x = \frac{p}{2a}$. The Legendre transform of f is

$$\begin{aligned} L[f(x)] &= f(x) - p \cdot x = ax^2 - 2ax^2 = \frac{p^2}{4a} - \frac{p^2}{2a} = -\frac{p^2}{4a} \\ &= g(p). \end{aligned} \quad (\text{E.8.6})$$

On the other hand, $g(p) = -\frac{p^2}{4a}$, $\frac{dg(p)}{dp} = -\frac{p}{2a} = -x$, and the Legendre transform of $g(p)$ is given as

$$\begin{aligned} L[g(p)] &= g(p) - p \cdot (-x) = -\frac{p^2}{4a} + \frac{p^2}{2a} = \frac{p^2}{4a} = ax^2 \\ &= f(x). \end{aligned} \quad (\text{E.8.7})$$

Remark To avoid the minus sign in Eq. (E.8.4), the Legendre transform can alternatively be defined as

$$g = px - f \quad (\text{E.8.8})$$

(for functions of several variables: $g(p_1, x_2, \dots, x_m) = p_1 \cdot x_1(p_1) - f(x_1(p_1), x_2, \dots, x_m)$), in which case the Legendre transform is its own inverse, since $f = px - g$, rather than being the negative of its inverse. This opposite-sign alternative definition has the advantage that it gives rise to the symmetric identity $f + g = px$ which in words says that the sum of a function and its Legendre transform equals the product of the conjugate pair of variables. It is worth to emphasize the dimensional consistency of this identity.

$f + g$ is actually a function of either p or x but not both, because one variable implicitly depends on the other via a Legendre transform.

Usually, the definition given in Eq. (M.68) is preferred in thermodynamics.

Example #9 Consider the function

$$f(x, z) = x^2 + y^2. \quad (\text{E.9.1})$$

The partial derivatives are $\frac{\partial f}{\partial x} = 2x = p_1$, $\frac{\partial f}{\partial y} = 2y = p_2$, $x = \frac{p_1}{2}$, and $y = \frac{p_2}{2}$.

The Legendre transforms of f are

$$g(x, p_2) = x^2 + y^2 - p_2 \cdot y = x^2 + \frac{p_2^2}{4} - \frac{p_2^2}{2} = x^2 - \frac{p_2^2}{4}, \quad (\text{E.9.2})$$

$$g(p_1, y) = x^2 + y^2 - p_1 \cdot x = \frac{p_1^2}{4} + y^2 - \frac{p_1^2}{2} = y^2 - \frac{p_1^2}{4}, \quad (\text{E.9.3})$$

$$\begin{aligned} g(p_1, p_2) &= x^2 + y^2 - p_1 \cdot x - p_2 \cdot y = \frac{p_1^2}{4} + \frac{p_2^2}{4} - \frac{p_1^2}{2} - \frac{p_2^2}{2} \\ &= -\frac{1}{4}(p_1^2 + p_2^2). \end{aligned} \quad (\text{E.9.4})$$

Example #10 Consider the function

$$f(x, y, z) = -\frac{x^3}{yz}. \quad (\text{E.10.1})$$

The partial derivatives are $\frac{\partial f}{\partial x} = -\frac{3x^2}{yz} = f_x$, $\frac{\partial f}{\partial y} = \frac{x^3}{y^2z} = f_y$, and $\frac{\partial f}{\partial z} = \frac{x^3}{yz^2} = f_z$.

The variable y can be expressed as $y = \frac{x^{3/2}}{z^{1/2}f_y^{1/2}}$.

Define the new function $f_2(x, f_y, z)$ as follows:

$$\begin{aligned} f_2(x, f_y, z) &= -\frac{x^3}{yz} - yf_y = -\frac{x^3 z^{1/2} f_y^{1/2}}{z x^{3/2}} - \frac{x^{3/2}}{z^{1/2} f_y^{1/2}} f_y \\ &= -\frac{2x^{3/2} f_y^{1/2}}{z^{1/2}}. \end{aligned} \quad (\text{E.10.2})$$

It is obvious from this definition that f_2 is the Legendre transform of f with respect to y . Taking into account that

$$\frac{\partial f_2}{\partial z} = -2x^{3/2} f_y^{1/2} \left(-\frac{1}{2} z^{-3/2} \right) = \frac{x^{3/2} f_y^{1/2}}{z^{3/2}} = f_z, \quad (\text{E.10.3})$$

and

$$z = \frac{x f_y^{1/3}}{f_z^{2/3}}, \quad (\text{E.10.4})$$

the Legendre transformation of f_2 (with respect to z) yields

$$\begin{aligned}
 f_3(x, f_y, f_z) &= f_2(x, f_y, z) - zf_z \\
 &= -\frac{2x^{3/2}f_y^{1/2}}{x^{1/2}f_y^{1/6}}f_z^{1/3} - \frac{xf_y^{1/3}}{f_z^{2/3}}f_z = -3xf_y^{1/3}f_z^{1/3}.
 \end{aligned}
 \tag{E.10.5}$$

Alternatively, Eq. (E.10.5) can be derived directly by performing two successive Legendre transformations

$$f_3(x, f_y, f_z) = f(x, y, z) - yf_y - zf_z \tag{E.10.6}$$

with $f(x, y, z) = -\frac{x^3}{yz}$, $\frac{\partial f}{\partial y} = \frac{x^3}{y^2z} = f_y$, $\frac{\partial f}{\partial z} = \frac{x^3}{yz^2} = f_z$, $y = xf_y^{-2/3}f_z^{1/3}$, and $z = xf_y^{1/3}f_z^{-2/3}$.

Thus

$$\begin{aligned}
 f(x, y, z) - yf_y - zf_z &= \frac{-x}{xf_y^{-2/3}f_z^{1/3} \cdot xf_y^{1/3}f_z^{-2/3}} - xf_y^{-2/3}f_z^{1/3} \\
 &\quad \cdot f_y - xf_y^{1/3}f_z^{-2/3} \cdot f_z \\
 &= -3xf_y^{1/3}f_z^{1/3}.
 \end{aligned}
 \tag{E.10.6}$$

We remark that while f is a homogeneous function of the first degree in the variables x , y , and z (see Example #1), the Legendre transforms $f_2(x, f_y, z)$ and $f_3(x, f_y, f_z)$ are only partly homogeneous (the first with respect to x and z , and the second with respect to only x).

Example #11 Consider the function

$$f(x, y, u, w) = -\frac{x^2w}{y} + u^5x. \tag{E.11.1}$$

Since $f_y = \frac{\partial f}{\partial y} = \frac{x^2w}{y^2}$, the Legendre transformation of f with respect to y yields

$$L_y[f(x, y, u, w)] = f_2(x, f_y, u, w) = -2xw^{1/2}f_y^{1/2} + u^5x. \tag{E.11.2}$$

Note that $f(x, y, u, w)$ is a partly homogeneous function of degree one in the variables x and y . The Legendre transform is also a partly homogeneous function, but only with respect to x .

Consider the function

$$f(x, y, u, w) = -\frac{x^2}{y} + u^5x + w^2. \tag{E.11.3}$$

Since $f_y = \frac{\partial f}{\partial y} = \frac{x^2}{y^2}$, and therefore $y = \frac{x}{f_y^{1/2}}$, the Legendre transformation of f with respect to y yields

$$\begin{aligned}
 f_2(x, f_y, u, w) &= -\frac{x^2f_y^{1/2}}{x} + u^5x + w^2 - \frac{x}{f_y^{1/2}} \left(\frac{x^2f_y}{x^2} \right) \\
 &= -2xf_y^{1/2} + u^5x + w^2.
 \end{aligned}
 \tag{E.11.4}$$

Example #12 The Gibbs free energy function ($G(T, p, n_1, \dots, n_m)$) is obtained from the internal energy function ($U = U(S, V, n_1, \dots, n_m)$) via appropriate Legendre transformations as

$$G = U - TS + pV, \tag{E.12.1}$$

where S is the entropy, V is the volume, p is the pressure, T is the temperature, and n_i is the chemical amount of component i . p and T are given, respectively, as $p = -\frac{\partial U}{\partial V}$ and $T = \frac{\partial U}{\partial S}$. Note that the function G is a typical example of a partly homogeneous function (see “[The Gibbs–Duhem equation](#)” section).

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