

Chapter 2

Elements of the Thermodynamic Theory of Electrified Interfaces

2.1 Introduction

Despite the advent of surface-sensitive techniques, thermodynamic measurements remain a valuable tool for the investigation of surfaces and interfaces. 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 electrified interfaces is of importance to all surface scientists and electrochemists. The topic may also be of some interest to the general reader because thermodynamics relates quantities that can be measured directly to quantities that are needed for the purposes of understanding or calculations.

The aim of this chapter is to present a simple and concise treatment of electrified interfaces within the framework of classical thermodynamics. More detailed discussions can be found in several excellent reviews and research papers [1–15].

2.2 Basic Concepts and Notions

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 ideally marking the boundary between the phase and the environment is called the surface of the phase.

The region between two phases where the properties vary between those in the bulk is the “interfacial or interface region.” It is sometimes regarded as a distinct—though not autonomous—phase and is called the interphase.

A surface does not exist in isolation. It is the interface region in a two-phase system 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

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.

With few exceptions, solid surfaces are not flat. The geometric area, as represented by the product of the length and breadth of a rectangle enclosing part of a surface, is not the same as the actual surface area which takes into account the areas of the hills and valleys within the rectangle. If the surface is very rough, with very pronounced and irregular asperities, the geometric area is considerably smaller than the actual area. (Such a surface is unlikely to be in a state of equilibrium and caution should be exercised when considering systems containing such surfaces.) The properties of a portion of surface are dependent on orientation, and if there are many portions of different orientation, correct summation over the whole surface may be a difficult task. Consideration will be restricted here to systems in which the difference between geometric and actual areas is not of overriding importance. (This complication is not always dealt with in standard texts because they tend to concentrate on the surface thermodynamics of liquid systems which usually possess smooth surfaces.)

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

$$\Psi^\sigma = \int_{\alpha\alpha}^{\beta\beta} \Xi(\xi) d\xi, \quad (2.1)$$

where Ξ is the local value of any physical quantity in the interfacial region, ξ is the coordinate perpendicular to the plane of the interface, Ψ^σ is the integrated quantity, and $\alpha\alpha$ and $\beta\beta$ are the two adjacent phases.

2.3 Gibbs and Guggenheim Model of the Interface

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. 2.1a.

There are two approaches to describing the thermodynamic properties of interfaces.

The first, the classical Gibbs approach, is based on a model in which a real interface layer is replaced by a dividing surface [16]. Gibbs found it mathematically

convenient to consider an idealized system depicted in Fig. 2.1b, 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. 2.1b. A disadvantage of

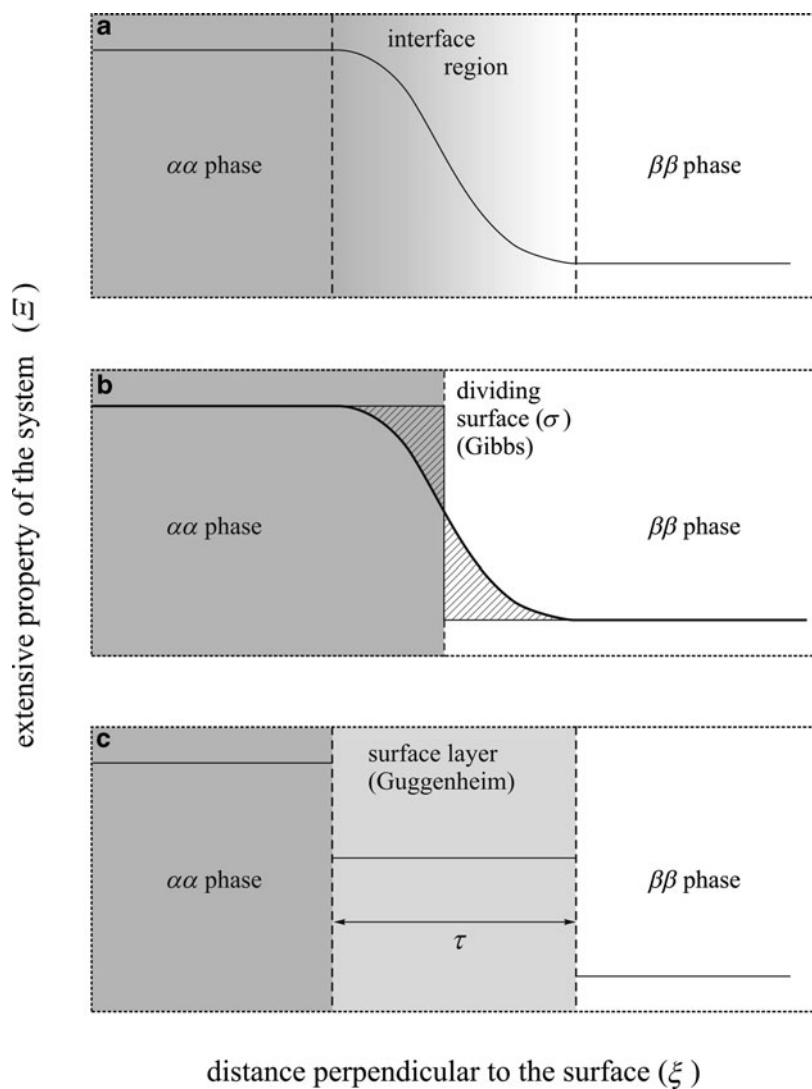


Fig. 2.1 (a) The real interface. (b) The Gibbs model of the interface. (c) The Guggenheim model of the interface (“interphase”)

this approach is that the position of the dividing surface alters according to the property considered. This is of particular importance when considering adsorption.

An alternative approach is that of Guggenheim in which the surface is considered as a region possessing thickness (and volume), the boundaries of which lie at the positions where the actual bulk phase properties cease to be uniform (Fig. 2.1c).

In this approach, two dividing surfaces, one at each boundary, are employed. A disadvantage is that terms dependent on surface volume are present in the equations, but it is difficult to assign values to these terms.

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 WXYZ rectangle (Fig. 2.2). It may be expedient to be more explicit and to define 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. (For very highly curved surfaces (radii of curvature of the same magnitude as τ), the notion of a surface layer may lose its usefulness.)

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 V volume 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:

$$V = V^{\alpha\alpha} + V^{\beta\beta} + V^{\text{inh}}. \quad (2.2)$$

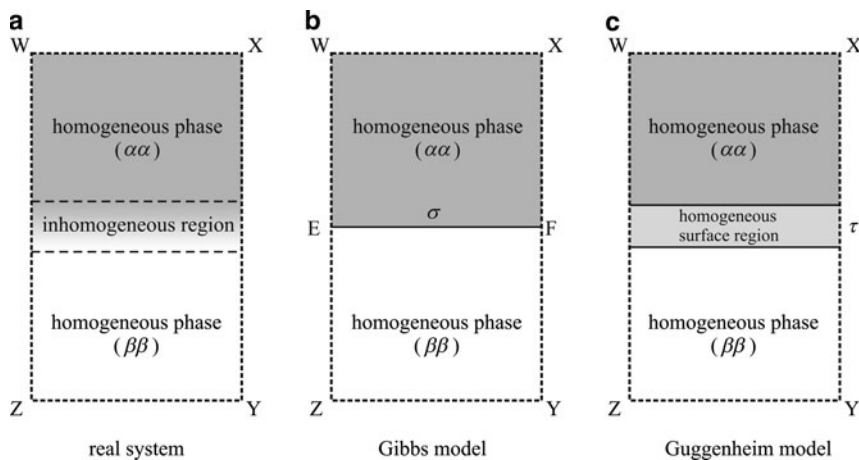


Fig. 2.2 The macroscopic subsystem selected for investigation, the Gibbs model, and the Guggenheim model

The internal energy can be given as follows:

$$U = U^{\alpha\alpha} + U^{\beta\beta} + U^{\text{inh}}. \quad (2.3)$$

Of course, this division is completely arbitrary since the values on the right-hand sides of Eqs. (2.2) and (2.3) depend on the (arbitrary) choice of the dividing surface(s). In the Guggenheim model, the V^σ volume of the interfacial layer is

$$V^\sigma = \tau A. \quad (2.4)$$

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,

$$V = V^{\alpha\alpha} + V^{\beta\beta}. \quad (2.5)$$

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

2.4 Adsorption

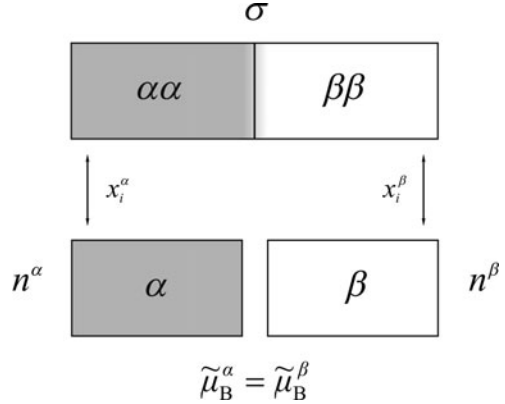
A quantitative measure of adsorption may be, and usually is, based on the following general definition: Adsorption of one or more of the components, at one or more of the phase boundaries of a multicomponent, multiphase system, is said to occur if the concentrations in the interfacial layers are different from those in the adjoining bulk phases. Consequently, the overall stoichiometry of the system deviates from that corresponding to a reference system of homogeneous bulk phases whose volumes and/or amounts are defined by suitably chosen dividing surfaces or by a suitable algebraic method.

In the Gibbs method, to treat the thermodynamics of surfaces, the interface is regarded as a mathematical dividing surface. Thus, the Gibbs interface is a two-dimensional homogeneous phase without thickness. 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 $\alpha\alpha$ and $\beta\beta$ (see Fig. 2.3). 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—the conditions of temperature, pressure, composition, etc., being identical to those in the adsorption equilibrium. Both reference systems consist of suitably defined amounts of the components. Each of the chosen reference amounts is characterized by its respective molar or specific properties.

Fig. 2.3 The real system (an idealized surface or surface phase is separating two homogeneous bulk phases $\alpha\alpha$ and $\beta\beta$) and the reference systems α and β



- 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 system.

If a Gibbs dividing surface 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. Evidently, the volume of the chosen 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.

However, there is a very 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” [17], with a “parallelepiped” [18], simply as a “section” of the interface cut out by perpendicular planes [19–21], etc.

The surface excess amount or Gibbs adsorption of component i is n_i^σ , which may be positive or negative, 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:

$$n_i^\sigma = n_i - n_i^\alpha - n_i^\beta = n_i - n_i^\alpha x_i^\alpha - n_i^\beta x_i^\beta = n_i - n_i^\alpha x_i^{\alpha\alpha} - n_i^\beta x_i^{\beta\beta}, \quad (2.6)$$

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 $\alpha(\alpha\alpha)$ and $\beta(\beta\beta)$, respectively. 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. (2.6) 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 of n_i^σ .

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

$$X^\sigma = X - X^\alpha - X^\beta, \quad (2.7)$$

where X denotes the value of the property for the whole system and X^α , X^β the values for the reference systems. The internal energy U is an extensive property.

The relation that gives the internal energy 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 [22].

The internal energies of the reference phases are given by

$$U^\alpha = U^\alpha(S^\alpha, V^\alpha, n_1^\alpha \dots n_m^\alpha) \quad (2.8)$$

and

$$U^\beta = U^\beta(S^\beta, V^\beta, n_1^\beta \dots n_m^\beta). \quad (2.9)$$

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

$$U = U(S, V, A, n_1 \dots n_m). \quad (2.10)$$

Thus, the excess of the internal energy is given by

$$U^\sigma = U - U^\alpha - U^\beta \quad (2.11)$$

and the excess of the entropy is

$$S^\sigma = S - S^\alpha - S^\beta. \quad (2.12)$$

Evidently, the excess internal energy function

$$U^\sigma = U^\sigma(S^\sigma, V^\sigma, A, n_1^\sigma \dots n_m^\sigma), \quad (2.13)$$

is a homogeneous function of degree one with respect to all variables, if $V^\sigma \equiv 0$ (Gibbs model), or $V^\sigma = A\tau$ (Guggenheim model), since in these cases

$$U^\sigma(kS^\sigma, kV^\sigma, kA, kn_i^\sigma \dots kn_m^\sigma) = kU^\sigma(S^\sigma, V^\sigma, A, n_i^\sigma \dots n_m^\sigma) \quad (2.14)$$

for all $k > 0$ real numbers (see Chap. 8). In the frames of the Gibbs model,

$$U^\sigma = U^\sigma(S^\sigma, A, n_1^\sigma \dots n_m^\sigma) \quad (2.15)$$

and

$$U^\sigma(kS^\sigma, kA, kn_i^\sigma \dots kn_m^\sigma) = kU^\sigma(S^\sigma, A, n_i^\sigma \dots n_m^\sigma), \quad (2.16)$$

according to Euler's theorem (Chap. 8):

$$U^\sigma = T^\sigma S^\sigma + \gamma A + \sum_i \mu_i^\sigma n_i^\sigma, \quad (2.17)$$

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

It should be noted that one of the most important questions in interfacial thermodynamics is related to the existence of a fundamental relation (fundamental function) of the form given in Eq. (2.13) or Eq. (2.15). If such a function exists, then every thermodynamic attribute is completely and precisely determined.

Due to the thermodynamic equilibrium,

$$T^\sigma = T^\alpha = T^\beta = T^{\alpha\alpha} = T^{\beta\beta} = T,$$

$$\mu_i^\sigma = \mu_i^\alpha = \mu_i^\beta = \mu_i^{\alpha\alpha} = \mu_i^{\beta\beta} = \mu_i$$

and so on.

Consequently, there is no need to add superscripts to T , $\mu_1 \dots \mu_m$, because these must have values uniform throughout α , β , $\alpha\alpha$, $\beta\beta$, and σ in order that there may be thermal, hydrostatic, and physicochemical equilibrium.

In the reference phases, the following relationships are valid:

$$U^\alpha = TS^\alpha - pV^\alpha + \sum_i \mu_i n_i^\alpha \quad (2.18)$$

and

$$U^\beta = TS^\beta - pV^\beta + \sum_i \mu_i n_i^\beta. \quad (2.19)$$

According to Eqs. (2.15) and (2.17), the intensive parameter (γ) is defined by

$$\gamma = \left(\frac{\partial U^\sigma}{\partial A} \right)_{S^\sigma, n_1^\sigma \dots n_m^\sigma}. \quad (2.20)$$

This expression is mathematically correct; however, it is not really useful for practical purposes. Equation (2.15) expresses the dependence of the energy U on the basis of independent variables $S^\sigma, A, n_1^\sigma \dots n_m^\sigma$. 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 , obtained from U by two Legendre transformations (see Chap. 8). According to this,

$$G^\alpha = U^\alpha + pV^\alpha - TS^\alpha, \quad (2.21)$$

$$G^\beta = U^\beta + pV^\beta - TS^\beta. \quad (2.22)$$

Consequently,

$$G^\alpha = \sum_i \mu_i n_i^\alpha, \quad (2.23)$$

$$G^\beta = \sum_i \mu_i n_i^\beta \quad (2.24)$$

and the excess Gibbs free energy is given as

$$G^\sigma = \gamma A + \sum_i \mu_i n_i^\sigma. \quad (2.25)$$

By using the G function, γ is defined by

$$\gamma = \left(\frac{\partial G^\sigma}{\partial A} \right)_{T, n_1^\sigma \dots n_m^\sigma}. \quad (2.26)$$

Unfortunately, this new 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 follows:

$$G = \gamma A + \sum_i \mu_i n_i^\alpha + \sum_i \mu_i n_i^\beta + \sum_i \mu_i n_i^\sigma = \gamma A + \sum_i \mu_i (n_i^\alpha + n_i^\beta + n_i^\sigma). \quad (2.27)$$

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

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T,p,n_1 \dots n_m}, \quad (2.28)$$

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

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T,V,n_1 \dots n_m}. \quad (2.28A)$$

(The Helmholtz energy or “free energy” function is defined as the Legendre transform of the internal energy function, $F = U - TS$.)

It should be noted that since no volume term appears in Eq. (2.15), there is no distinction between the surface Helmholtz and Gibbs free energies.

According to the foregoing considerations, G^σ is a partly homogeneous function of degree one in the variables A and $n_1^\sigma \dots n_m^\sigma$ (see Chap. 8). The expression for the total differential of G^σ is

$$dG^\sigma = \left(\frac{\partial G^\sigma}{\partial T} \right)_{A,n_1^\sigma \dots n_m^\sigma} dT + \left(\frac{\partial G^\sigma}{\partial A} \right)_{T,n_1^\sigma \dots n_m^\sigma} dA + \sum_i \left(\frac{\partial G^\sigma}{\partial A} \right)_{T,A,n_{j \neq i}^\sigma} dn_i^\sigma. \quad (2.29)$$

Taking into account that

$$\left(\frac{\partial G^\sigma}{\partial T} \right)_{A,n_1^\sigma \dots n_m^\sigma} = -S^\sigma, \quad \left(\frac{\partial G^\sigma}{\partial A} \right)_{T,n_1^\sigma \dots n_m^\sigma} = \gamma, \quad \text{and} \quad \left(\frac{\partial G^\sigma}{\partial A} \right)_{T,A,n_{j \neq i}^\sigma} = \mu_i,$$

Eq. (2.29) can be written as follows:

$$dG^\sigma = -S^\sigma dT + \gamma dA + \sum_i \mu_i dn_i^\sigma. \quad (2.30)$$

In order to get an expression for dG^σ from Eq. (2.25) comparable with Eqs. (2.29) and (2.30), we must differentiate G^σ “generally,” that is, with respect to the same variables as in Eq. (2.25), expressed explicitly or implicitly. These are T , A , and $n_1^\sigma \dots n_m^\sigma$. This gives

$$dG^\sigma = \gamma dA + A d\gamma + \sum_i \mu_i dn_i^\sigma + \sum_i n_i^\sigma d\mu_i. \quad (2.31)$$

There are thus two (general) expressions for dG^σ [Eqs. (2.30) and (2.31)], both of which are correct. This can only be the case if

$$S^\sigma dT + A d\gamma + \sum_i n_i^\sigma d\mu_i = 0, \quad (2.32)$$

which is the so-called Gibbs–Duhem equation for interfaces. (A more detailed derivation of the Gibbs–Duhem equation for “partly homogeneous functions” can be found in Chap. 8.)

It should be noted that as it has been shown earlier, the existence of a relationship among the various intensive parameters is a consequence of the linear homogeneous property of the fundamental relation. This means that Eq. (2.31) is a pure mathematical consequence of the homogeneity condition.

At constant temperature,

$$-A d\gamma = \sum_i n_i^\sigma d\mu_i. \quad (2.33)$$

Dividing both sides of the equation by A yields

$$-d\gamma = \sum_i \frac{n_i^\sigma}{A} d\mu_i = \sum_i \Gamma_i d\mu_i, \quad (2.34)$$

where Γ_i is the surface excess concentration of species i . This expression is commonly called the Gibbs adsorption equation.

In the case of liquid/liquid interfaces, the interfacial intensive parameter can be identified with the interfacial tension. It is sometimes called specific surface energy [19, 23].

Two important points should be noted here:

1. In the case of charged species (ionic components) “electrochemical potentials” ($\tilde{\mu}_i$) may be used instead of “chemical potentials” in the corresponding equations.
2. It follows from the definition equation [Eq. (2.6)] that the Γ_i values are uncertain since they depend on the arbitrary selection of n^z and n^β .

However, when examining the thermodynamic properties of interfaces, it is important to find measurable quantities that do not depend on the size of the reference phases. For this purpose, the following procedure can be used:

At constant temperature and pressure, the Gibbs–Duhem relationships for the two reference bulk phases are:

$$\sum_i x_i^z d\mu_i = 0 \quad (2.35)$$

and

$$\sum_i x_i^\beta d\mu_i = 0. \quad (2.36)$$

Using Eqs. (2.35) and (2.36), 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

$$d\mu_1 = -\frac{x_2^\alpha}{x_1^\alpha} d\mu_2 - \sum_{i \neq 1,2} \frac{x_i^\alpha}{x_1^\alpha} d\mu_i \quad (2.37)$$

and

$$d\mu_2 = -\frac{x_1^\beta}{x_2^\beta} d\mu_1 - \sum_{i \neq 1,2} \frac{x_i^\beta}{x_2^\beta} d\mu_i. \quad (2.38)$$

Solving the set of equations (2.37) and (2.38) for $d\mu_1$ and $d\mu_2$ and substituting the results into Eqs. (2.33) and (2.34), we obtain

$$-d\gamma = \frac{1}{A} \sum_{i \neq 1,2} \left(n_i^\sigma + \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} n_1^\sigma + \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} n_2^\sigma \right) d\mu_i, \quad (2.39)$$

or

$$-d\gamma = \sum_{i \neq 1,2} \left(\Gamma_i + \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} \Gamma_1 + \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} \Gamma_2 \right) d\mu_i. \quad (2.40)$$

Since

$$\Gamma_i = \frac{1}{A} (n_i - n^\alpha x_i^\alpha - n^\beta x_i^\beta), \quad (2.41)$$

we get

$$-d\gamma = \frac{1}{A} \sum_{i \neq 1,2} \left(n_i + n_1 \frac{x_2^\alpha x_i^\beta - x_2^\beta x_i^\alpha}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} + n_2 \frac{x_1^\beta x_i^\alpha - x_1^\alpha x_i^\beta}{x_1^\alpha x_2^\beta - x_2^\alpha x_1^\beta} \right) d\mu_i, \quad (2.42)$$

Equation (2.42) can be written in the simpler form:

$$-d\gamma = \sum_{i \neq 1,2} \Gamma'_i d\mu_i, \quad (2.43)$$

where Γ'_i denotes the (relative) surface excess of component i with respect to the two selected components. It is clear that the (relative) surface excesses does not depend any more on the selection of the reference systems (i.e., on the selection of n^α and n^β).

2.5 The Electrocapillary Equation and the Lippmann Equation

In the case of electrodes and electrolyte solutions, the expressions derived above should be modified.

The term “electrode” is used here to denote heterogeneous electrochemical systems, in which at least two phases are connected and one of them is an electronic conductor or a semiconductor, while the other is an ionic conductor, usually an electrolyte solution (see Chap. 1).

In case of an electronic conductor (metal)/electrolyte solution interface, we should take into account that the solvent of the electrolyte solution is not a component of the electronic conductor or semiconductor phase. The same may be true for other components. Let α denote an ionic conductor phase (e.g., an aqueous electrolyte solution), and let β denote the electronic conductor (or semiconductor) phase. In the aqueous electrolyte solution, component 1 (the solvent) is water (or another component which is absent from the electronic conductor/semiconductor phase). We denote the mole fraction of this component by x_v^α .

In this case

$$x_1^\alpha = x_v^\alpha$$

and

$$x_1^\beta = x_v^\beta = 0.$$

Similarly, we can select a component (constituent) of the metal phase (component 2), which is absent from the electrolyte solution, that is,

$$x_2^\beta = x_M^\beta$$

and

$$x_2^\alpha = x_M^\alpha = 0.$$

We can consider that in the metal phase, there is a formal electrochemical (dissociation) equilibrium between atoms of metal M_i and the corresponding cations $M_i^{z_i}$ of ionic charge z_i and the electrons (i.e., we can consider these species as constituents of the metal phase). The condition of electroneutrality can be temporally relaxed, so all the extensive variables appearing in Eq. (2.43) may be treated as independent. The electron is the only component besides metal ions in a pure metal phase. Of course, in case of alloys, we have several components.

Taking into account the above considerations, Eq. (2.43) can be written as

$$-d\gamma = \sum_{i \neq 1,2} \left(\Gamma_i - \Gamma_v \frac{x_i^\alpha}{x_v^\alpha} - \Gamma_M \frac{x_i^\beta}{x_M^\beta} \right) d\tilde{\mu}_i. \quad (2.44)$$

In case of ideally polarizable electrodes,

$$-d\gamma = \sum \left(\Gamma_j - \Gamma_v \frac{x_j}{x_v} \right) d\tilde{\mu}_j + \sum \left(\Gamma_k - \Gamma_M \frac{x_k}{x_M} \right) d\tilde{\mu}_k, \quad (2.45)$$

where index j denotes components in the electrolyte solution and index k refers to components of the metal phase.

Electrocapillary measurements, like any other electrochemical measurements, require the use of a complete cell, that is, one with two electrodes. One electrode is the ideal polarized electrode; the other electrode is a reversible charge-transfer electrode. However, it is important to realize from the outset that this second electrode is not an ordinary “constant-potential” reference electrode like the saturated calomel electrode (SCE). Rather, it is simply some electrode dipping into the solution S , which is reversible (in the Nernstian sense) to one of the ions of that solution. This second electrode of the electrocapillary cell is called the indicator electrode and denoted by the symbol IN.

The particular ion of the solution to which electrode IN is reversible will be called the indicator ion.

A solution S containing c cationic species and a anionic species could be prepared in many different ways. However, for the purpose of the thermodynamic treatment, the most general electrocapillary equation can be derived if we assume that the ions of the solution are furnished by neutral binary salts. Of the $c \times a$ different binary salts that could be chosen, we shall select $c + a - 1$ binary salts in the following way: If the indicator electrode IN is reversible to cation j' , we arbitrarily select an anion, say k' . If the indicator electrode is reversible to anion k' , we arbitrarily select a cation, say j' . In either case, we have selected a binary salt containing ions j' and k' . We call this salt the indicator salt. The electrolyte solution is then considered to have been made up by dissolving $c + a - 2$ additional binary salts of which $c - 1$ have anion k' in common with the indicator salt; the remaining $a - 1$ salts have cation j' in common with the indicator salt.

Thus, the Gibbs adsorption equation for an ideally polarizable electrode and for the cation-reversible indicator electrode at constant temperature T and pressure p can be given in the following form [3, 24]:

$$\begin{aligned} d\gamma = & -q_M dE_+ - \sum_{i \neq i'} \Gamma_{ii'} d\mu_i - \sum_{j \neq j'} \frac{\Gamma_{jh'}}{v_{jk'}^+} d\mu_{jk'} - \sum_{k \neq k'} \frac{\Gamma_{kh'}}{v_{jk}^-} d\mu_{jk} \\ & - \sum_{h \neq h'} \Gamma_{hh'} d\mu_h - \left[\left(\frac{\Gamma_{k'h'}}{v_{j'k'}^-} \right) - \left(\frac{1}{|z_{k'}| v_{j'k'}^-} \right) \sum_{j \neq j'} \Gamma_{jh'} z_j \right] d\mu_{j'k'}, \end{aligned} \quad (2.46)$$

where q_M is the charge density on the metal side of the interface, subscript i indicates the components (metals) in the metallic phase (a single phase alloy), subscript h designates the neutral molecular species in the solution, γ is the interfacial intensive parameter, the z 's are the ionic charges, the Γ and μ values are the surface excesses and chemical potentials of the various components, respectively, and the v 's indicate the number of moles of cations (or anions) per formula weight of the salt.

This equation or more generally, the equation

$$\begin{aligned} d\gamma = & -s^\sigma dT - q_M dE_+ - \sum_{i \neq i'} \Gamma_{ii'} d\mu_i - \sum_{j \neq j'} \frac{\Gamma_{jh'}}{v_{jk'}^+} d\mu_{jk'} - \sum_{k \neq k'} \frac{\Gamma_{kh'}}{v_{jk}^-} d\mu_{jk} \\ & - \sum_{h \neq h'} \Gamma_{hh'} d\mu_h - \left[\left(\frac{\Gamma_{k'h'}}{v_{j'k'}^-} \right) - \left(\frac{1}{|z_{k'}| v_{j'k'}^-} \right) \sum_{j \neq j'} \Gamma_{jh'} z_j \right] d\mu_{j'k'}, \end{aligned} \quad (2.47)$$

is called the “electrocapillary equation.” Equation (2.46) can be written in a somewhat simpler form [25]; however, all these results show that even in the case of a very simple system, the Gibbs adsorption equation could take various forms depending on the choice of independent components, the indicator electrolyte, and the indicator ion, and it cannot be given in a simple generalized form as done, e.g., in [26].

From Eq. (2.46),

$$-\left(\frac{\partial \gamma}{\partial E} \right)_{p, T, \mu_j, \mu_k} = q_M, \quad (2.48)$$

where

$$q_M = F \sum_j z_j \Gamma_j = -F \sum_k z_k \Gamma_k. \quad (2.49)$$

Equation (2.48) is usually called the Lippmann equation. The Lippmann equation and the electrocapillary equation are strictly valid for liquid/liquid interfaces.

However, at least in principle, they do not apply to “solid electrodes” under elastic strain.

An illustrative example will serve to highlight the differences between the two cases.

2.5.1 Example for the Application of the Electrocapillary Equation

The phase α is supposed to be an electrolyte with cations K^+ and anions A^- in a not-dissociated solvent L. The phase p is a pure liquid metal thought to dissociate into metal ions M^+ and electrons e^- . The amounts of a component i in the two bulk phases and in the interphase are n^α , n^β , and n_i^σ , respectively. The total differential of the internal energy of the plane interface is

$$dU^\sigma = TdS^\sigma + \gamma dA + \sum_i \tilde{\mu}_i^\sigma dn_i^\sigma, \quad (2.50)$$

with the intensive interfacial parameter γ . The Gibbs–Duhem equation can be written as

$$S^\sigma dT + Ad\gamma + \sum_i n_i^\sigma d\tilde{\mu}_i^\sigma = 0. \quad (2.51)$$

Electroneutrality in the whole system corresponds to

$$n_{K^+} - n_{A^-} + n_{M^+} - n_{e^-} = 0 \quad (2.51)$$

and electroneutrality in the bulk phases to

$$x_{K^+}^\alpha = x_{A^-}^\alpha, \quad (2.52)$$

$$x_{M^+}^\beta = x_{e^-}^\beta. \quad (2.53)$$

The following material balances yield the excess amounts in the interface:

$$n_{K^+}^\sigma = n_{K^+} - x_{K^+}^\alpha n_{K^+}^\alpha, \quad (2.54)$$

$$n_{A^-}^\sigma = n_{A^-} - x_{A^-}^\alpha n_{A^-}^\alpha, \quad (2.55)$$

$$n_{M^+}^\sigma = n_{M^+} - x_{M^+}^\beta n_{M^+}^\beta, \quad (2.56)$$

$$n_{e^-}^\sigma = n_{e^-} - x_{e^-}^\beta n_{e^-}^\beta, \quad (2.57)$$

$$n_L^\sigma = n_L - x_L^\alpha n_L^\alpha. \quad (2.58)$$

The Gibbs adsorption equation at constant T is

$$A d\gamma + n_{K^+}^\sigma d\tilde{\mu}_{K^+}^\sigma + n_{A^-}^\sigma d\tilde{\mu}_{A^-}^\sigma + n_L^\sigma d\mu_L^\sigma + n_{M^+}^\sigma d\tilde{\mu}_{M^+}^\sigma + n_{e^-}^\sigma d\tilde{\mu}_{e^-}^\sigma = 0. \quad (2.59)$$

In chemical equilibrium, the electrochemical potentials

$$\tilde{\mu}_i^z = \mu_i^z + zF\varphi^z.$$

of the particles with the charges $z = \pm 1$ are all the same in all phases (F is the Faraday constant, the superscript indicates the corresponding phase):

$$\tilde{\mu}_{K^+} = \tilde{\mu}_{K^+}^\sigma = \tilde{\mu}_{K^+}^z = \mu_{K^+}^\alpha + F\varphi^\alpha, \quad (2.60)$$

$$\tilde{\mu}_{A^-} = \tilde{\mu}_{A^-}^\sigma = \tilde{\mu}_{A^-}^z = \mu_{A^-}^\alpha - F\varphi^\alpha, \quad (2.61)$$

$$\mu_L = \mu_L^\sigma = \mu_L^z, \quad (2.62)$$

$$\tilde{\mu}_{M^+} = \tilde{\mu}_{M^+}^\sigma = \tilde{\mu}_{M^+}^\beta = \mu_{M^+}^\beta + F\varphi^\beta, \quad (2.63)$$

$$\tilde{\mu}_{e^-} = \tilde{\mu}_{e^-}^\sigma = \tilde{\mu}_{e^-}^\beta = \mu_{e^-}^\beta - F\varphi^\beta, \quad (2.64)$$

$$\tilde{\mu}_{K^+} + \tilde{\mu}_{A^-} = \mu_{K^+} + \mu_{A^-} = \mu_{KA} = \mu_{KA}^\sigma, \quad (2.65)$$

The Gibbs–Duhem equations for the bulk phases at constant T and p are

$$n_{K^+}^\alpha d\tilde{\mu}_{K^+}^\alpha + n_{A^-}^\alpha d\tilde{\mu}_{A^-}^\alpha + n_L^\alpha d\mu_L^\alpha = 0, \quad (2.66)$$

$$n_{M^+}^\beta d\tilde{\mu}_{M^+}^\beta + n_{e^-}^\beta d\tilde{\mu}_{e^-}^\beta = 0. \quad (2.67)$$

From Eqs. (2.51) to (2.67), one obtains

$$-d\gamma = \frac{1}{A} \left[\left(n_{K^+} - \frac{x_{K^+}^\alpha}{x_L^\alpha} n_L \right) d\mu_{KA} + (n_{K^+} - n_{A^-}) d\tilde{\mu}_{e^-}^\beta + F d(\varphi^\alpha - \varphi^\beta) \right]. \quad (2.68)$$

The change in the potential difference between the two phases can only be measured in an electrochemical cell containing a reference electrode. If the reference electrode is reversible with respect to the anion A^- , the change in the (measurable) electrode potential can be expressed as

$$dE = \frac{1}{F} (d\mu_{A^-}^\alpha - d\mu_{e^-}^\beta) - d(\varphi^\alpha - \varphi^\beta). \quad (2.69)$$

With Eqs. (2.68) and (2.69), we obtain

$$-d\gamma = \frac{1}{A} \left[\left(n_{K^+} - \frac{x_{K^+}^z}{x_L^z} n_L \right) d\mu_{KA} + F(n_{A^-} - n_{K^+}) dE \right] = \Gamma'_{K^+} d\mu_{KA} + q_M dE, \quad (2.70)$$

with the relative surface excess of the cation on the solution side and the surface charge q_M on the metal side. The classical Lippmann equation follows from Eq. (2.70):

$$- \left(\frac{\partial \gamma}{\partial E} \right)_{T, p, \mu_{KA}} = q_M. \quad (2.71)$$

2.5.2 *The Ideally Polarizable Electrode when There Is no Complete Equilibrium Established Between the Bulk of a Solid and the Interface*

The charging of an interface/interphase results in a certain movement of the atoms in the interfacial region and an exchange of material between the interfacial region and the bulk. In case of a plane interface, equilibrium is attained if the temperature, pressure, and the chemical potentials of all components are equal in the whole system. The transport of material is relatively fast in a liquid. However, in a real solid, the movement of material is usually very slow. Adsorption may change the specific surface energy of different crystal faces in a different way requiring adjustment of the equilibrium shape with a corresponding stress distribution. The nonequilibrium stresses change the chemical potential of the metal [7, 27].

In an ideal solid phase which is free of vacancies and interstitials, there is no transport of the “immobile” components or constituents (atoms or ions), but electrons may be mobile. Nevertheless, the interfacial region can be in equilibrium with the adjacent fluid phase [17, 23]. However, the chemical potentials of the immobile components (or constituents) in the interfacial region can differ from those in the bulk solid, i.e., although mechanical equilibrium is maintained, chemical equilibrium cannot be established between the bulk and the interfacial region.

This means that Eq. (2.63) is not valid, and

$$\tilde{\mu}_{M^+}^\sigma \neq \tilde{\mu}_{M^+}^\beta. \quad (2.72)$$

Instead of Eq. (2.70), one obtains

$$\begin{aligned}
-d\gamma^s = & \frac{1}{A} \left[\left(n_{K^+} - \frac{x_{K^+}^\alpha}{x_L^\alpha} n_L \right) d\mu_{KA} + \left(n_{M^+} - x_{M^+}^\beta n_{M^+}^\beta \right) (d\tilde{\mu}_{M^+}^\sigma + d\tilde{\mu}_{e^-}) \right] \\
& + \frac{1}{A} F(n_{A^-} - n_{K^+}) dE = \Gamma'_{K^+} d\mu_{KA} + \Gamma_{M^+} (d\tilde{\mu}_{M^+}^\sigma + d\tilde{\mu}_{e^-}) + q_M dE.
\end{aligned} \tag{2.73}$$

Experimentally, one may obtain the path-dependent “specific surface energy” or “interfacial stress” γ^s . The chemical and the mechanical contributions to the irreversible part of the excess Gibbs free energy of the surface occur in combinations given by the equilibrium reference state and the adsorption equilibrium toward the fluid phase. According to the local equilibrium in the interfacial region,

$$d\tilde{\mu}_{M^+}^\sigma + d\tilde{\mu}_{e^-} = \tilde{\mu}_M^\sigma, \tag{2.74}$$

thus,

$$-d\gamma^s = \Gamma'_{K^+} d\mu_{KA} + \Gamma_{M^+} d\tilde{\mu}_M^\sigma + q_M dE \tag{2.75}$$

and instead of Eq. (2.71), we get

$$-\left(\frac{\partial \gamma^s}{\partial E}\right)_{T,p,\mu_{KA}} = q_M + \Gamma_{M^+} \left(\frac{\partial \tilde{\mu}_M^\sigma}{\partial E}\right)_{T,p,\mu_{KA}} = q_M + q^s. \tag{2.76}$$

Thus, for a solid electrode, there is an additional contribution to the equilibrium superficial charge. This quantity is connected with the deviation from the equilibrium between the interfacial region and the bulk of the solid; however, its value depends on the selection of the reference system. On the other hand, in case of a real solid containing a high concentration of point defects, the additional charge and the corresponding nonequilibrium specific surface energy (interfacial stress) may be time dependent on a long time scale.

2.5.3 Additional Remarks

Concerning the variables of the fundamental relation (function), the question may arise whether the area of the interface (A) is an appropriate state variable or not. There are two limiting cases (models) for which the answer seems obvious (we limit ourselves to isotropic conditions for simplicity): (1) All constituents are mobile in the adjacent phases. (2) The solid phase is ideally elastic.

In the first case, there is no thermodynamic difference between a liquid/liquid and a solid/liquid interface. On the other hand, the area of the interface and the other thermodynamic variables unequivocally determine the surface state of an isotropic

ideally elastic solid. However, in conventional measurements of interfacial stress changes of solid electrodes, the deformation practically always remains within the elastic limit. Consequently, A can reasonably be considered as an independent thermodynamic variable.

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