Chapter 9
Extension of Thermodynamics for Additional Interactions (Non-Simple Systems)

In previous chapters, we have discussed the thermodynamic description of systems, which contained several phases, allowing also for chemical reactions to occur. However, we have supposed that only mechanical and thermal interactions can take place between the system and its surroundings, and considered the system consisting of electrically neutral and non-magnetic particles; we have also excluded interactions with external fields, and supposed that the system (or its phases) is isotropic and has a small surface whose changes can be neglected. In this chapter, we shall briefly discuss the possibility of including further interactions and the release of the mentioned constraints in the thermodynamic description. We also treat somewhat more detailed the thermodynamics of a few interactions that occur more frequently in the chemical praxis.

As stated by Postulate 1, the equilibrium state of simple systems consisting of K chemical components can completely be described by $K + 2$ extensive variables, which – in case of energy representation – are entropy S, volume V and composition specified by the amounts of components $n_1, n_2, \ldots, n_K$. In other words, a simple system has $K + 2$ degrees of freedom. The total differential of the energy function, according to (2.22), contains terms of energy dimension, each of them being the product of an intensive variable and the increment of an extensive variable. The intensive variable in this product is the partial derivative of the energy function with respect to the variable whose increment is the factor in the actual term. These terms contribute as *work* to the increment of energy, except for the term $T\mathrm{d}S$, which is the *heat* contribution. Thus, we call $-P\mathrm{d}V$ the volume work and the sum of the terms $\mu_i \mathrm{d}n_i$ the chemical work. The former is the consequence of mechanical interactions, while the latter is the consequence of chemical interactions contributing to the change in energy.

If we allow for other interactions between the system and its surroundings, we should add other variables to specify the state and its energy. Accordingly, additional products of similar structure will also appear in the total differential of the energy function, which also contains the new intensive variables multiplied by the increments of the respective extensive variable. These terms account for the change in energy as a consequence of the new interactions.

E. Keszei, *Chemical Thermodynamics*,
DOI 10.1007/978-3-642-19864-9_9,

When adding these new terms and variables to the fundamental equation, we should of course take into account the physical nature of the new interactions. In case of simple systems, all the variables were scalar quantities; consequently, the derivatives of the energy function were also scalar. Including, for example, magnetic interactions, both the extensive variable and the derivative of the energy with respect to this variable – the corresponding intensive quantity – are vectors. Treating vector variables does not mean any problems in thermodynamics (only complicates the mathematics); we should apply the corresponding formulae used in magnetostatics to calculate the work associated with the change of magnetic interactions. Let us discuss now the extensive variables and the corresponding intensive ones characteristic of the most important interactions, which can be used to determine the work done while the actual interaction would change.

As a first case, let us release the isotropy of mechanical interactions and allow for a direction-dependent deformation as the response of the system to a direction-dependent force. In a homogeneous isotropic system, Pascal's law is valid; the deforming force – which acts to change the volume – is transmitted equally in all directions, and the resistance against this force – expressed by the pressure P – is also the same in all directions.

Solid bodies can have a much more complicated behavior; in addition to compression, we can stretch, bend, shear, or twist them. Solid bodies can respond to forces of different directions with several kinds of deformations. Their shape can be distorted in a complex way especially in case of crystals, which can suffer different deformations in different directions. Accordingly, both force and deformation should be treated as vectors. For relatively small forces, the validity of Hooke's law holds; deformation is proportional to the force. This proportionality is valid for all components of the vector; every component of force (a vector) has an effect on every component of the deformation (also a vector). In terms of linear algebra, we can say that the scalar compressibility κ is replaced by a *tensor* of many elements which transforms the force vector into the deformation vector, depending on the actual direction. We should also note that in solid-state physics, the force acting relative to a unit surface is called *stress*, with its direction outward of the surface – contrarily to pressure. Consequently, we should write the product of this stress multiplied by deformation in place of the term $-P\mathrm{d}V$ in (2.22).[1] As the deformation of crystals is not of primary interest in chemistry, we would not deal with it any further.

The mathematical formalism associated with magnetic interactions is also quite complicated. The simplest case is a system where only paramagnetic or diamagnetic interactions occur in a homogeneous magnetic field (i.e., where the field strength is uniform.) In this case, the direction of the magnetization vector[2] $\boldsymbol{M}$ is

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[1] Note that stress has an opposite sign with respect to pressure, thus the term to enter into the energy increment is positive.

[2] In many cases, the magnetization $\boldsymbol{M}$ is that of the unit volume or molar volume. Here, it means the total magnetization of the whole system, i.e., the unit volume magnetization multiplied by the volume.

parallel to the magnetic induction (or magnetic flux density) vector $\boldsymbol{B}$. If the system has the shape of an ellipsoid and one of its symmetry axes is parallel to the vector $\boldsymbol{B}$, then the fundamental equation of the system can be given as $U = U(S, V, \boldsymbol{M}, \boldsymbol{n})$, and the differential fundamental equation as:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + B\mathrm{d}M + \sum_{i=1}^{K} \mu_i \,\mathrm{d}n_i. \tag{9.1}$$

In a more general case, the magnetic moment $\boldsymbol{M}$ in the term $\boldsymbol{B}\mathrm{d}\boldsymbol{M}$ in (9.1) should be replaced by an integral over the entire system of the position-dependent intensive magnetic moment $\boldsymbol{m(r)}$. In magnetically anisotropic crystals, magnetization is a tensor – similarly to the deformation tensor – and the expression of magnetic work in (9.1) becomes more complicated mathematically, but dU can be calculated anyway. In case of magnetic interactions, there is another peculiarity; there exist no walls that could restrict magnetization. However, this imposes no problem when describing the equilibrium of magnetic interactions.

The thermodynamic description of a system having an electric dipole moment in an electric field is similar to the magnetic case. The corresponding formulae are simplest if the direction of the *electric dipole moment* (vector) of the system is parallel to the direction of the external electric field (vector), the system has the shape of an ellipsoid and one of its symmetry axes is parallel to the dipole moment vector. In this case, the electric dipole moment $\boldsymbol{P}$ (extensive variable) can be characterized with one value, as well as the external electric field strength $\boldsymbol{E}$ (intensive variable) for a homogeneous isotropic system. The fundamental equation of this electrically polarized system can be given as $U = U(S,\ V,\ \boldsymbol{P},\ \boldsymbol{n})$, and the differential fundamental equation as:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + E\mathrm{d}P + \sum_{i=1}^{K} \mu_i \,\mathrm{d}n_i. \tag{9.2}$$

If the system and/or the spatial arrangement is more complicated, the treatment of the equilibrium is similar to that of the magnetic case.

In electrostatics, there exists the “electric monopole”, i.e., the electric charge as well. This charge is a scalar quantity and it does not depend on the external field strength – contrarily to the electric or magnetic dipole moment. Accordingly, the thermodynamic description of electrically charged systems is quite simpler than that of dipoles. If the electric field is homogeneous, the interaction of the electric *potential* E (intensive) and the charge q (extensive) can be described by the energy increment calculated as the product of the intensive potential and the increment of the extensive charge, $E\mathrm{d}q$. The fundamental equation of the electrically charged system can be given as $U = U\ (S,\ V,\ q,\ \boldsymbol{n})$, and the differential fundamental equation as:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + E\mathrm{d}q + \sum_{i=1}^{K} \mu_i \,\mathrm{d}n_i. \tag{9.3}$$

Many systems of practical interest in chemistry contain charged particles – mostly ions –, thus it is important to discuss the thermodynamics of these systems. For this reason, a whole section is dedicated to the description of systems containing electrically charged particles.

The description of the interaction of thermodynamic systems with a gravitational field can be similarly described as an electrically charged system interacting with an external electric field. The gravitational field also interacts with the field-independent extensive quantity, the mass. The intensive quantity characteristic of the field is the gravitational potential (sometimes simply referred to as potential); when multiplied with mass, it yields the gravitational energy. In a gravitational field, mass should also be a variable of the internal energy function. However, as the mass of a system is uniquely determined by its composition $\boldsymbol{n}$, it is not necessary to deal with it as an additional variable. Accordingly, the number of degrees of freedom of a system is not greater in a gravitational field with respect to the case when the effect of the field is neglected. This cannot be neglected if the gravitational potential changes within the system. In this case, a position-dependent gravitational potential multiplied by the increment of mass should be included in the differential fundamental equation. Within earthly conditions, this potential depends on the height h:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + (gh)\,\mathrm{d}m + \sum_{i=1}^{K} \mu_i\,\mathrm{d}n_i. \tag{9.4}$$

The quantity g is the gravitational acceleration, which can be considered constant within moderately large height differences. It is important to know that the mass increment $\mathrm{d}m$ is a unique function of the increments of amounts of components $\mathrm{d}n_i$, which should be taken into account when calculating the internal energy. If the thermodynamic system has a small height which does not change, the contribution of gravitational potential is negligibly small compared to other terms. It is important, for example, in systems where sedimentation occurs.

In multiphase systems, there is an *interface layer* between two adjacent phases. While intensive properties (e.g., molar values of extensive quantities) are identical within homogeneous phases independently of the position, there should be a "transition region" between the two phases where differences get matched within a distance of a few molecules. A single-phase system also has an interface at the walls of the container. Describing this system, we usually treat this interface as the surface of the homogeneous phase. Interface layers can have great importance in chemistry, thus it is worth to discuss them in some detail. For this reason, a whole section is dedicated to the thermodynamics of interfaces. Here, we shall only mention the case of a homogeneous phase whose surface interactions cannot be neglected and should be considered in the internal energy. To take surface effects into account, the two-dimensional analogue of pressure is used as an intensive variable, and the corresponding extensive variable is surface. The product of the intensive *surface tension* γ multiplied by the surface A has energy dimension, thus the fundamental equation accounting for surface interactions can be given as $U = U(S, V, A, \boldsymbol{n})$, and the corresponding differential fundamental equation is:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \gamma\mathrm{d}A + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i. \tag{9.5}$$

In summary, we can conclude that, in case of every new interaction in addition to those of a simple system, we should add a new extensive variable characteristic of this interaction to the variables of internal energy specified by the fundamental equation. In the differential form of the fundamental equation, a new term appears that contains the appropriate intensive variable (the partial derivative of the internal energy function with respect to the new variable) multiplied by the increment of the new extensive variable. The additional term is not necessarily as simple as those for the simple system; the new variables are neither always isotropic scalar quantities nor homogeneously distributed within the system. They can also have more specific properties, thus their inclusion needs special care. It is also important that a new interaction always increases the number of degrees of freedom $K + 2$ of the simple system.

9.1 Thermodynamics of Interfaces: Two-Dimensional Equations of State

As we have seen in the chapter on mixtures, condensed phases do not always mix. Between two (non-mixing) condensed phases (solid–liquid, solid–solid, liquid–liquid) and between a condensed phase and the gas phase (solid–gas, liquid–gas), there is always an interface; a "transition region" where differences between the two phases get matched within a layer of a few molecules.

Let us discuss one of the most simple cases; the equilibrium of a pure (single-component) liquid with its vapor. The density of the liquid is so high that molecules are almost closely packed, while in the gas phase, they can freely move at large distances compared to their size.[3] Accordingly, molecules in the liquid phase are closely surrounded by their neighbors, while they do not have close neighbors in the vapor. This is illustrated schematically in Fig. 9.1. The real-life picture is of course three-dimensional both in the liquid and the vapor, but a two-dimensional sketch is simpler to show on a surface. Looking at the figure we can state that – in case of a pure substance – molecules are almost closely packed, which would mean 12 neighbors in three dimensions. However, in the surface layer – the edge of the liquid – molecules only have 8 or 9 close neighbors, depending on the actual liquid structure. Even if there is neither a strict structure nor true close packing in liquids, it is certainly true that molecules adjacent to the gas phase have fewer neighbors

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[3] This difference is typical only in states not too close to the critical point.

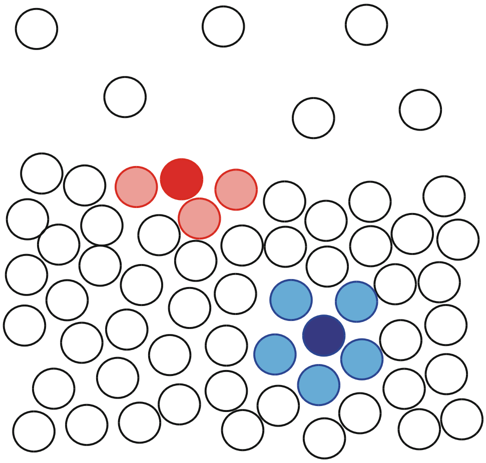

Fig. 9.1 Schematic representation of a liquid–vapor interface. The bottom part crowded by circles represents the molecules of the liquid phase, the upper part with distant circles those of the vapor phase. It can clearly be seen that more molecules are in the close vicinity of a chosen molecule (five in the case shown) inside the liquid than at the phase boundary (three in the case shown)

than their counterparts in the liquid. There are attractive interactions between molecules in liquids – this holds them closely packed. Consequently, if we want to move them onto the surface from an inner position, we should "detach" them from some of their neighbors, for what we need to invest energy. If the change in energy associated with the change of the surface is not negligible compared to the energy change of the entire system, we have to include this extra surface energy in the internal energy. This *excess surface energy* of a material compared to the bulk is proportional to the surface, thus we have to write a term proportional to the increment of the surface into the increment of the internal energy, and the surface becomes a variable of the energy function.

Taking into account the excess surface energy in a simple system, the surface A becomes an additional variable in the internal energy function: $U = U(S, V, A, \boldsymbol{n})$. Its total differential can be written with the appropriate extension of (2.15):

$$\begin{aligned} \mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_{V,A,\boldsymbol{n}} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,A,\boldsymbol{n}} \mathrm{d}V + \left(\frac{\partial U}{\partial A}\right)_{S,V,\boldsymbol{n}} \mathrm{d}A \\ + \sum_{i=1}^{K} \left(\frac{\partial U}{\partial n_i}\right)_{S,V,A,\,n_{j \neq i}} \mathrm{d}n_i. \end{aligned} \tag{9.6}$$

The partial derivatives with respect to S, V, and n_i are, as known, the temperature T, the negative pressure $-P$ and the chemical potentials μ_i. The partial derivative with respect to the surface A is called the *surface tension* and we shall denote it by the lower-case Greek letter γ. Accordingly, the differential fundamental equation can be written in the form already provided above:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \gamma \mathrm{d}A + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i. \tag{9.7}$$

We can also deduce the thermodynamic definition of the surface tension in the following form:

$$\gamma(S, V, A, \boldsymbol{n}) \equiv \left(\frac{\partial U}{\partial A}\right)_{S,V,\boldsymbol{n}}. \tag{9.8}$$

Furthermore, we can also state that the definitions of the thermodynamic functions $H = U + PV$, $F = U - TS$ and $G = U + PV - TS$ do not change the variables A and n_i, thus the total differentials of these functions given by the fundamental equations $H = H(S, P, A, \boldsymbol{n})$, $F = F(T, V, A, \boldsymbol{n})$, and $G = G(T, P, A, \boldsymbol{n})$ can be written similarly as:

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \gamma\mathrm{d}A + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i, \tag{9.9}$$

$$\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \gamma\mathrm{d}A + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i, \tag{9.10}$$

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \gamma\mathrm{d}A + \sum_{i=1}^{K} \mu_i \mathrm{d}n_i. \tag{9.11}$$

The definition of the surface tension can also be written from these latter equations in the following forms:

$$\gamma(S, P, A, \boldsymbol{n}) = \left(\frac{\partial H}{\partial A}\right)_{S,P,\boldsymbol{n}}, \tag{9.12}$$

$$\gamma(T, V, A, \boldsymbol{n}) = \left(\frac{\partial F}{\partial A}\right)_{T,V,\boldsymbol{n}}, \tag{9.13}$$

$$\gamma(T, P, A, \boldsymbol{n}) = \left(\frac{\partial G}{\partial A}\right)_{T,P,\boldsymbol{n}}. \tag{9.14}$$

It is interesting to note that surface tension can also be interpreted by analogy with pressure, which can be considered as the (three-dimensional) force acting on the surface of the system, relative to the surface area. Accordingly, surface tension is the (two-dimensional) force acting on a line within the surface of the system, relative to the length of the line. (There is a basic difference between the two quantities; the pressure P exerts a force to *increase* the volume while the surface tension γ to *decrease* the surface. Accordingly, the respective terms in the total differential of the internal energy function have opposite signs.) It is obvious that the dimensions energy/area and force/length are also identical. We can easily calculate the work done increasing a rectangular surface, e.g. in a slanted rectangular container when we put it into a less slanted position. Increasing the surface along the direction x from position x_0 to x_1 in a container of width b leads to a surface increment of $bx_1 - bx_0$. The energy increment associated with this surface increment if the composition remains constant is

$$\Delta G = \int_{bx_0}^{bx_1} \gamma \mathrm{d}A = \int_{x_0}^{x_1} \gamma b \mathrm{d}x. \tag{9.15}$$

This extra energy ΔG has obviously been generated by the work done to increase the surface. This work has been done against a force f along the direction x. Consequently, the same extra energy ΔG can be calculated from this work:

$$\Delta G = \int_{x_0}^{x_1} f \mathrm{d}x. \tag{9.16}$$

Comparing the two above equations leads to the equality $\gamma b = f$, or, rearranged, $\gamma = f/b$. This clearly supports that the surface tension can be considered from a mechanical point of view as the force acting *within the surface along a line*, relative to the length of the line. This force tends to *decrease* the surface in case of a liquid–gas (or solid–gas) surface, as the increase of the surface needs the investment of energy. It is worth to note that this force is much easier to measure, and appropriate methods lead to a more accurate value of the surface tension, than measuring energy changes described by (9.8) or (9.14).

The thermodynamic description discussed in the example of Fig. 9.1 is valid for any interface. However, in case of two adjacent condensed phases, molecules are nearly close packed in each of the phases; i.e., the number of neighboring molecules is roughly the same in the interface layer as in the bulk of either phases. Consequently, it is the difference in the attraction of molecules present in the two different phases that will determine which phase has a greater attraction on the molecule in the interface region. Accordingly, the excess surface energy at the boundary of a phase can be either positive or negative. It is also interesting to note that the excess surface energy might be different on different crystal surfaces, as the molecular structure is not necessarily the same at all crystal surfaces. In further discussions, we only deal with liquid–gas surfaces, where the excess surface energy is always positive.

9.1.1 Thermodynamic Properties of Curved Surfaces

According to the above conclusions, in systems of constant entropy and volume – where the minimum of energy is the condition of equilibrium – the liquid of the least possible surface is in equilibrium with the gas phase, as it has the least energy. As the three-dimensional body of minimal surface for a given volume is a sphere, the equilibrium shape of a liquid system – if the effect of gravitation is negligible – is spherical. (A liquid body of large mass is deformed by gravitation; thus, a large liquid drop on a flat surface has a flattened shape. However, if a liquid droplet is small enough, its shape is really spherical. Lack of gravitation – e.g., in the state of weightlessness – leads to spherical shape even for larger drops. If the liquid has an interface with other liquids or solids, surface energetics is different, thus the shape is usually no more spherical. This latter effect is called *wetting* what we do not discuss here.)

Let us examine the equilibrium between the liquid and gas phase in case of a pure (single-component) liquid, taking into account the excess surface energy. Consider as one of the two subsystems the liquid with the spherical surface; the other is the gas phase in contact with the liquid. Let us discuss first the example of a small droplet whose spherical shape is not distorted by gravitation, in equilibrium with its vapor. The droplet and the saturated vapor are enclosed in a constant-temperature rigid container in an arrangement shown schematically in Fig. 9.2.

As both volume and amount are constant within the container, the equalities $-\mathrm{d}V^g = \mathrm{d}V^l$ and $-\mathrm{d}n^g = \mathrm{d}n^l$ hold. Temperature cannot change in the thermostatted system, thus $\mathrm{d}T^g = \mathrm{d}T^l = 0$. The condition of equilibrium in a system of constant volume, temperature and amount is the minimum of the free energy function, which can be written as the mathematical condition $\mathrm{d}F = 0$. In the total differential of $F = F^g(T^g, V^g, n^g) + F^l(T^l, V^l, A^l, n^l)$, the term containing the derivative with respect to T multiplied by the increment $\mathrm{d}T$ is zero, as the temperature is constant. The resulting equation for the equilibrium condition can be written with the respective intensive variables substituted for the partial derivatives. According to the figure, P_{in} denotes the pressure inside the drop, while P_{ex} the pressure in the gas phase:

$$\mathrm{d}F = -P_{\text{ex}}\mathrm{d}V^g + \mu^g\mathrm{d}n^g - P_{\text{in}}\mathrm{d}V^l + \gamma^l\mathrm{d}A^l + \mu^l\mathrm{d}n^l = 0. \tag{9.17}$$

Making use of the equalities $-\mathrm{d}V^g = \mathrm{d}V^l$ and $-\mathrm{d}n^g = \mathrm{d}n^l$, and regrouping terms we get:

$$\mathrm{d}F = (P_{\text{ex}} - P_{\text{in}})\mathrm{d}V^l + (\mu^l - \mu^g)\mathrm{d}n^l + \gamma^l\mathrm{d}A^l = 0. \tag{9.18}$$

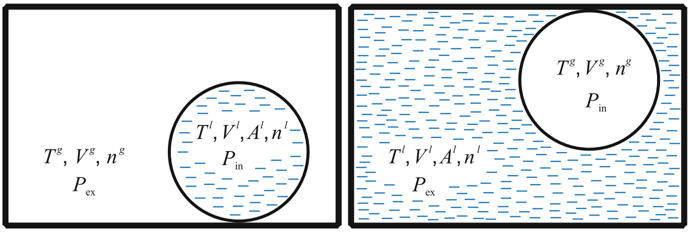

Fig. 9.2 Schematic representation of the equilibrium of spherical liquid–gas interfaces. A liquid drop is shown on the left-hand side, and a bubble or cavity on the right-hand side. Both containers (thick *rectangular boxes*) have rigid, impermeable walls and are immersed into a thermostat (have a constant temperature)

Molecules of the liquid can freely move between the two phases, thus the intensive condition of the equilibrium is the equality of the chemical potentials μ^l and μ^g, from which it follows that $(\mu^l - \mu^g)\ \mathrm{d}n^l = 0$. The resulting equation reads as:

$$(P_{\mathrm{ex}} - P_{\mathrm{in}})\mathrm{d}V^l + \gamma^l \mathrm{d}A^l = 0. \tag{9.19}$$

Let us calculate the relationship between the curvature of the liquid surface and the pressure inside the spherical drop. The curvature of the sphere can be characterized by its radius r. In case of a sphere of radius r, the increment of both the surface and the volume can be given by the increment of the radius $\mathrm{d}r$. To calculate this increment, let us first express the second and third power of $r + \mathrm{d}r$.

$$(r + \mathrm{d}r)^3 = r^3 + 3r^2\mathrm{d}r + 3r(\mathrm{d}r)^2 + (\mathrm{d}r)^3 \cong r^3 + 3r^2\mathrm{d}r, \tag{9.20}$$

$$(r + \mathrm{d}r)^2 = r^2 + 2r\mathrm{d}r + (\mathrm{d}r)^2 \cong r^2 + 2r\mathrm{d}r. \tag{9.21}$$

(We have made use of the fact that the second and third power of the infinitesimally small quantity $\mathrm{d}r$ can be neglected compared to the other two terms remaining.) Using the above results, we can write:

$$\mathrm{d}V = (V + \mathrm{d}V) - V = \frac{4(r + \mathrm{d}r)^3\pi}{3} - \frac{4r^3\pi}{3} \cong 4r^2\pi\mathrm{d}r, \tag{9.22}$$

$$\mathrm{d}A = (A + \mathrm{d}A) - A = 4(r + \mathrm{d}r)^2\pi - 4r^2\pi \cong 8r\pi\mathrm{d}r. \tag{9.23}$$

Let us substitute the above results for the increments $\mathrm{d}V$ and $\mathrm{d}A$ into (9.19), and rearrange the equation:

$$-(P_{\mathrm{ex}} - P_{\mathrm{in}}) \cdot 4r^2\pi\mathrm{d}r = \gamma \cdot 8r\pi\mathrm{d}r \tag{9.24}$$

This equation should hold for any value of $\mathrm{d}r$ (equivalently, we can "simplify" by $\mathrm{d}r$), thus we can express the equilibrium pressure within the drop as:

$$P_{\mathrm{in}}(\mathrm{drop}) = P_{\mathrm{ex}} + \frac{2\gamma}{r}. \tag{9.25}$$

In case of a spherical bubble, equilibrium calculations are quite similar. The only difference is that the liquid surface is *not convex but concave* in this case, i.e., its curvature is not positive but negative. As a consequence, we get the result for the equilibrium pressure *inside a bubble* by simply replacing $1/r$ by $-1/r$ in the above equation:

$$P_{\mathrm{in}}(\mathrm{bubble}) = P_{\mathrm{ex}} - \frac{2\gamma}{r}. \tag{9.26}$$

We can see from the results that the pressure inside a drop is greater than in the surrounding gas phase, while it is smaller in a bubble than in the surrounding liquid phase.

Equations (9.25) and (9.26) describe the pressure within spherically curved liquid surfaces. The general form of the equation for any shape is the Young–Laplace equation:

$$P_{\mathrm{in}} = P_{\mathrm{ex}} + \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right). \tag{9.27}$$

Here, r_1 and r_2 are the so-called *principal radii of curvature* at a given point of the surface. In case of a sphere, these are identical, thus we get back the term $2\gamma/r$. Based on (9.25)–(9.27), we can also state that the pressure inside a liquid of flat surface is identical to the pressure of the adjacent gas phase, as $r = \infty$ in this case. The difference of the inner pressure of droplets or bubbles from the gas phase in equilibrium with a flat surface is proportional to the surface tension, and inversely proportional to the radius of the droplet. Thus, the smaller the size of droplets or bubbles, the greater is the difference in pressure.

Curved liquid surfaces occur not only in drops or bubbles. It is well known that in thin tubes called *capillaries* the liquid surface is not flat but curved, and the liquid level is either above or below the flat level outside the capillary. In the light of the Young–Laplace equation, it is obvious that the two effects are related; the pressure inside the capillary at the curved surface is different from that of a flat surface. The direction of the curving depends on the interactions between the solid tubing material and the liquid inside. If the interaction between the molecules of the solid and those of the liquid (*adhesion*) is more attractive than the interaction between the molecules of the liquid (*cohesion*), the liquid *wets* the capillary surface and creeps up the wall. If adhesion is weaker than cohesion, the liquid does not wet the capillary surface and descends the wall. The Young–Laplace equation enables to calculate the capillary rise (or descent) from the curvature of the liquid surface. To perform the calculations, let us consider the cases shown in Fig. 9.3.

Let us suppose that wetting is strong enough (or weak enough in case of a non-wetting liquid) and the diameter of the capillary is small enough for the liquid to

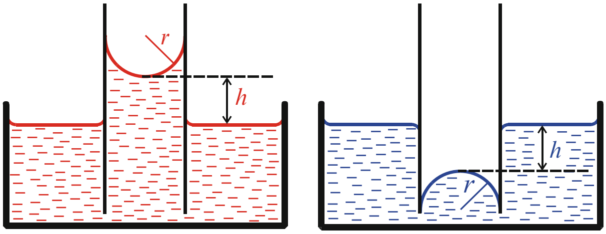

Fig. 9.3 The surface, curvature and height of the liquid in a capillary tube. The liquid wets the surface of the capillary on the left-hand side and does not wet it on the right-hand side

form an undistorted hemispherical surface. In this case, the radius r of the surface (called *meniscus*[4]) is the same as that of the capillary tube, and (9.25) or (9.26) can be used to calculate the pressure at the curved surface in the liquid.[5] If the liquid wets the tube (e.g., water in a glass tube) the surface inside the liquid is concave, thus its pressure is lower than the external pressure P by $2\gamma/r$. As a consequence, the liquid *rises* in the capillary tube until a height h where the hydrostatic pressure decreases the pressure at the liquid surface to P, thus maintaining hydrostatic equilibrium within the liquid:

$$\rho g h = \frac{2\gamma}{r}. \tag{9.28}$$

(The lower-case Greek letter ρ denotes the density of the liquid, while g the gravitational acceleration.) From this equation, we can express the *capillary rise*:

$$h = \frac{2\gamma}{\rho g r}. \tag{9.29}$$

If the liquid does not wet the tube (e.g., mercury in a glass tube) the surface inside the liquid is convex, thus its pressure is *higher* than the external pressure P by $2\gamma/r$. As a consequence, the meniscus *falls* in the capillary tube until the hydrostatic equilibrium is achieved within the liquid. The *capillary depression* h is also described by (9.29).

Capillary action has a great role in the transport through porous materials. This is the reason that sponges absorb a considerable amount of water. Water uptake of plants from the soil is also partly due to capillary action, partly to osmosis, already discussed in this book.

Above curved surfaces, the equilibrium vapor pressure is also different compared to the vapor above flat surfaces. The reason for this is that, in addition to the mechanical equilibrium described by (9.25) or (9.26), chemical equilibrium between the liquid and the vapor should also hold. The condition of this equilibrium is the equality of the chemical potentials in both phases. Let us write the condition of the two equilibria in case of a drop of radius r, using the subscripts v for vapor and l for liquid:

$$P^l - P^v = \frac{2\gamma}{r}, \tag{9.30}$$

$$\mu^l(T, P^l) = \mu^v(T, P^v). \tag{9.31}$$

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[4] The word makes allusion to the shape of the crescent Moon. The diminutive form *μηνισκος* of the Greek word *μηνη* (a name for the Moon) means the waning crescent. (It survived in the Latin name *mensis* meaning a month.)

[5] If the conditions mentioned are not fulfilled, i.e., the surface is not hemispherical, the pressure acting on the surface can be evaluated as a consequence of the mechanical equilibrium taking into account the actual geometry of the surface. This is the case if wetting is weak, or if the surface is flatter than spherical in a thicker tube.

In the second equation, $\mu^l(T, P^l)$ is the chemical potential of the liquid at the equilibrium temperature T and the equilibrium pressure P^l inside the drop, while $\mu^v(T, P^v)$ is the chemical potential of the vapor at the same temperature T and the pressure of the vapor phase P^v. The equilibrium should hold for an infinitesimal change of the pressure as well:

$$P^l + \mathrm{d}P^l - (P^v + \mathrm{d}P^v) = \frac{2\gamma}{r} + \mathrm{d}\left(\frac{2\gamma}{r}\right), \tag{9.32}$$

$$\mu^l(T, P^l) + \mathrm{d}\mu^l = \mu^v(T, P^v) + \mathrm{d}\mu^v. \tag{9.33}$$

Accordingly, equilibrium is only maintained if both equalities

$$\mathrm{d}P^l - \mathrm{d}P^v = \mathrm{d}\left(\frac{2\gamma}{r}\right). \tag{9.34}$$

and

$$\mathrm{d}\mu^l = \mathrm{d}\mu^v \tag{9.35}$$

holds. Note that the equilibrium is described similarly to the phase equilibrium discussed in Sect. 7.2.3, adding the condition of mechanical equilibrium. Thus, we can use (6.13) to express the total differential of the chemical potential in terms of the increments of temperature and pressure. At constant temperature, the term containing $\mathrm{d}T$ is zero, so it can be dropped. The term containing $\mathrm{d}x$ can also be dropped as we deal with a pure substance, i.e., x is always unit. Let us denote the molar volumes of the corresponding phases in the surviving term by v^l and v^v. Thus, (9.35) can be rewritten as:

$$v^l\mathrm{d}P^l = v^v\mathrm{d}P^v. \tag{9.36}$$

Let us substitute $\mathrm{d}P^l$ as expressed from (9.34):

$$v^l\mathrm{d}P^v + v^l\mathrm{d}\left(\frac{2\gamma}{r}\right) = v^v\mathrm{d}P^v. \tag{9.37}$$

Rearranging we get:

$$\mathrm{d}\left(\frac{2\gamma}{r}\right) = \frac{v^v - v^l}{v^l}\,\mathrm{d}P^v \tag{9.38}$$

Taking into account that the molar volume of the liquid v^l is negligible compared to that of the vapor v^v, the ratio $(v^v - v^l)/v^l$ can be replaced by v^v/v^l. Supposing that the vapor behaves as an ideal gas, we can substitute RT/P^v for the molar volume v^l:

$$\mathrm{d}\left(\frac{2\gamma}{r}\right) = \frac{RT}{v^l}\frac{1}{P^v}\mathrm{d}P^v. \tag{9.39}$$

To calculate the excess vapor pressure, let us integrate the left side from $r = \infty$ (flat surface) to the actual drop radius r, and the right side from the pressure P_0 over the flat surface to P_r, the equilibrium pressure over the surface of the drop. (While doing so, it is reasonable to change the integration variable from r to s.)

$$\int_{s=\infty}^{s=r} \mathrm{d}\left(\frac{2\gamma}{s}\right) = \frac{RT}{v^l} \int_{P^v=P_0}^{P^v=P_r} \frac{1}{P^v}\mathrm{d}P^v. \tag{9.40}$$

Integrating we obtain the result

$$\frac{2\gamma}{r} = \frac{RT}{v^l} \ln\frac{P_r}{P_0}, \tag{9.41}$$

which is readily rearranged to provide the vapor pressure in equilibrium with the liquid surface of a drop of radius r:

$$P_r(\text{drop}) = P_0 \mathrm{e}^{\frac{2\gamma v^l}{RTr}}. \tag{9.42}$$

It is convenient to write the molar volume v^l as the ratio of the molar mass M and the density ρ:

$$P_r(\text{drop}) = P_0 \mathrm{e}^{\frac{2\gamma M}{RTr\rho}}. \tag{9.43}$$

Both equations are usually called as the *Kelvin equation* for spherical drops. (The general form of the Kelvin equation is also given in terms of the two principal radii of curvature; cf. (9.27).)

In case of a spherical bubble, equilibrium calculations are quite similar. The only difference is that the convex curvature $1/r$ should be replaced by the concave curvature $-\ 1/r$ to get the equilibrium vapor pressure inside a *bubble*:

$$P_r(\text{bubble}) = P_0 \mathrm{e}^{-\frac{2\gamma M}{RTr\rho}}. \tag{9.44}$$

Let us recall the two approximations used to get the above expressions; the molar volume of the liquid has been ignored in the difference $v^v - v^l$, and the vapor was supposed to be an ideal gas. To have an idea of the first approximation, consider the molar volume 18 cm^3 of liquid water at 25°C compared to that of the vapor in equilibrium with it at 3.169 kPa being 780 480 cm^3. Thus, the difference arising from substituting v^v/v^l in place of $(v^v - v^l)/v^l$ is merely 0.0024%. The molar volume of an ideal gas at the same temperature and pressure is 782 253 cm^3, leading to a difference of 0.227% only. The overall difference thus does not exceed 0.23%. The difference diminishes with decreasing temperature but increases with increasing temperature, mainly due to the ideal gas approximation, but even at 100°C, it is only 1.68%. Thus, it is not worth using (9.38) and the exact pressure-dependent v^v and v^l but (9.43) when making only approximate calculations.

The effect of the change of vapor pressure according to (9.43) and (9.44) over curved surfaces has important consequences. One of them is the *isothermal distillation* of liquids when smaller droplets having greater vapor pressure get vaporized while the vapor condenses onto the greater droplets. Thus, greater droplets get growing and smaller droplets get reduced in size – as it happens in clouds. In a saturated vapor, the formation of the first droplets is hindered by the fact that the vapor pressure in equilibrium with these droplets is larger than the equilibrium pressure over a flat surface, or even larger droplets. Consequently, stable droplets can only be formed from a supersaturated vapor, thus condensation begins at higher than the equilibrium pressure. This supersaturation does not occur if there are solid particles present in the gas phase; on their surface, there is a possibility to form a liquid layer of greater radius. Contrails (or vapor trails) in the wake of aircrafts also develop by condensation on the soot particles emanating from the exhaust of the engine.

In a similar manner, boiling inside liquids is also hindered by the fact that the pressure inside the small bubbles to form at the beginning of boiling is smaller than the outer pressure above the flat liquid surface. Accordingly, small bubbles can only be formed at higher vapor pressure – thus at higher temperature – leading to the superheating of the liquid. (To avoid superheating, boiling chips are used, containing relatively large cavities to help evaporation.)

The equilibrium of small crystallites with a saturated solution can be described similarly to the case of droplets and their vapor. In this case, the solubility of small crystallites is greater than that of greater size crystals. From this, it follows that solutions get typically oversaturated before crystallization, as the solution saturated for large crystals is still undersaturated for the first-to-appear small crystallites.

9.2 Thermodynamic Description of Systems Containing Electrically Charged Particles

Systems containing electrically charged particles have two interesting and important properties in addition to the formal description provided by (9.3) shown at the beginning of this chapter. One of these properties is that there exists no electric charge without a *charge carrier*, which is a molecular entity. Within earthly conditions, such a charge carrier can be the *electron* or *ions*. The charge of individual ions can be the multiple of either the charge of an electron (these are the *negatively charged ions*) or the multiple of the charge of a proton (these are the *positively charged ions*). The charge of the electron and that of the proton has equal absolute values but opposite sign. The charge of the proton is called the *elementary charge*, and its value is $1.602176487 \times 10^{-19}$C. Accordingly, 1C is 6.24151×10^{18} elementary particles. However, in chemistry we do not use this value but the macroscopic quantity of 1 mol elementary charges as a unit. This unit is the product of the elementary charge and the Avogadro constant:

$$\begin{aligned} 1F &= 1.602176487 \times 10^{-19}\,\mathrm{C} \cdot 6.02214179 \times 10^{23}\mathrm{mol}^{-1} \\ &= 96485.33977\,\mathrm{Cmol}^{-1} \end{aligned} \tag{9.45}$$

The quantity F is called the *Faraday constant*.[6]

The charge of ions is characterized by their *charge number*, which is the number of elementary charges carried by a single ion. Accordingly, the charge number of an Na^{+} ion is $+1$, that of the Cl^{-} ion is -1, that of the Al^{+3} ion is $+3$, and that of the ion SO_4^{2-} is -2. The charge number of the common charge carrier electron (which is not considered as an ion) is -1. It is important to note that the property of electric charge being always connected to a charge carrier particle implies that to change the quantity of charge is always connected to moving particles, as there is no electric charge without a carrier particle.[7]

Another important property of systems containing electrically charged particles is the *electroneutrality principle*. According to this, the sum of the absolute value of the negative and the positive charges is always equal, thus macroscopic systems are always *electrically neutral*. We have learnt in electrostatics that electrically charged macroscopic bodies do exist, so this principle needs some considerations. Let us imagine a spherical piece of aluminum containing exactly 1 mol atoms. The density of aluminium is 2.700 g cm^{-3}, its molar mass is 26.9815 g mol^{-1}, whence its molar volume is 9.99315 $\mathrm{cm}^3\,\mathrm{mol}^{-1}$, thus the radius of the sphere is 1.3362 cm. If the sphere is electrically neutral, it contains 0 charge and we can measure a voltage of 0 V on its surface with respect to earth potential. Let us calculate the potential of the same size aluminum sphere if we "withdraw" 3×10^{-10} mol electrons, thus creating 10^{-10} mol Al^{3+} ions, which means a positive excess charge of $3 \times 10^{-10}\,F$. The potential of a conducting sphere in vacuum having an excess charge Q can be calculated as:

$$E = \frac{Q}{4\pi\varepsilon_0 r}. \tag{9.46}$$

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[6] Michael Faraday (1791–1867) was an English chemist and physicist. His most important achievements are in the field of electrochemistry and electromagnetism. He discovered the laws named after him, stating that the transport of a given amount of substance always means the transport of a well-determined amount of electric charge. The unit of capacity, *farad* is also named after him. (Not to be confused with the chemical unit of charge, *faraday*.)

[7] The person who laid down the principles of electric theory is the American inventor, scientist and politician Benjamin Franklin (1706–1790). He imagined electricity – similarly to heat – as a liquid. According to his interpretation, the charge of bodies containing a lot of electric fluid is "positive" (or "vitreous" using an elder name, as this property occurs when rubbing glass), while the charge of bodies containing little electric fluid is "negative" (or "resinous" using an elder name, as this property occurs when rubbing amber). The movement of the liquid is the electric current. This interpretation still survives in the theory of electricity, where charge carriers are not considered but "the quantity of electric charge".

Substituting the charge $3 \times 10^{-10} F = 3 \times 9.64853 \times 10^{-19}\,\mathrm{C}$, the vacuum permittivity $\varepsilon_0 = 8.854187817 \times 10^{-12}\,\mathrm{F\,m^{-1}}$, the radius $r = 0.013362\,\mathrm{m}$, we get the potential 19 469 408 V for the sphere. It means that, in case of 1 mol aluminum, 1×10^{-10} mol free Al^{3+} ions provide a voltage of nearly 20 million V with respect to earth. This quantity of ions in 1 mol is 0.0001 millionths of a mol, or in analytical terms, 0.1 ppb, which is chemically undetectable.[8] (It means that the neutral sphere cannot be distinguished by *chemical methods* from the one at 20 million V potential.) It is obvious that such high potentials cannot be treated in the chemical laboratory. However, they cannot occur either; as the discharge across the air to the nearest neutral object (at earth potential) would radically diminish this potential. It is also obvious that in case of smaller potentials, the associated charges are also smaller, thus their chemical detectability is even more impossible. The voltage of usual electrochemical devices does not exceed 10 V, which is equivalent to approximately 1.5×10^{-16} mol free Al^{3+} ions. The distinction between the charged and the neutral sphere is completely impossible with any chemical methods in this case.

Based on the above considerations, we can conclude that we cannot make any chemical difference between a neutral and a charged system. Thus, we always accept the validity of the electroneutrality principle – even if our system is electrically charged. Let us formulate the principle from the thermodynamical point of view. Consider a system of K components, out of which J are ionic components. The amount of components be n_i and their charge number z_i. The system is electrically neutral if

$$\sum_{i=1}^{J} n_i z_i = 0 \tag{9.47}$$

holds. Dividing the above equation by the volume of the system or the mass of the solvent, we get two equivalent equations in terms of molar concentrations c_i or molalities m_i:

$$\sum_{i=1}^{J} c_i z_i = 0; \qquad \sum_{i=1}^{J} m_i z_i = 0. \tag{9.48}$$

Any one of the three equations expresses the principle of electroneutrality, thus we can use any of them for the thermodynamic description.

The electroneutrality principle imposes a constraint for the ionic components, which is not needed if the system contains only electrically neutral particles. This constraint results in a reduction of the number of degrees of freedom by one, even if there is no electric field present; i.e., the number of degrees of freedom is only $K + F - 1$ instead of $K + F - 2$ if the system contains ionic species as well.

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[8] The unit ppb is the acronym of "parts per billion". The ratio 0.1 ppb is roughly equivalent to one person over the entire population of Earth.

9.2.1 Thermodynamic Consequences of the Electroneutrality Principle: The Chemical Potential of Electrolytes and the Mean Activity Coefficient

An important consequence of the electroneutrality principle is that the chemical potential of individual ions cannot be determined. To demonstrate this, let us recall the expression of the chemical potential as a function of temperature, pressure and composition already stated in (6.8):

$$\mu_i(T, P, x_1, x_2, \ldots, x_K) = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}.$$

Obviously, to calculate the chemical potentials, we have to know the Gibbs potential as a function of the amount n_i of every components. This function should be measured, or calculated from related measured data. To do this measurement, we should change *the amount of a single ion* independently of other ions. However, this is impossible, as the electroneutrality principle only allows changes of the amounts of ions which fulfill (9.47).

Fortunately, we do not need the knowledge of the chemical potential of individual ions either to describe equilibria of systems containing ionic species – which is also the consequence of the electroneutrality principle. As an example, let us discuss a system where a substance dissociating to produce ions – say, $\mathrm{AlCl_3}$ – distributes between two phases α and β. The condition of equilibrium at constant temperature and pressure – as stated in (8.5) – can be written as:

$$\mu^{\alpha}_{\mathrm{Al^{3+}}} \mathrm{d}n^{\alpha}_{\mathrm{Al^{3+}}} + \mu^{\alpha}_{\mathrm{Cl^{-}}} \mathrm{d}n^{\alpha}_{\mathrm{Cl^{-}}} + \mu^{\beta}_{\mathrm{Al^{3+}}} \mathrm{d}n^{\beta}_{\mathrm{Al^{3+}}} + \mu^{\beta}_{\mathrm{Cl^{-}}} \mathrm{d}n^{\beta}_{\mathrm{Cl^{-}}} = 0. \tag{9.49}$$

As we do not consider chemical reactions, the amount of the species can only change by transfer across the phase boundary, hence we can write $\mathrm{d}n^{\alpha}_{\mathrm{Al^{3+}}} = -\mathrm{d}n^{\beta}_{\mathrm{Al^{3+}}}$ and $\mathrm{d}n^{\alpha}_{\mathrm{Cl^{-}}} = -\mathrm{d}n^{\beta}_{\mathrm{Cl^{-}}}$. Substituting these into the above equation and rearranging, we get:

$$\left(\mu^{\alpha}_{\mathrm{Al^{3+}}} - \mu^{\beta}_{\mathrm{Al^{3+}}}\right) \mathrm{d}n^{\alpha}_{\mathrm{Al^{3+}}} + \left(\mu^{\alpha}_{\mathrm{Cl^{-}}} - \mu^{\beta}_{\mathrm{Cl^{-}}}\right) \mathrm{d}n^{\alpha}_{\mathrm{Cl^{-}}} = 0. \tag{9.50}$$

The electroneutrality principle can be written in the following form:

$$z_{\mathrm{Al^{3+}}} n^{\alpha}_{\mathrm{Al^{3+}}} + z_{\mathrm{Cl^{-}}} n^{\alpha}_{\mathrm{Cl^{-}}} = 0. \tag{9.51}$$

This principle is valid also if there is a transfer of the ions from one phase to the other, from which it follows:

$$z_{\mathrm{Al^{3+}}} \mathrm{d}n^{\alpha}_{\mathrm{Al^{3+}}} - z_{\mathrm{Cl^{-}}} \mathrm{d}n^{\alpha}_{\mathrm{Cl^{-}}} = 0. \tag{9.52}$$

As the ions are formed by dissociation of the $AlCl_3$, between the quantities $n^{\alpha}_{Al^{3+}}$ and $n^{\alpha}_{Cl^-}$, as well as between $dn^{\alpha}_{Al^{3+}}$ and $dn^{\alpha}_{Cl^-}$, the conditions arising from the stoichiometric equation should also be fulfilled. The stoichiometric equation can be written as:

$$AlCl_3 = \nu_{Al^{3+}} \, Al^{3+} + \nu_{Cl^-} \, Cl^-. \tag{9.53}$$

(A reasonable choice is of course $\nu_{Al^{3+}} = 1$ and $\nu_{Cl^-} = 3$.) Thus, the conditions following from the dissociation can be written as

$$n^{\alpha}_{Al^{3+}} = \nu_{Al^{3+}} \, n^{\alpha}_{AlCl_3} \quad \text{and} \quad n^{\alpha}_{Cl^-} = \nu_{Cl^{3-}} \, n^{\alpha}_{AlCl_3}, \tag{9.54}$$

as well as

$$dn^{\beta}_{Al^{3+}} = \nu_{Al^{3+}} \, dn^{\beta}_{AlCl_3} \quad \text{and} \quad dn^{\beta}_{Cl^-} = \nu_{Cl^{3-}} \, dn^{\beta}_{AlCl_3}. \tag{9.55}$$

Using the latter two equations, the condition in (9.50) can be written in the following form:

$$\nu_{Al^{3+}} \left(\mu^{\alpha}_{Al^{3+}} - \mu^{\beta}_{Al^{3+}} \right) dn^{\alpha}_{AlCl_3} + \nu_{Cl^{3-}} \left(\mu^{\alpha}_{Cl^-} - \mu^{\beta}_{Cl^-} \right) dn^{\alpha}_{AlCl_3} = 0. \tag{9.56}$$

This equation should hold for arbitrary $dn^{\alpha}_{AlCl_3}$, thus

$$\nu_{Al^{3+}} \left(\mu^{\alpha}_{Al^{3+}} - \mu^{\beta}_{Al^{3+}} \right) + \nu_{Cl^-} \left(\mu^{\alpha}_{Cl^-} - \mu^{\beta}_{Cl^-} \right) = 0. \tag{9.57}$$

Upon rearrangement, this yields the following result:

$$\nu_{Al^{3+}} \mu^{\alpha}_{Al^{3+}} + \nu_{Cl^-} \mu^{\alpha}_{Cl^-} = \nu_{Al^{3+}} \mu^{\beta}_{Al^{3+}} + \nu_{Cl^-} \mu^{\beta}_{Cl^-}. \tag{9.58}$$

The meaning of this result is more obvious after substituting the stoichiometric numbers:

$$\mu^{\alpha}_{Al^{3+}} + 3\mu^{\alpha}_{Cl^-} = \mu^{\beta}_{Al^{3+}} + 3\mu^{\beta}_{Cl^-} \tag{9.59}$$

From the above discussion, we can conclude that in case of electrolytes (which dissociate into ionic species), we do not need to know the chemical potential of the individual ions to characterize the equilibrium state; it is sufficient to know the chemical potential of the neutral combination of anions and cations. If the melt or solution containing the ions is in equilibrium with the solid electrolyte, this combination should be equal to the chemical potential of the solid. For this reason, the neutral combination can be called the *chemical potential of the electrolyte*. In the above example, this can be written as:

$$\mu_{Al^{3+}} + 3\mu_{Cl^-} = \mu_{AlCl_3} \tag{9.60}$$

Note that the term "electrolyte" in this respect should be interpreted in a general sense; it designates the neutral combination of oppositely charged species of any system where these charged species can move. Thus, the above considerations are equally valid, e.g., for metals or metal oxides. In metals, the equilibrium is determined by the combination of the chemical potentials of metal cations and electrons, while in metal oxides, by those of the metal cations and the oxygen ions.

We can generalize the conclusions of the example. Using a general notation for the electrolyte $C_{\nu_+}A_{\nu_-}$, which dissociates to ν_+C^{z+} cations and ν_-A^{z-} anions, we can write the dissociation as:

$$C_{\nu_+}A_{\nu_-} = \nu_+C^{z+} + \nu_-A^{z-}. \tag{9.61}$$

The number of charges should be the same (in this case, zero) on both sides of the equation, thus the electroneutrality can be written in terms of the stoichiometric numbers:

$$\nu_+z_+ + \nu_-z_- = 0. \tag{9.62}$$

To describe the equilibrium, it is sufficient to know the chemical potential of the electrolyte:

$$\mu_{C_{\nu_+}A_{\nu_-}} = \nu_+\mu_{C^{z+}} + \nu_-\mu_{A^{z-}}. \tag{9.63}$$

It is important to add that the *difference* of the chemical potential of individual ions is well defined. This can be illustrated by the following example. Let us write (9.63) for aluminum-chloride and aluminum-nitrate:

$$\mu_{Al^{3+}} + 3\mu_{Cl^-} = \mu_{AlCl_3}, \tag{9.64}$$

$$\mu_{Al^{3+}} + 3\mu_{NO_3^-} = \mu_{AlNO_3}. \tag{9.65}$$

Dividing the difference of the two equations by 3, we get the result

$$\mu_{Cl^-} - \mu_{NO_3^-} = \frac{1}{3}\left(\mu_{AlCl_3} - \mu_{AlNO_3}\right), \tag{9.66}$$

which is well determined, as the right-hand side of the equation contains the difference of two well-determined (and measurable) chemical potentials. Similarly, we can calculate the difference of the following two equations:

$$\mu_{Zn^{2+}} + 2\mu_{Cl^-} = \mu_{ZnlCl_2}, \tag{9.67}$$

$$\mu_{Ca^{2+}} + 2\mu_{Cl^-} = \mu_{CaCl_2}, \tag{9.68}$$

to get the well-determined difference

$$\mu_{\mathrm{Zn}^{2+}} - \mu_{\mathrm{Ca}^{2+}} = \frac{1}{2}\left(\mu_{\mathrm{ZnCl}_2} - \mu_{\mathrm{CaCl}_2}\right). \tag{9.69}$$

Let us examine the consequences of the above discussions for the *activity* of individual ionic species. According to (6.70), the absolute activity λ_i of a species i can be expressed with the help of its chemical potential:

$$\mu_i = RT \ln \lambda_i.$$

Applying this relation to each term in (9.63), we can write:

$$RT \ln \lambda_{\mathrm{C}_{\nu_+}\mathrm{A}_{\nu_-}} = RT\nu_+ \ln \lambda_{\mathrm{C}^{z+}} + RT\nu_- \ln \lambda_{\mathrm{A}^{z-}}. \tag{9.70}$$

Let us divide the equation by RT, rewrite the multiplication of the logarithms as the power of the arguments and the sum of the logarithms as the logarithm of the product of the arguments:

$$\ln \lambda_{\mathrm{C}_{\nu_+}\mathrm{A}_{\nu_-}} = \ln\left[(\lambda_{\mathrm{C}^{z+}})^{\nu_+}(\lambda_{\mathrm{A}^{z-}})^{\nu_-}\right] \tag{9.71}$$

Inverting the logarithm, we obtain the thermodynamically sound activity of the electrolyte $\mathrm{C}_{\nu_+}\mathrm{A}_{\nu_-}$ as the product in the above equation:

$$\lambda_{\mathrm{C}_{\nu_+}\mathrm{A}_{\nu_-}} = (\lambda_{\mathrm{C}^{z+}})^{\nu_+}(\lambda_{\mathrm{A}^{z-}})^{\nu_-}. \tag{9.72}$$

Denoting the number of ions produced upon the dissociation of the electrolyte $\mathrm{C}_{\nu_+}\mathrm{A}_{\nu_-}$ by $\nu = \nu_+ + \nu_-$, we can interpret the mean absolute activity of one of them from the following equation:

$$\left(\lambda_{\nu_+\mathrm{C}^{z+},\,\nu_-\mathrm{A}^{z-}}\right)^{\nu} = (\lambda_{\mathrm{C}^{z+}})^{\nu_+}(\lambda_{\mathrm{A}^{z-}})^{\nu_-}. \tag{9.73}$$

From this, we can express the *mean absolute activity* related to a single ion as the *geometric mean* of the activities of individual ions:

$$\lambda_{\nu_+\mathrm{C}^{z+},\,\nu_-\mathrm{A}^{z-}} = \sqrt[\nu]{(\lambda_{\mathrm{C}^{z+}})^{\nu_+}(\lambda_{\mathrm{A}^{z-}})^{\nu_-}} \tag{9.74}$$

We can interpret this definition as an equal redistribution of the activity of the electrolyte among the ions formed during dissociation.

As the notation is considerably complex in the above definition, it is common practice to use a simplified notation. If anions and cations are well defined, it is sufficient to write λ_+ and λ_- instead of $\lambda_{\mathrm{C}^{z+}}$ and $\lambda_{\mathrm{A}^{z-}}$, and $\lambda_\pm$ instead of $\lambda_{\nu_+\mathrm{C}^{z+},\,\nu_-\mathrm{A}^{z-}}$. Thus, the simplified definition of the mean activity can be written as:

$$\lambda_\pm = \sqrt[\nu]{(\lambda_+)^{\nu_+}(\lambda_-)^{\nu_-}}. \tag{9.75}$$

In mixtures containing charged particles, interactions between the ions are determined by long-range electrostatic interactions, thus they cannot be treated as ideal mixtures even in case of considerably dilute solutions. Let us write the mean activity for the standard state of a real mixture:

$$\lambda_{\pm}^{\ominus} = \sqrt[\nu]{\left(\lambda_{+}^{\ominus}\right)^{\nu_+}\left(\lambda_{-}^{\ominus}\right)^{\nu_-}}. \tag{9.76}$$

In analogy with (6.71), we can write

$$\mu_{\pm} - \mu_{\pm}^{\ominus} = RT \ln \frac{\lambda_{\pm}}{\lambda_{\pm}^{\ominus}}. \tag{9.77}$$

The argument of the logarithm is the *mean relative activity* $a_{\pm}$ which is simply called as *mean activity* in the chemical praxis. The ratio can be expressed in terms of the relative activities of the individual ions:

$$a_{\pm} = \frac{\lambda_{\pm}}{\lambda_{\pm}^{\ominus}} = \sqrt[\nu]{\frac{\left(\lambda_{+}\right)^{\nu_+}\left(\lambda_{-}\right)^{\nu_-}}{\left(\lambda_{+}^{\ominus}\right)^{\nu_+}\left(\lambda_{-}^{\ominus}\right)^{\nu_-}}} = \sqrt[\nu]{\frac{\left(\lambda_{+}\right)^{\nu_+}}{\left(\lambda_{+}^{\ominus}\right)^{\nu_+}}\,\frac{\left(\lambda_{-}\right)^{\nu_-}}{\left(\lambda_{-}^{\ominus}\right)^{\nu_-}}} = \sqrt[\nu]{\left(a_{+}\right)^{\nu_+}\left(a_{-}\right)^{\nu_-}}. \tag{9.78}$$

From the last two equations, we can express the *mean chemical potential* $\mu_{\pm}$ of the electrolyte:

$$\mu_{\pm} = \mu_{\pm}^{\ominus} + RT \ln a_{\pm}. \tag{9.79}$$

The practical choice in electrochemistry is to refer the standard chemical potential $\mu_{\pm}^{\ominus}$ to the molality $m_{\pm}$ in the following sense. Writing the relative activity as a function of molality according to (6.92), we get:

$$\mu_{\pm} = \mu_{m,\pm}^{\ominus} + RT \ln \gamma_{m,\pm}\left(\frac{m_{\pm}}{m_{\pm}^{\ominus}}\right). \tag{9.80}$$

Let us simplify this notation by dropping the subscripts m, and assign to the symbol $m_{\pm}$ the molality divided by the standard molality $m_i^{\ominus}$, i.e., the measured value in units of the standard molality. As a result, we get the commonly used expression of the mean chemical potential:

$$\mu_{\pm} = \mu_{\pm}^{\ominus} + RT \ln \gamma_{\pm} m_{\pm}. \tag{9.81}$$

In this expression, $m_{\pm}$ is the mean chemical potential of any one of the ionic species formed from the electrolyte, and the standard potential $\mu_i^{\ominus}$ refers to the (hypothetical) state of this ion in which the activity $a_{\pm} = \gamma_{\pm}\, m_{\pm}$ is unit.

In accordance with the reasoning in Sect. 6.3.3, it is practical to reference the standard state to the infinitely dilute solution:

$$\lim_{m_{\pm}\to 0} \gamma_{\pm} = 1. \tag{9.82}$$

In this case, the standard refers to the hypothetical concentration of $m_{\pm} = 1\ \text{mol kg}^{-1}$ of molecules in the infinitely dilute state.

We can summarize the results the following way. Substances dissociating to yield ions in a solution or melt are called electrolytes. The chemical potential or the activity of individual ions thus formed cannot be determined, but it is not necessary to know them either to characterize thermodynamic equilibria of ionic systems. Instead, we need to know only the chemical potential or the activity of the neutral combination of ions corresponding to the composition of the electrolyte to characterize equilibrium, which can be determined. In case of an electrolyte dissociating into v_+ cations and v_- anions, this chemical potential is defined as:

$$\mu_{\pm} = v_+\mu_+ + v_-\mu_-. \tag{9.83}$$

Accordingly, the individual chemical potentials μ_+ and μ_- are only determined up to an arbitrary additive constant. In other words, only their difference is uniquely determined.

The *mean* (*relative*) *activity* associated to one single ion out of the $v = v_+ + v_-$ ions formed from the electrolyte upon dissociation can also be derived from the individual ionic activities according to the following formula:

$$a_{\pm} = \sqrt[v]{(a_+)^{v_+}(a_-)^{v_-}}. \tag{9.84}$$

Consequently, the individual activities a_+ and a_- are only determined up to an arbitrary multiplicative constant. In other words, only their ratio is uniquely determined. If the individual ionic activities a_+ and a_- are expressed in terms of molalities, then the mean activity $a_{\pm}$ can be decomposed the following way:

$$\begin{aligned} a_{\pm} &= \sqrt[v]{(\gamma_+ m_+)^{v_+}(\gamma_- m_-)^{v_-}} \\ &= \sqrt[v]{(\gamma_+)^{v_+}(\gamma_-)^{v_-}}\ \sqrt[v]{(m_+)^{v_+}(m_-)^{v_-}} = \gamma_{\pm} m_{\pm}. \end{aligned} \tag{9.85}$$

The quantity $\gamma_{\pm}$ thus defined is called the *mean activity coefficient*. Although this quantity is a state function, its determination is not an easy task. The molecular structure of melts and solutions of electrolytes is rather complicated and strongly depends on the composition. Thus, the calculation of the fundamental equation – as well as the mean activity coefficient – based on statistical thermodynamical methods is usually not feasible. The experimental determination of the mean activity coefficient can be done by the usual methods (e.g., osmotic pressure or vapor pressure measurements), or with the help of suitable galvanic cells discussed in a subsequent section. However, it can be calculated for the case of considerably dilute ionic solutions, using pertinent approximations. The result of these calculations is called the *Debye–Hückel limiting law* – named after the first scientists to do the calculations.[9] According to this law, the logarithm to base 10 of the mean activity coefficient of an ion in a sufficiently dilute electrolyte solution can be given as

$$\log_{10}\gamma_{\pm} = -A\left|z_+z_-\right|\sqrt{\frac{I}{m^{\ominus}}}, \tag{9.86}$$

where I is the *ionic strength*, defined on a molality basis as

$$I = \frac{1}{2}\sum_{i=1}^{J} z_i^2 m_i, \tag{9.87}$$

and the factor A (also called as the *Debye–Hückel constant*) is

$$A = \frac{\ln 10 \cdot F^3}{4\pi N_A}\sqrt{\frac{\rho m^{\ominus}}{2\varepsilon^3 R^3 T^3}}. \tag{9.88}$$

In this expression, ln 10 relates the natural logarithm (to base e) to base 10, F is the Faraday constant, N_A the Avogadro constant, R the gas constant, T the temperature, ε the electric permittivity and ρ the density of the solution. The value of A for water as a solvent at $T = 298$ K and $\rho = 0.997$ kg dm^{-3}, using $m^{\ominus} = 1$mol kg^{-1} and $\varepsilon = 78.54\ \varepsilon_0$ is 0.509. Using this value, we can calculate the mean activity coefficient in highly dilute solutions.

It is important to know that (9.86)–(9.88) can only be applied if the validity of approximations used to derive the Debye–Hückel law holds; i.e., in ideally dilute solutions where the ions are completely solvated and the structure of the solvation shell does not change upon further dilution. In addition to supposing spherical electric field around the ions, the thermal energy of the ions kT is also supposed to be much smaller than the electrostatic interaction energy between the (distant) ions. These conditions are satisfactorily fulfilled at electrolyte concentrations below some 10^{-5} mol kg^{-1}, but the formula gives reasonable approximation up to 10^{-4}–10^{-3} mol kg^{-1}. (There exist also "extended" versions of (9.86) which give better approximations at somewhat higher concentrations as well.) From this we can

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[9] Peter Joseph Wilhelm Debye (1884–1966) was a Dutch physicist, working at German and Swiss universities, and finally at Cornell University in the United States. He received the Nobel-prize in chemistry in 1936, also for contributions to the knowledge of molecular structure through his investigations on dipole moments. He published the theory for dilute electrolyte solutions – later named after the two scientists – together with Hückel in 1923. Erich Armand Joseph Hückel (1896–1980) was a German physicist and mathematician. His most important work is the introduction of simplified quantum mechanical methods to describe molecular orbitals (later called the Hückel MO theory), which also led to the interpretation of the aromatic structure. He co-authored the Debye-Hückel theory while working with Debye in Zürich.

conclude that, while solutions containing uncharged particles can be considered as ideal solutions at high dilutions, in ionic solutions, the deviation from ideality outlast for quite high dilutions. This is the reason to call the formula in (9.86) as the Debye–Hückel *limiting* law. Note also that – within the range of validity of the limiting law – the ionic activity decreases with increasing ionic strength of the solution.

An important result of the limiting law is the description of the change of the activity coefficient as a function of the electrolyte concentration $m_{\pm}$. This enables to determine the standard chemical potential $\mu_{\pm}^{\ominus}$ by extrapolating experimental results to $m_{\pm} = 0$. For example, in a solution containing only one electrolyte dissociating into two ions of charge number $+1$ and -1 (a so-called *1:1 binary electrolyte*), the ionic strength calculated using (9.87) is:

$$I = \frac{1}{2} \sum_{i=1}^{2} z_i^2 m_i = \frac{1}{2} \left(m_{+} + m_{-} \right) = m_{\pm}. \tag{9.89}$$

Substituting this in (9.86), we get:

$$\log_{10} \gamma_{\pm} = -A \left| z_{+} z_{-} \right| \sqrt{\frac{m_{\pm}}{m^{\ominus}}}. \tag{9.90}$$

According to this result, the logarithm of the mean activity coefficient goes to zero (i.e., $\gamma_{\pm}$ goes to one, the value in an ideal solution) proportional to the square root of the molality as the concentration goes to zero. From this, we can conclude that $\gamma_{\pm}$ cannot become unit for arbitrarily small but finite concentration, only at exactly zero concentration.

9.2.2 Chemical Potential of Ions in an Electric Field: The Electrochemical Potential

Let us write the Euler relation (2.33) for a system containing electric charge q in an electric field of strength φ, according to (9.3):

$$U = TS - PV + \sum_{i=1}^{K} \mu_i n_i + \varphi q. \tag{9.91}$$

Let us also take into consideration that electric charge can only be present in the form of *charge carriers*; thus, we can write the charge q as the sum of the charges “carried” by the J ionic species:

$$q = \sum_{j=1}^{J} z_j F n_j. \tag{9.92}$$

Obviously, the charge carried by the ionic species is proportional to their amount n_j; thus, their electric contribution to the internal energy is also proportional to n_j – similarly to the contribution of the chemical potential μ_i of the species. The chemical potential determines the change in internal energy if the amount of a given species changes. However, in an electric field, the change of the amount of an ionic species necessarily involves the change of the carried charge as well. Thus, the change in the amount of an ionic species includes the change of energy due to the accompanying change of its charge, so we have to include the change of electric energy into the chemical potential. The change of the "pure chemical" energy and the electric energy are not and cannot be independent; therefore, it is practical to treat them as one quantity. This quantity is called the *electrochemical potential*:

$$\mu_j = \tilde{\mu}_j + z_j F\varphi. \tag{9.93}$$

This definition reflects that the charge belongs to the chemical "character" of the charge carrier. We get the same result by derivation of the U function given in (9.91) with respect to the amount of the component n_j – which is the very definition of the chemical potential. Consequently, the above quantity μ_j is the chemical potential in an electric field. However, to stress the fact that it includes a nonzero electric contribution, it is often called the electrochemical potential.

An important property of the electrochemical potential defined by (9.93) is that the "pure chemical" part $\tilde{\mu}_j$ (the value of the chemical potential in a zero-potential field) cannot be separated uniquely from the electric part $z_j F\varphi$, as the chemical potential of the individual ion is not uniquely determined either. (As it has been concluded in the previous section, even in case of zero potential we can only determine μ_j up to an arbitrary additive constant, and thus the potential $\tilde{\mu}_j$ as well.) However, if we want to stress the electric interaction separately, the Euler relation for the internal energy can then be written in the following form:

$$U = TS - PV + \sum_{i=1}^{K-J} \mu_i n_i + \sum_{j=1}^{J} \left(\tilde{\mu}_j + z_j F\varphi\right) n_i. \tag{9.94}$$

As a result of the above considerations, we can state that chemical equilibria of charge carriers can be treated similarly to any other species the way we treated them before; the condition of electrochemical equilibrium in case of charged species which can move freely between two phases is the equality of their electrochemical potentials within the two phases. For any (freely moving) ions, the equality

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{9.95}$$

should hold; even if the electric potential φ^{α} and φ^{β} of the phases α and β are not equal.[10] Based on the formal decomposition of the electrochemical potential according to (9.93), we can write this condition in the following form:

$$\tilde{\mu}_i^{\alpha} + z_i F \varphi^{\alpha} = \tilde{\mu}_i^{\beta} + z_i F \varphi^{\beta}. \tag{9.96}$$

The equilibrium electric potential difference between the two phases can be given based on this equation:

$$\mu_i^{\beta} - \mu_i^{\alpha} = \tilde{\mu}_i^{\beta} - \tilde{\mu}_i^{\alpha} + z_i F \left(\varphi^{\beta} - \varphi^{\alpha} \right). \tag{9.97}$$

However, as the "pure chemical" part $\tilde{\mu}_j$ cannot be separated uniquely from the electric part $z_j F \varphi$, the difference $\tilde{\mu}_i^{\beta} - \tilde{\mu}_i^{\alpha}$ is not unique either; i.e., it is not a thermodynamically sound quantity. Accordingly, the electric potential difference $\varphi^{\beta} - \varphi^{\alpha}$ cannot be determined either. Fortunately, there is an exception; if the chemical composition of the two phases is identical, then the "purely chemical" terms $\tilde{\mu}_i^{\beta}$ and $\tilde{\mu}_i^{\alpha}$ are also identical, thus their difference is zero. Consequently, only the electric potential difference of phases of *identical chemical composition* can be defined according to the relation:

$$\mu_i^{\beta} - \mu_i^{\alpha} = z_i F \left(\varphi^{\beta} - \varphi^{\alpha} \right). \tag{9.98}$$

Based on this relation, we can obtain the condition of electric equilibrium between two phases from the general condition $\mu_i^{\beta} = \mu_i^{\alpha}$ for phases of identical composition:

$$\varphi^{\beta} = \varphi^{\alpha}. \tag{9.99}$$

It is in accordance with the general condition of equilibrium that the intensive variables characteristic to the given interaction are identical within the entire system.

9.2.3 *Heterogeneous Electrochemical Equilibria: The Galvanic Cell*

The most important electrochemical device in everyday life is the *galvanic cell*.[11] This device usually contains two ion-conducting phases and two

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[10] We consider as the potential of the phase the *inner potential*, which can be measured inside the phase, in contrast with the *outer potential*, which can be measured on the surface of the phase at an infinitely small distance.

[11] The name is derived from the family name of the Bolognese medical doctor, Luigi Galvani (1737–1798). He was the first to describe the device nowadays called an electrochemical cell, which he discovered while dissecting frogs, and first interpreted its electric power as the product of living cells. The galvanic cell is the version where – if joining the terminal wires – a spontaneous

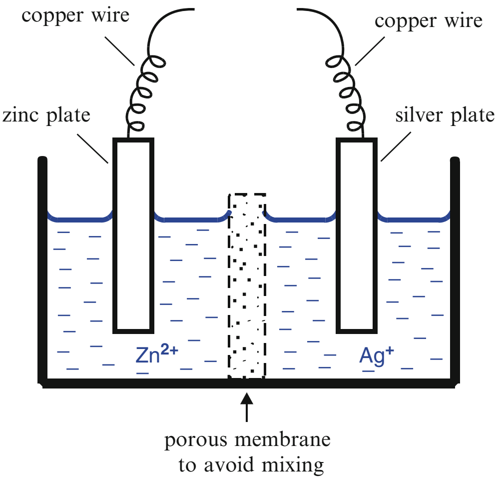

Fig. 9.4 Possible arrangement of a silver-zinc galvanic cell with copper terminals

electron-conducting phases arranged in a way that each electron-conducting phase is in contact with an ion-conducting phase, and the two ion-conducting phases are in contact with each other. It is common practice to include also the terminal wires (of the same metal) attached to the electron-conducting phases.

We shall demonstrate the thermodynamic description on the example of a galvanic cell consisting of zinc metal immersed into an aqueous solution containing zinc ions, and of silver metal immersed into an aqueous solution containing silver ions, along with a couple of copper terminal wires. A possible physical arrangement of the cell is shown in Fig. 9.4.

The cell can be described symbolically by the *cell diagram*, which contains the following elements from left to right, in a fixed order: left terminal metal, left electron-conducting phase, left ion-conducting phase, right ion-conducting phase, right electron-conducting phase, and right terminal metal. (Some special cells may contain more elements than these. In that case, additional elements are written in the appropriate places.) The diagram of the example cell can be written the following way:

$$\underset{l}{\mathrm{Cu}}\;\Big|\;\underset{\mathrm{Zn}}{\mathrm{Zn}}\;\Big|\;\text{aqueous }\underset{z}{\mathrm{Zn}^{2+}}\text{ solution}\;\vdots\;\text{aqueous }\underset{a}{\mathrm{Ag}^{+}}\text{ solution}\;\Big|\;\underset{\mathrm{Ag}}{\mathrm{Ag}}\;\Big|\;\underset{r}{\mathrm{Cu}} \tag{9.100}$$

Solid vertical bars symbolize solid | solid or solid | liquid phase boundaries, while dotted bars a miscible liquid ⋮ liquid phase boundary. To identify actual phases, we use the short symbols written below the diagram.

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electric current is flowing. The other version is called an *electrolytic cell*, in which an external voltage drives a current of opposite direction to that of the galvanic cell.

Let us write the condition of electrochemical equilibria for phases in contact with each other. Between the metals, it is the electron that can freely pass:

$$\mu_{\mathrm{e}^-}^{l} = \mu_{\mathrm{e}^-}^{\mathrm{Zn}}, \tag{9.101}$$

$$\mu_{\mathrm{e}^-}^{r} = \mu_{\mathrm{e}^-}^{\mathrm{Ag}}. \tag{9.102}$$

Between metals and metallic ion solutions, it is the metal ion that can freely pass (i.e., get solved from the metal or precipitated onto it):

$$\mu_{\mathrm{Zn}^{2+}}^{\mathrm{Zn}} = \mu_{\mathrm{Zn}^{2+}}^{z}, \tag{9.103}$$

$$\mu_{\mathrm{Ag}^+}^{a} = \mu_{\mathrm{Ag}^+}^{\mathrm{Ag}}. \tag{9.104}$$

The electric potential difference between the right and the left terminals is well determined, as they are chemically identical. The nonzero potential difference is the result of a constrained equilibrium; phases are in contact only pairwise, preventing an unconstrained overall chemical and electric equilibrium. Substituting the charge number of electron $z_{\mathrm{e}^-} = -1$ into (9.98), we get:

$$-F\left(\varphi^{r} - \varphi^{l}\right) = \mu_{\mathrm{e}^-}^{r} - \mu_{\mathrm{e}^-}^{l}. \tag{9.105}$$

Using the previous equations for equilibrium condition, we can rewrite it as:

$$-F\left(\varphi^{r} - \varphi^{l}\right) = \mu_{\mathrm{e}^-}^{\mathrm{Ag}} - \mu_{\mathrm{e}^-}^{\mathrm{Zn}}. \tag{9.106}$$

Let us make use of the possibility that the chemical potential of metals – similarly to that of electrolytes – can be written as the sum of the metal ion and electron. Writing this identity for one electron, we get:

$$\frac{1}{2}\mu_{\mathrm{Zn}}^{\mathrm{Zn}} = \frac{1}{2}\mu_{\mathrm{Zn}^{2+}}^{\mathrm{Zn}} + \mu_{\mathrm{e}-}^{\mathrm{Zn}}, \tag{9.107}$$

$$\mu_{\mathrm{Ag}}^{\mathrm{Ag}} = \mu_{\mathrm{Ag}^+}^{\mathrm{Ag}} + \mu_{\mathrm{e}-}^{\mathrm{Ag}}. \tag{9.108}$$

With the help of the above equations, we can express the chemical potential difference $\mu_{\mathrm{e}^-}^{\mathrm{Ag}} - \mu_{\mathrm{e}^-}^{\mathrm{Zn}}$ in terms of the chemical potentials of the metal ions instead of the electron:

$$-F\left(\varphi^{r} - \varphi^{l}\right) = \mu_{\mathrm{Ag}}^{\mathrm{Ag}} - \mu_{\mathrm{Ag}^+}^{\mathrm{Ag}} - \frac{1}{2}\mu_{\mathrm{Zn}}^{\mathrm{Zn}} + \frac{1}{2}\mu_{\mathrm{Zn}^{2+}}^{\mathrm{Zn}}. \tag{9.109}$$

Making use of the equalities (9.103) and (9.110), after some rearrangement, we can write this in the following form:

$$-F\left(\varphi^{r} - \varphi^{l}\right) = \mu_{\mathrm{Ag}}^{\mathrm{Ag}} + \frac{1}{2}\mu_{\mathrm{Zn}^{2+}}^{z} - \frac{1}{2}\mu_{\mathrm{Zn}}^{\mathrm{Zn}} - \mu_{\mathrm{Ag}^{+}}^{a}. \tag{9.110}$$

The difference on the right-hand side

$$\left(\mu_{\mathrm{Ag}}^{Ag} + 1/2\mu_{\mathrm{Zn}^{2+}}^{z}\right) - \left(1/2\mu_{\mathrm{Zn}}^{Zn} + \mu_{\mathrm{Ag}^{+}}^{a}\right)$$

can be interpreted – in analogy of (8.15) – as the Gibbs potential $\Delta_{\mathrm{r}}\, G$ of the reaction

$$\tfrac{1}{2}\,\mathrm{Zn}(s) + \mathrm{Ag}^{+}(aq) \rightarrow \tfrac{1}{2}\,\mathrm{Zn}^{2+}(aq) + \mathrm{Ag}(s). \tag{9.111}$$

Based on these results, we can conclude that the equilibrium potential difference of a galvanic cell is independent of the terminal metal; it depends only of the cell reaction (i.e., the setup of the cell). This is the reason we can call the difference as the *potential of the cell reaction*. To formulate the general thermodynamic expression of this potential, we have to consider another important property of contact equilibria. In the example, we have written the conditions of equilibrium for one single electron. Of course, we could write the same equations for an arbitrary number of electrons – in the example, two electrons are also a natural choice. It is obvious that the electric potential difference of the cell cannot depend on this choice. To show this, we can consider the results obtained by writing the appropriate equations for two electrons instead of one. We should write the double of the chemical potentials and $z = -2$ instead of $z_{\mathrm{e}^-} = -1$:

$$-2F\left(\varphi^{r} - \varphi^{l}\right) = 2\mu_{\mathrm{Ag}}^{\mathrm{Ag}} + \mu_{\mathrm{Zn}^{2+}}^{z} - \mu_{\mathrm{Zn}}^{\mathrm{Zn}} - 2\mu_{\mathrm{Ag}^{+}}^{a}. \tag{9.112}$$

The cell reaction should be also written accordingly as:

$$\mathrm{Zn}(s) + 2\ \mathrm{Ag}^{+}(aq) \rightarrow \mathrm{Zn}^{2+}(aq) + 2\ \mathrm{Ag}(s). \tag{9.113}$$

Comparing the two stoichiometric equations we can see that, when writing the equation for one electron, a single elementary charge is exchanged between ½ Zn and Ag^{+}, while in case of two electrons, the number of elementary charges exchanged is 2. The number of elementary charges exchanged in a reaction is called the *charge number of the cell reaction*; it is an integer number denoted by *n*. Thus, the potential of the cell reaction *E* can be written as:

$$-nFE = \Delta_{\mathrm{r}}G. \tag{9.114}$$

As the Gibbs potential of the reaction $\Delta_{\mathrm{r}}G$ is proportional to the charge number *n*, it is immaterial how we write the cell reaction – which supports the reliability of the equations for contact equilibria. It can also be seen from the equation that the correct sign of the cell potential can only be obtained if we write the stoichiometric equation in the proper direction. In the example discussed, this is the direction according to which Zn is oxidized at the left-hand side metal-solution boundary (and gets dissolved in the solution), while Ag^+ ions are reduced at the right-hand side metal-solution boundary (and precipitated onto the metal surface). As the cell potential, E is always calculated by subtracting the potential of the left terminal from that of the right terminal, the cell reaction should always be written in a way that oxidation should occur on the surface of the left electron conducting phase and reduction on the surface of the right electron conducting phase. The sign of the cell potential at the actual concentrations is determined by the sign of the reaction Gibbs potential $\Delta_r G$. If its sign is negative (i.e., the reaction spontaneously proceeds from left to right at constant temperature and pressure), then E is positive, and vice versa. It follows from the above arguments that, if the cell diagram is reversed, the stoichiometric equation should also be reversed. Consequently, the stoichiometric equation determines the arrangement of the cell diagram.

Having in mind the thermodynamics of chemical reactions discussed in Chap. 8, it seems to be worth to relate the reaction Gibbs potential to the standard reaction Gibbs potential, thus connecting the potential of the cell reaction to the equilibrium constant. Let us start by expressing the chemical potentials in (9.112) as a function of composition. The composition of pure metals does not change, that of the ions in the solution can be given as a function of their activity:

$$\mu^{a}_{\mathrm{Ag}^+} = \mu^{\ominus a}_{\mathrm{Ag}^+} + RT\ln a^{a}_{\mathrm{Ag}^+}, \tag{9.115}$$

$$\mu^{z}_{\mathrm{Zn}^{2+}} = \mu^{\ominus z}_{\mathrm{Zn}^{2+}} + RT\ln a^{z}_{\mathrm{Zn}^{2+}}. \tag{9.116}$$

Upon substitution into (9.112) and rearrangement, we get:

$$\begin{aligned} -2F\left(\varphi^r - \varphi^l\right) = {} & 2\mu^{\mathrm{Ag}}_{\mathrm{Ag}} - 2\mu^{\ominus a}_{\mathrm{Ag}^+} - 2RT\ln a^{a}_{\mathrm{Ag}^+} \\ & - \left(\mu^{\mathrm{Zn}}_{\mathrm{Zn}} - \mu^{\ominus z}_{\mathrm{Zn}^{2+}} - RT\ln a^{z}_{\mathrm{Zn}^{2+}}\right). \end{aligned} \tag{9.117}$$

Let us express from this equation the potential difference $E = \varphi^r - \varphi^l$:

$$2E = \left(2\frac{\mu^{\ominus a}_{\mathrm{Ag}^+} - \mu^{\mathrm{Ag}}_{\mathrm{Ag}}}{F} + \frac{2RT}{F}\ln a^{a}_{\mathrm{Ag}^+}\right) - \left(\frac{\mu^{\ominus z}_{\mathrm{Zn}^{2+}} - \mu^{\mathrm{Zn}}_{\mathrm{Zn}}}{F} + \frac{RT}{F}\ln a^{z}_{\mathrm{Zn}^{2+}}\right). \tag{9.118}$$

The first and third terms do not depend on the composition and contain standard chemical potentials, thus their difference can be considered as the standard (electric) potential. Let us denote this difference by $2E^{\ominus}$; from which we obtain the standard potential as

$$E^{\ominus} = 2\frac{\mu^{\ominus a}_{\mathrm{Ag}^+} - \mu^{\mathrm{Ag}}_{\mathrm{Ag}}}{F} - \frac{\mu^{\ominus z}_{\mathrm{Zn}^{2+}} - \mu^{\mathrm{Zn}}_{\mathrm{Zn}}}{F}. \tag{9.119}$$

Using this notation and combining the two other (logarithmic) terms in a fraction, we obtain the following relation:

$$E = E^{\ominus} + \frac{RT}{2F} \ln \frac{\left(a^{a}_{\mathrm{Ag}^{+}} \right)^{2}}{a^{z}_{\mathrm{Zn}^{2+}}}. \tag{9.120}$$

This is called the *Nernst equation* (for the given cell).

The standard potential $E^{\ominus}$ can also be obtained in a different way. Based on (9.114), we can write

$$-\,nFE^{\ominus} = \Delta_{\mathrm{r}} G^{\ominus}. \tag{9.121}$$

From (8.19), the standard reaction Gibbs potential $\Delta_{\mathrm{r}} G^{\ominus}$ can be written in the form – $RT \ln K_a$, where K_a is the equilibrium constant of the reaction. Combining these, we can express the standard potential from the thermodynamic data of the cell reaction in the following form:

$$E^{\ominus} = -\frac{\Delta_{\mathrm{r}} G^{\ominus}}{nF} = \frac{RT}{nF} \ln K_a. \tag{9.122}$$

We can arrive to this result also by considering that the state according to a purely chemical equilibrium occurs in the cell if there is no potential difference between the two terminal metals, that is, $E = 0$. In this case, the argument of the logarithmic term of (9.120) contains the equilibrium activities, thus it gives the equilibrium constant. Upon substitution and rearrangement, we get the above result.

We can summarize the above results by extending it to a general case. If in a cell that is characterized by the cell diagram

$$\begin{array}{c|c|ccc|c|c} \text{left} & \text{left electron} & \text{left} & \vdots & \text{right} & \text{right electron} & \text{right} \\ \text{terminal} & \text{conductor} & \text{ion conductor} & \vdots & \text{ion conductor} & \text{conductor} & \text{terminal} \end{array} \tag{9.123}$$

the general *charge transfer reaction*

$$\sum_{i=1}^{R} \nu_i A_i = 0 \tag{9.124}$$

occurs, whose charge number is n, then the equilibrium electric potential difference between the right and the left terminal – the potential of the cell reaction – is given by the Nernst equation:

$$E = E^{\ominus} + \frac{RT}{nF} \ln \prod_{i=1}^{J} \left(a_i \right)^{\nu_i}. \tag{9.125}$$

The product contains the activities of the J components of the reaction present in the solution, raised to the power of their stoichiometric numbers. (Pure solid phases are not included.) The standard potential $E^{\ominus}$ can be calculated from the standard reaction Gibbs potential $\Delta_r G^{\ominus}$ according to (9.122):

$$E^{\ominus} = -\frac{\Delta_r G^{\ominus}}{nF}$$

9.2.4 Electrodes and Electrode Potentials

The discussion of the above example of a galvanic cell led us to the expression (9.118) of the electric potential difference containing two terms. One term depends only on the properties of the left electrolyte solution and the electron conductor submerged into this solution, the other term depends only on those of the right electrolyte solution and the right electron conductor. This is also true for any galvanic cell; they can be divided into a *left half cell* and a *right half cell*, whose contributions to the electric potential difference can be treated separately. These half cells are also called *electrodes*.[12]

Accordingly, the cell diagram (9.100) can be decomposed into two electrodes:

$$\text{aqueous Ag}^+ \text{ solution} \mid \text{Ag} \,, \tag{9.126}$$

$$\text{aqueous Zn}^{2+} \text{ solution} \mid \text{Zn} \,. \tag{9.127}$$

Writing the diagram of half cells, we drop the terminal metal as it has no importance if it is alone at one side only, and the ionic conductor is always on the left side – the reason for this will be explained soon. Equation (9.118) already suggested that we can express the *electrode potential*, and thus the *electrode reaction* as well, for individual electrodes. To obey the principle of the conservation of charge, the electrode reaction should also contain the electron. The two electrode reactions in the example can be written as follows:

$$\text{Ag}^+(aq) + \text{e}^- \rightarrow \text{Ag}(s), \tag{9.128}$$

$$\tfrac{1}{2}\,\text{Zn}^{2+}(aq) + \text{e}^- \rightarrow \tfrac{1}{2}\,\text{Zn}(s). \tag{9.129}$$

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[12] The names *anode, cathode*, and *electrode* have been introduced by Faraday who discovered the migration of ions. The actual forms of these names were proposed to Faraday by the scientist and priest William Whewell (1794–1866). The Greek word *ανοδος* refers to the rising sun, while *καθοδος* to the setting sun, thus expressing the opposite direction of the current at the two terminals with respect to the cell. The (positive) current enters the cell on the anode and leaves the cell on the cathode. The word electrode is a generalized expression referring to a current passing thorough a half cell.

We can obtain the cell reaction (9.113) by subtracting the twofold of the zinc electrode reaction from the twofold of the silver electrode reaction (i.e., we add the twofold opposite reaction of the zinc electrode). The factor two arises as a consequence of writing electrode reactions always for one electron transfer, while (9.118) refers to two electrons. Accordingly, the potential of the silver electrode is half of the first term of (9.118):

$$\varepsilon_{\mathrm{Ag}^+/\mathrm{Ag}} = \frac{\mu^{\ominus a}_{\mathrm{Ag}^+} - \mu^{\mathrm{Ag}}_{\mathrm{Ag}}}{F} + \frac{RT}{F} \ln a^{a}_{\mathrm{Ag}^+}, \tag{9.130}$$

and that of the zinc electrode is half of the second term of the equation:

$$\varepsilon_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = \frac{\mu^{\ominus z}_{\mathrm{Zn}^{2+}} - \mu^{\mathrm{Zn}}_{\mathrm{Zn}}}{2F} + \frac{RT}{2F} \ln a^{z}_{\mathrm{Zn}^{2+}}. \tag{9.131}$$

The potential difference of the cell can be calculated from these results the same way as the stoichiometric equation of the cell reaction from the electrode reactions; we should subtract the twofold of the potential of the $\mathrm{Zn}^+/\mathrm{Zn}$ electrode from the twofold of the potential of the $\mathrm{Ag}^+/\mathrm{Ag}$ electrode.

It is easy to see why we write the diagram of the electrodes as a "right-hand side half cell"; the equilibrium electric potential of the entire cell is obtained by subtracting the left-hand side half cell from the right-hand side half cell. To calculate the potential difference of the cell, the cell reaction should have been written in a way that reduction should occur on the right electrode and oxidation on the left electrode. If electrode reactions are always written as reductions, the potential to be subtracted will always mean the opposite reaction, that is, oxidation.

Similarly to the potential of the cell reaction, we can also divide the potential of the electrode reaction into a *standard electrode potential* and a second term containing a composition-dependent quantity:

$$\varepsilon_{\mathrm{Ag}^+/\mathrm{Ag}} = \varepsilon^{\ominus}_{\mathrm{Ag}^+/\mathrm{Ag}} + \frac{RT}{F} \ln a_{\mathrm{Ag}^+}, \tag{9.132}$$

$$\varepsilon_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = \varepsilon^{\ominus}_{\mathrm{Zn}^{2+}/\mathrm{Zn}} + \frac{RT}{2F} \ln a_{\mathrm{Zn}^{2+}}. \tag{9.133}$$

As it can be seen from these expressions, the standard potential of the electrodes corresponds to the solution of unit activity. We could say that it can be *measured* if the solution is of unit activity; however, this raises a problem that has emerged already when dividing the cell into electrodes (half cells). While (9.118) and (9.120) describing the potential difference of the cell contain only well-determined thermodynamic quantities (differences of chemical potentials and ratios of activities), (9.132) and (9.133) describing electrode potentials contain the chemical potential and the activity of individual ions, which are not well determined. Consequently, these latter do not have a unique physical significance. There are two possibilities to overcome this ambiguity. We could either fix the undetermined additive constant in the chemical potential of the ions (which is equivalent to fixing the undetermined multiplicative constant in their activity), or fix the additive constant in the electrode potentials derived from the chemical potentials. In the praxis, this latter has been implemented; the standard electrode potential of the *hydrogen electrode* has been fixed to zero.

According to this convention, to calculate the potential difference of a cell whose left electrode is a standard hydrogen electrode, we should subtract from the potential of the right electrode exactly zero volts. In other words, the cell potential of this galvanic cell is exactly the electrode potential of the right electrode. The *standard hydrogen electrode* is given by the following diagram:

$$\mathrm{HCl}\,(aq,\ a_{\pm} = 1)\ |\ \mathrm{H_2}(g, P = 1\ \mathrm{bar})\ |\ \mathrm{Pt} \tag{9.134}$$

Here, HCl(aq, $a_{\pm} = 1$) designates the aqueous solution of HCl where the activity of the H^+ ion is unit, and H_2 ($g, P = 1$ bar) specifies that this HCl solution is saturated by hydrogen gas of 1 bar pressure.[13] By definition, this half cell has an electrode potential of exactly 0 V.

By expressing the potential of the hydrogen electrode from the equilibrium conditions, we get the result

$$\varepsilon_{\mathrm{H^+}/\frac{1}{2}\mathrm{H_2}} = \frac{\mu^{\ominus}_{\mathrm{H^+}} - 1/2\,\mu_{\mathrm{H_2}}}{F} + \frac{RT}{F}\ln a_{\mathrm{H^+}}, \tag{9.135}$$

from which we can conclude that the standard potential $\varepsilon^{\ominus}_{\mathrm{H^+}/\frac{1}{2}\mathrm{H_2}}$ is only zero if the standard chemical potential of the aqueous H^+ ion is zero. (The chemical potential of the pure hydrogen gas – being a stable element – is zero by definition.) In other words, fixing the electrode potential of the standard hydrogen electrode at zero is equivalent to fixing the standard chemical potential of the aqueous H^+ ion at zero.

The electrode reaction in the hydrogen electrode can be written as:

$$\mathrm{H^+}(aq) + \mathrm{e^-} \rightarrow \tfrac{1}{2}\mathrm{H_2}(g). \tag{9.136}$$

The peculiarity of this reaction is that its product is a gas, not a solid. However, as we can see from the "electrode diagram", the electron conductor is platinum metal, which dissolves a considerable amount of hydrogen. As a consequence, the oxidation of the hydrogen gas or the reduction of the H^+ ions occurs on the surface of platinum. Electrodes of similar constitution (i.e., containing a dissolved reactive gas in an electron conductor) are called *gas electrodes*.

Although we can calculate the cell potential after having fixed the standard potential of the hydrogen electrode to zero, this potential is not necessarily the one we could measure in a cell in electrochemical equilibrium. An *equilibrium cell* is the one in which there is no net current flowing, and there is equilibrium at each phase

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[13] Prior to the introduction of the SI, the reference pressure was 1 atm = 1.01325 bar. As a consequence, electrode potentials found in tables referenced to a hydrogen pressure of 1.01325 bar are higher than the currently used values referenced to 1 bar by 0.169 mV (0.000169 V).

boundary – except for the liquid–liquid phase boundary. At this boundary, charge carriers should pass freely from one phase to the other, but the (miscible) liquids are not allowed to mix. (Equilibrium at this boundary could have been achieved by complete mixing, but the porous membrane separating the liquids does not allow for mixing. In case of the example cell, this mixing would lead to the precipitation of silver onto the surface of the zinc metal. The membrane acts to avoid this process.) Charge carriers passing across the membrane will give rise to a liquid-liquid junction potential (usually called liquid junction potential or simply junction potential), which adds to the potential difference of the electrodes. The origin of the liquid junction potential is that the eventual different concentration and the different diffusion velocity across the boundary leads to different spatial distribution of ions, which gives rise to a potential across the boundary. (This is the reason to call it as *diffusion potential.*) Thus, it is not an equilibrium property but is a result of ionic migration.

An equilibrium description of the liquid junction potential can be illustrated in the example of the zinc–silver cell discussed above. Let us start from (9.110) writing E in place of the potential difference $\varphi^r - \varphi^l$:

$$-FE = \mu_{\mathrm{Ag}}^{\mathrm{Ag}} - \mu_{\mathrm{Ag}^+}^{a} - \frac{1}{2}\mu_{\mathrm{Zn}}^{\mathrm{Zn}} + \frac{1}{2}\mu_{\mathrm{Zn}^{2+}}^{z} \tag{9.137}$$

Let us write the chemical potentials for the case when $\mathrm{AgNO_3}$ is the source of Ag^+ ions and $\mathrm{Zn(NO_3)_2}$ is the source of Zn^{2+} ions. Using the relation between the chemical potential of the electrolytes and the constituting ions, we can write:

$$\mu_{\mathrm{Ag}^+}^{a} = \mu_{\mathrm{AgNO_3}}^{a} - \mu_{\mathrm{NO_3^-}}^{a}, \tag{9.138}$$

$$1/2\mu_{\mathrm{Zn}^{2+}}^{z} = 1/2\mu_{\mathrm{Zn(NO_3)_2}}^{z} - \mu_{\mathrm{NO_3^-}}^{a}. \tag{9.139}$$

Upon substitution into the equation describing the cell potential, we get:

$$-FE = \mu_{\mathrm{Ag}}^{Ag} - \mu_{\mathrm{AgNO_3}}^{a} + \mu_{\mathrm{NO_3^-}}^{a} - 1/2\mu_{\mathrm{Zn}}^{Zn} + 1/2\mu_{\mathrm{Zn(NO_3)_2}}^{z} - \mu_{\mathrm{NO_3^-}}^{z} \tag{9.140}$$

Let us expand this equation by terms that cancel[14] and rewrite it by regrouping terms:

$$\begin{aligned}-FE = {} & \left(1/2\mu_{\mathrm{Zn}}^{Zn} - 1/2\mu_{\mathrm{Zn(NO_3)_2}}^{z} + RT\ln m_{\mathrm{NO_3^-}}^{z}\right), \\ & + \left(\mu_{\mathrm{NO_3^-}}^{z} - \mu_{\mathrm{NO_3^-}}^{a} + RT\ln\frac{m_{\mathrm{NO_3^-}}^{a}}{m_{\mathrm{NO_3^-}}^{z}}\right), \\ & - \left(\mu_{\mathrm{Ag}}^{Ag} - \mu_{\mathrm{AgNO_3}}^{a} + RT\ln m_{\mathrm{NO_3^-}}^{a}\right).\end{aligned} \tag{9.141}$$

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[14] To expand, let us add the term $RT\left(\ln m_{\mathrm{NO_3^-}}^{z} - \ln m_{\mathrm{NO_3^-}}^{a} + \ln\frac{m_{\mathrm{NO_3^-}}^{a}}{m_{\mathrm{NO_3^-}}^{z}}\right) = 0$.

Considering this result we can state that the first term on the right-hand side (in the first line) is only related to the zinc electrode (including its electrolyte solution), and the third term (in the third line) is only related to the silver electrode (including its electrolyte solution). The second term is only related to the two electrolyte solutions. Consequently, we could say that the first term is the potential of the zinc electrode, the third term is that of the silver electrode, while the middle term is the liquid junction potential. However, we should keep in mind that several other ions can also take part in the charge transfer in addition to the NO_3^- ion, thus writing and regrouping terms in the above equation is arbitrary. At the same time, we can also conclude that, if the concentration of the solutions *a* and *z* are identical, there is no potential difference at the boundary of the solutions. This can be approximated for example, by adding a large amount of KNO_3 into both solutions in addition to $AgNO_3$ and $Zn(NO_3)_2$ so that the composition of the two solutions is only slightly different. In this case, the liquid junction potential can be neglected compared to the cell potential. If necessary, we can calculate the diffusion potential by writing equations for the nonequilibrium transport of the ions.

If the nature of the cell enables to use a common solvent as ion conductor for both electrodes, it completely eliminates the liquid junction potential. Another method is the *salt bridge* that efficiently eliminates the junction potential. In the salt bridge, there is a high concentration electrolyte solution containing ions of nearly identical diffusion velocity (e.g., KCl or NH_4NO_3), which also diminishes the junction potential to a level that can be neglected. In the cell diagram of cells with negligible junction potential, the liquid–liquid phase boundary is symbolized by a double dotted bar (⋮⋮) instead of the usual single dotted bar (⋮). For reasons not discussed here, these are called as *cells without transference*.

Problems

1. At 18°C, water rises at a height of 5 cm in a glass capillary of 0.3 mm radius. The density of water at this temperature is $998.6\,\mathrm{kg\,m^{-3}}$. Based on the given data, calculate the equilibrium vapor pressure of water above a water drop with a radius of 10 nm. The vapor pressure over a plane water surface is 2.1 kPa. Suppose that the surface of water in the capillary is spherical with a zero contact angle at the glass wall.

Solution: First we shall determine the surface tension of water from (9.29):

$$\gamma = \frac{\rho g r h}{2} = 73.55\ \mathrm{N\,m^{-1}}.$$

The vapor pressure above the water droplet can be determined using the Kelvin equation (9.43)

$$P_r = P_0 e^{\frac{2\gamma M}{RTr\rho}} = 2.343\ \mathrm{kPa}.$$

Thus, the vapor pressure of a 10 nm radius water droplet is 11.6 % higher than the equilibrium pressure over a flat water surface.

2. An assumption of the Debye–Hückel theory is that the concentration distribution as a function of distance of the charged particles i around a chosen central ion is given as the first-power term of a power series of the function

$$c_i(r) = \bar{c}_i \exp\left[-\frac{ez_i\varphi(r)}{kT}\right].$$

Here, $\bar{c}_i$ is the average concentration of the charged particles i in the solution, e is the elementary charge, z_i is the charge number of the particles, $\varphi(r)$ is the electric potential at a distance r from the central ion, and k is the Boltzmann constant. To get the radial charge density around the central ion, the above function is summed for all charged particles in the solution.

Based on these considerations, argue why the theory works better for a solution of pure KCl than for that of pure $CaBr_2$.

Solution: Let us write the charge density $\rho(r)$ around the central ion as a power series expansion up to the second-order term in $\varphi(r)$ summing for all the ionic species, multiplied by the respective ionic charge z_iF:

$$\rho(r) = \sum_i \bar{c}_i z_i F - \sum_i \frac{\bar{c}_i F^2 z_i^2}{RT}\varphi(r) + \sum_i \frac{\bar{c}_i F^3 z_i^3}{R^2T^2}\varphi^2(r).$$

The first term of the above expression is the charge density at the position of the central ion (at $r = 0$). This is always zero, regardless of the nature of the electrolyte – based on the electroneutrality principle as expressed in (9.48). The second term is identical to the approximation used by Debye and Hückel. By inspecting the third term, we can state that for 1:1 electrolytes (and every higher term containing even powers of φ) it is also zero as odd powers of the charge number z_i sum to zero. This does not apply for electrolytes such as $CaBr_2$, where the absolute values of the charge numbers are not identical for the two ions. Thus, the truncation of the power series is a worse approximation than for 1:1 electrolytes.

Further Reading

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