Chapter 13
Potentials

13.1 Introduction

Potentials and potential gradients are important in battery systems. The difference in the potentials of the two electrodes determines the voltage of electrochemical cells, being larger when they are charged, and smaller when they are discharged. On the other hand, potential gradients are the driving forces for the transport of species within electrodes.

All potentials (potential energies) are relative, rather than having absolute values.

Since they cannot be measured on an absolute scale, it is desirable to establish useful references against which they can be measured. This is not the case in electrochemistry alone, but is true for all disciplines. For example, when dealing with the potential energies of electrons in solids, the solid-state physics community uses two different references, depending upon the problem being addressed. One is the potential energy of an electron at the bottom of the *valence band* in a solid, and the other is the so-called *vacuum level*, the energy of an isolated electron at an infinite distance from the solid in question. There is no universal relation between these two reference potentials, as the first is dependent upon the identity of the material involved, while the latter is not.

In electrochemical systems potential differences are measured electrically as voltages between some reference electrode system and an electrode of interest. The voltage that is measured is a measure of the difference in the electrochemical potentials of the electrons in the two electrodes.

The approaches to this matter are different between the conventional electrochemical community, whose interests have traditionally been mostly concerned with aqueous systems, and the solid-state electrochemical community, many of whose members have come from a solid-state materials background. This is despite

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the fact that some of the electrochemical systems of interest to the latter group also often include liquid electrolytes. It will be seen that one difference is the focus on the properties of neutral species in the solid-state electrochemical community, and upon ionic species in the aqueous electrochemical community.

The matter of the distribution of the different electrical and chemical potentials within electrochemical cells is often misunderstood. It will be seen that this often depends upon the experimental conditions.

13.2 Terminology

The term "potential" is often used for both a single potential and a potential difference. The standard practice in electrochemistry is to use certain reactions to provide reference electrode potentials against which other potentials can be measured. In aqueous systems a standard procedure is to use the reaction

$$2H^+ + 2e^- = H_2 \tag{13.1}$$

as the reference potential, and electrodes which involve this reaction are often called standard hydrogen electrodes (SHE), as discussed in Sect. 13A.9. On the same scale the potential of a lithium electrode at which the reaction is

$$Li^+ + e^- = Li \tag{13.2}$$

occurs at a potential that is -3.045 V with regard to the potential of the SHE. Further, a fluorine electrode operating at a pressure of 1 atm of fluorine gas and for which the reaction can be written as

$$2F^- - 2e^- = F_2 \tag{13.3}$$

has a potential of +2.87 V relative to the SHE at ambient temperature.

These potentials will be modified somewhat in other electrolytes because of differences in the *solvation energies*. If the solvation energy is not considered, the difference in electrode potential is always equal to that of the Nernst equation voltage for neutral species outside the electrolyte and one can always write

$$\Delta G_r^0 = -zFE \tag{13.4}$$

where ΔG_r^0 is the Gibbs free energy change of the relevant reaction, z is the number of electrons transferred in the reaction to which ΔG_r^0 refers, F is the Faraday constant, and E is the cell voltage, which is equal to the difference in the electrode potentials on the two sides.

13.3 Potential Scales

Another alternative way of looking at electrode potentials involves the use of a general potential scale based upon a particular reaction equilibrium. In molten salts, for example, it may be useful to use the chlorine or fluorine evolution electrode reaction as a reference against which other electrode potentials are measured.

In the subsequent chapters, reference will be made to chemical and electrostatic *macropotential differences* across a solid, as well as to gradients in those potentials within the solid. The chemical and electrostatic potentials are only two of a number of thermodynamic potentials. Since there is often a considerable amount of confusion relating to the different types of potentials inside solids and near their surfaces, this question will now be considered.

Understanding of the spatial distribution of the various thermodynamic potentials within a solid is important because of the relationship between the values of specific potentials and the local structure. Since many of the properties of solids are dependent upon the local structure, variations in properties with position are both possible and commonplace. Furthermore, under proper conditions, they can be controlled to advantage.

This relationship between local potentials, structure, and properties leads to two general types of application. Local values of some potentials may be experimentally observed by the proper use of appropriate probe techniques. This can lead to valuable information about the structure and can therefore be used as an analytical technique for a host of purposes. In addition, however, the situation can be reversed, and specific values of certain potentials can be imposed upon a material in order to change or control its structure and properties.

The total thermodynamic potential for a given species i at any point can arbitrarily be composed of several factors. Each of these factors has the dimensions of energy, as does the total thermodynamic potential. The total thermodynamic potential of a particular species has the properties of potential energy, and gradients in it produce forces tending to cause the superposition of a long range drift motion upon the local random motion of that species within the solid.

13.4 Electrical, Chemical, and Electrochemical Potentials in Metals

First, consider the matter of electrical potentials and the various related electrostatic potentials of individual species. In order to compare electrical potentials as well as the electrostatic energies of charged particles within and near different solids, it must be recognized that neither of these quantities has an absolute value. Therefore, it is desirable to establish some sort of reference level electric potential. For this purpose it is useful to compare the thermodynamic potential of a charged particle i within a solid phase with the potential of an isolated particle of the same chemical

composition in a vacuum at an infinite distance from all other charges. The value of the electrical potential at this charge-free infinity is defined arbitrarily as zero. This fixed reference value is called the *reference vacuum level*, E^{∞}. Unfortunately, the term *vacuum level* is also used in some of the current semiconductor literature for a different potential, as will be described later.

Consider a hypothetical experiment in which this charged particle is transferred from infinity to a position inside a solid. In the absence of any other potential gradients, the work that would be done can be divided into two parts. One of these is due to the interaction of the particle with the other particles within the bulk solid phase. This will typically include electrostatic, polarization, and repulsive interactions, and thus is dependent upon the identity of the particle, as well as the constitution of the bulk solid. It represents the chemical binding energy of the species in the solid, and is called the *chemical potential* of particle i, μ_i.

The second part of the work involved in transferring the particle from infinity to the interior of the solid is purely electrostatic, and is thus $z_i q(\Phi - E^{\infty})$, where z_i is the charge number of the particle (and represents both the sign and the number of elementary charges carried), q is the magnitude of the elementary charge (the value of the charge of the proton), and Φ is the local value of the *electrostatic macropotential* within the solid, which is called the *inner potential*.

The total work involved in this hypothetical experiment is called *the electrochemical potential* of the particle of species i, η_i, within the solid, and since $E^{\infty} = 0$, can thus be written as

$$\eta_i = \mu_i + z_i q \Phi \tag{13.5}$$

If the interior of the solid can be considered to be compositionally homogeneous, it will thus have a uniform value of the inner potential Φ. However, the solid phase must have an exterior surface that separates it from its surroundings whether vacuum, gas, liquid, or another solid phase.

For simplicity, consider the case of an isolated solid phase surrounded by vacuum. Because of the structural discontinuity at the surface, there must be local redistributions of both particles and electrical charge compared to the configurational structure within the bulk solid. There can also be differences in the concentrations of intrinsic species between the surface and the interior, as well as adsorbed foreign species upon the surface.

It is useful to utilize a simple model in which the solid is divided into two parts, a uniform interior and a separate surface region. The latter is sometimes called the *selvedge*, the term used for the edge region of a piece of cloth, which is often woven differently from the interior to prevent it from unraveling. The selvedge thus contains all of the various local redistributions and compositional effects, which can be described as producing an electrical double layer. In addition, this surface region contains all the excess charge if the solid has a net electrostatic charge different from E^{∞}.

Therefore, the value of the inner potential Φ can be divided into two terms, one called the *surface potential* X, which is related to the dipolar effects of the electrical

double layer in the selvedge. The second is known as the *outer potential* Ψ, and is the net externally measurable electrostatic potential of the solid.

The value of outer potential Ψ is dependent upon the amount of excess charge Q and the dimensions of the solid. For the case of a sphere of radius a,

$$\Psi = Q/a \tag{13.6}$$

The surface potential can be interpreted in terms of a simple model consisting of a uniform distribution of dipoles of moment M perpendicular to the surface with a concentration of N per cm^2 within the selvedge. If the positively charged ends of the dipoles are on the outside,

$$X = -4\pi NM \tag{13.7}$$

The relationship between these potentials for the case of two chemically identical solids with different amounts of excess charge, and thus different values of the outer potential, is shown in Fig. 13.1.

Changes in the charge on a solid body are actually accomplished by the transfer of charged particles, e.g., electrons, so that the composition is actually slightly changed when the net charge is varied. However, this involves such minor changes in the concentrations of the particles present in the solid that they can be neglected.

Now consider the question of the *energies* (also sometimes called *potentials*) of charged species. As mentioned already, the electrostatic part of the total potential energy of a particle i of charge $z_i q$ inside a solid with an inner potential Φ is $z_i\, q\Phi$. In

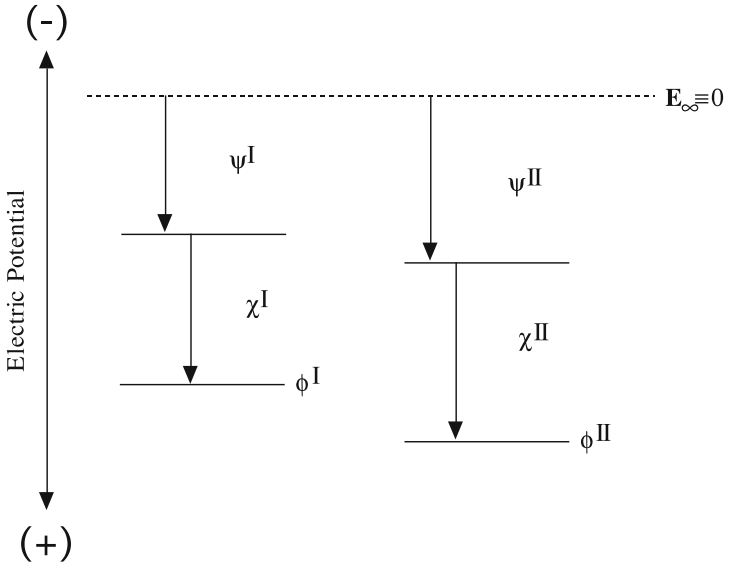

Fig. 13.1 Relationship between potentials related to two chemically identical solids with different values of outer potential

the case of electrons, $z_i = -1$. Thus this part of the total potential energy of an electron has an absolute magnitude that is greater and more positive the lower the value of Φ, since Φ is negative relative to the zero reference E^{∞},

Therefore, the total energy of an electron within a solid is its electrochemical potential $\mu_{e'}$, which has two components. One is related to the fact that the electron is within the solid and has the characteristics of a *chemical binding energy*, and the other is *purely electrostatic*. Thus

$$n_{e^-} = \mu_{e^-} + z_{e^-} q\Phi \tag{13.8}$$

and

$$\eta_{e^-} = \mu_{e^-} + \mathrm{RTln}a_{e^-} + z_{e^-} q(\Psi + X) \tag{13.9}$$

These energy relations for a single electron in the interior of a metal are shown in Fig. 13.2. Note that the value of the chemical potential for the electron is also negative.

To reinforce the understanding of these matters, a hypothetical experiment can be considered in which a single electron exists between two parallel plates of the same metal which are maintained in a vacuum, but are connected to the opposite terminals of a battery. This is illustrated in Fig. 13.3, in which the right-hand plate is connected to the positive pole, and the left-hand plate to the negative pole of the battery.

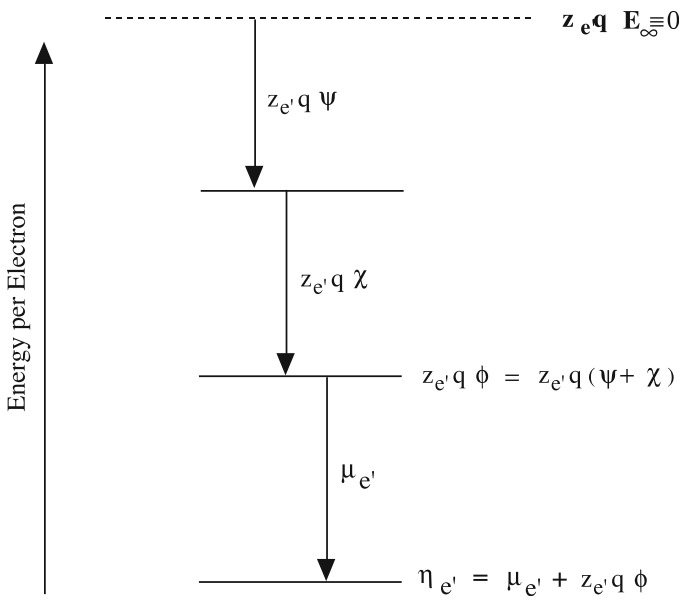

Fig. 13.2 Energy relations for a single electron in a metal

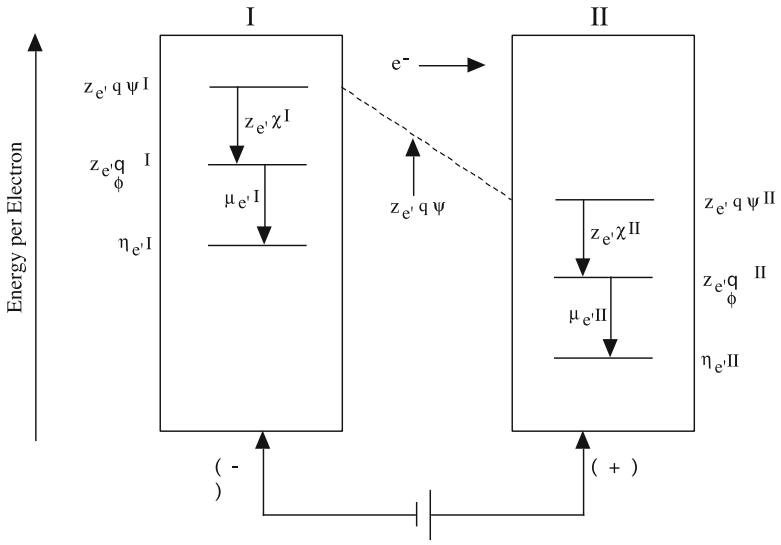

Fig. 13.3 Relationship between the potentials in two identical materials connected to the terminals of a battery

There will be a force acting upon the electron that is proportional to the negative value of the gradient in its potential energy in the vacuum $z_{e-}q\ d\Psi/dx$. This will cause it to accelerate from left to right. This is consistent with our expectation from general electrostatics that a negatively charged particle will be attracted to a positively charged electrode.

It can be seen from this example that the values of $z_i\ q\Psi$, μ_i and η_i all change as the externally measurable electrostatic potential of the solid Ψ is varied. However, if the chemical constitution is not altered, the values of X and μ_i remain the same, so that the relative values of $z_i\ q\Psi$, $z_i\ q\Phi$ *and* η_i do not change.

It will be seen later that the quantity Ψ can be varied externally, as in the above example, and also experimentally measured. It has therefore been found useful to define another quantity, the *real potential* α_i, which is independent of the value of Ψ. This is given as

$$a_i = \mu_i + z_i qX \tag{13.10}$$

For the case of an uncharged solid, where $\Psi = 0$, $\alpha_i = \mu_i$ and α_i, which generally has a negative value, is the work done in transferring a particle of species i from infinity to the interior of the uncharged solid.

The real potential of an electron $\alpha_{e'}$ thus has the same magnitude, but opposite sign, as the *electronic work function* $W_{e'}$, which is defined as the Gibbs free energy necessary to extract an electron from an uncharged solid into an exterior vacuum (at infinite distance). That is,

$$\alpha_{e^-} = W_{e^-} \tag{13.11}$$

The *binding energy* or chemical potential of species i can be written as

$$\mu_i = \mu_i^0 + \mathrm{RTln}a_i \tag{13.12}$$

where μ_i^0 is the chemical potential in some standard state. In the case of electrons in a metal, $\mu_{e^-}^0$ is chosen as the chemical potential of an electron in the chemically pure metal. The activity of the electron in the pure metal is also defined as unity, so that in this case

$$\mu_{e^-} = \mu_{e^-}^0 \tag{13.13}$$

The activity of any species i is related to its concentration $[i]$ by

$$a_i = \gamma_i[i] \tag{13.14}$$

where γ_i is the activity coefficient, expressed in appropriate units. Thus both the chemical potential μ_i and electrochemical potential η_i are composition-dependent.

In metals the concentration of electrons is typically very high, so that minor changes in composition due to impurities or doping produce negligible effects upon μ_{e-} and η_{e-}. However, this factor should be taken into consideration in more heavily alloyed metals as well as in non-metals. The two contributions to μ_i, and thus to η_i are shown in Fig. 13.4.

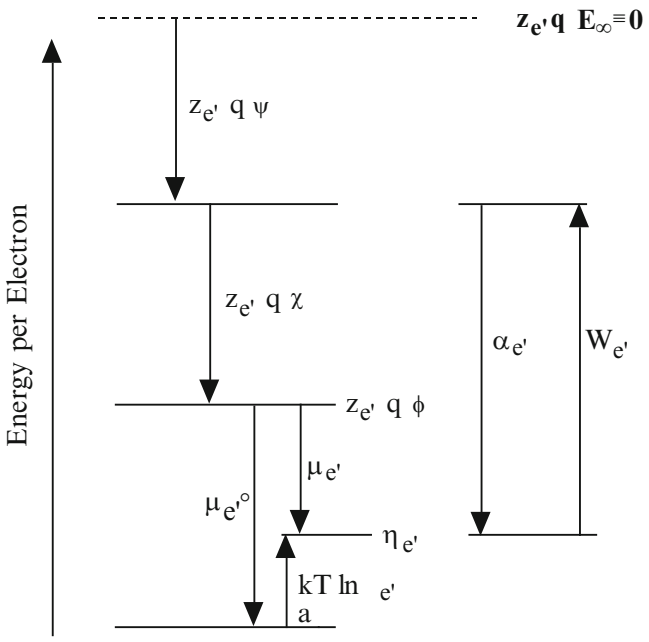

Fig. 13.4 The contributions to the chemical potential and the electrochemical potential

Table 13.1 Values of the electronic work function measured on polycrystals

Metal	Work function/eV
Ag	4.33
Ba	2.39
Be	3.92
Ca	2.71
Co	4.41
Cs	1.87
Fe	4.48
K	2.26
Li	2.28
Mg	3.67
Mo	4.20
Na	2.28
Ni	4.61
Rb	2.16
Ta	4.19
U	3.27
W	4.49
Zn	4.28

Table 13.2 Crystallographic orientation dependence of the work function: single crystals

Metal	Normal to Surface	Work Function/eV
Cu	111	4.39
Cu	100	5.64
Ag	111	4.75
Ag	100	4.81
W	111	4.39
W	112	4.69
W	001	4.56
W	110	4.68

Because the real potential and the work function include the term $z_{e-}qX$ that relates to the electrical double layer effects in the selvedge, these values are dependent upon the details of the structure in that region. Experiments have shown that this includes both the crystal face from which electrons are emitted and the presence of any impurities upon the surface. Some experimental values are given in Table 13.1 for polycrystalline metals. Table 13.2 shows the variation with crystal face on single crystals of several metals.

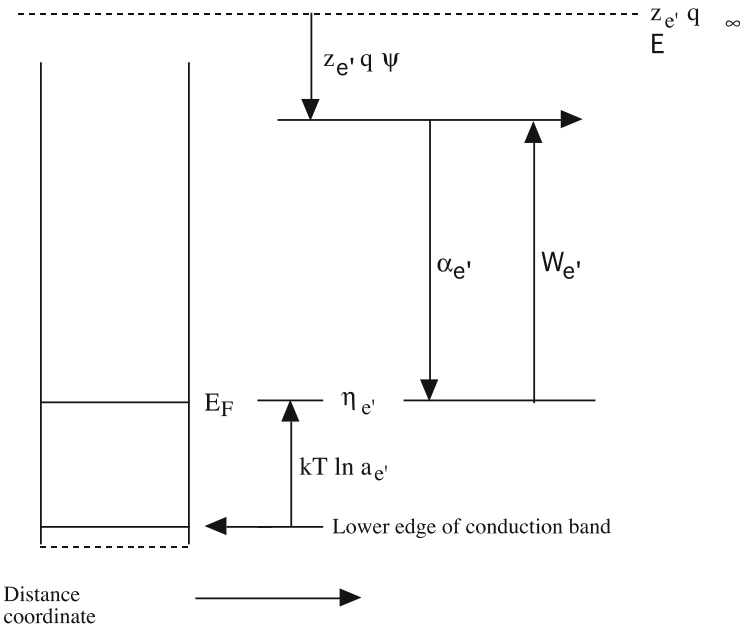

Fig. 13.5 Simple Band model of a metal

13.5 Relation to the Band Model of Electrons in Solids

A combination of knowledge about the variation of the density of energy states available for electron occupation with energy and the state occupation probability, which is expressed in terms of the Fermi-Dirac relation, provides information about the distribution of the electrons within a solid among their allowed energy states. This type of information is often displayed in simplified form by use of an *energy band model*, in which the energy per electron is plotted versus distance. An example of a simple band model of a metal is shown in Fig. 13.5. This figure also shows the relationship to the various thermodynamic potentials discussed here.

13.6 Potentials in Semiconductors

While the discussion thus far has centered upon metals, similar conclusions are found for semiconductors. In (undoped) intrinsic semiconductors, $\mu_{e-} = \mu_{e-}{}^{0}$ and the electrochemical potential is the same as the *Fermi level* E_F The Fermi level is midway between the electron energies at the top of the valence band E_V and the bottom of the conduction band E_C, regardless of the temperature. This situation is shown in Fig. 13.6.

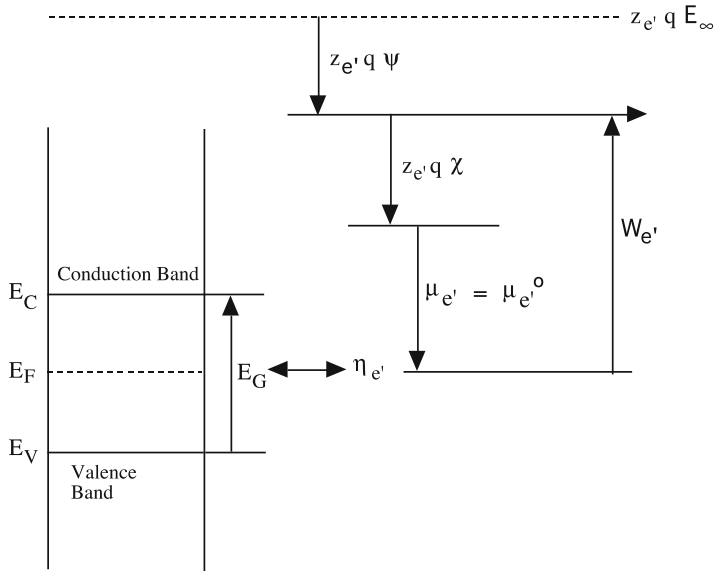

Fig. 13.6 Relation between thermodynamic potentials and potentials commonly used in the energy band model of an intrinsic semiconductor. E_G is the band gap (E_C–E_V). The potential of the Fermi level E_F is equal to the electrochemical potential of the electrons, η_{e-}

An important difference between metals and semiconductors, however, is that the electrostatic contribution to the total energy of an electron $z_{e-}q\Phi$ is generally not the same throughout the solid in semiconductors. It often increases or decreases significantly near the surface, or at locations where the chemical composition varies, such as at *p-n junctions*.

What if the semiconductor is doped with an *altervalent*, or *aliovalent*, species, an atom that carries a different amount of electrical charge from those that are normally present. The *electroneutrality requirement* causes the ratio of conduction electrons to holes to change to compensate for the charge of this *foreign species*, or *dopant*. As an example, if *donors* are present the concentration of itinerant conduction band electrons is increased. The activity of the electrons is thus greater in such an *extrinsic* semiconductor than in the corresponding *intrinsic* (undoped) material. This raises the values of kT ln a_{e-}, thus reducing μ_{e-} (which is negative), and raising η_{e-}. In semiconductor band model language this raises E_F toward E_C. This also, of course, decreases the work function W_{e-} since one can assume that X is not changed.

13.7 Interactions Between Different Materials

Many applications of these concepts involve interactions between the various potentials and energies that have been discussed here. In order to understand such matters a simple case will be considered.

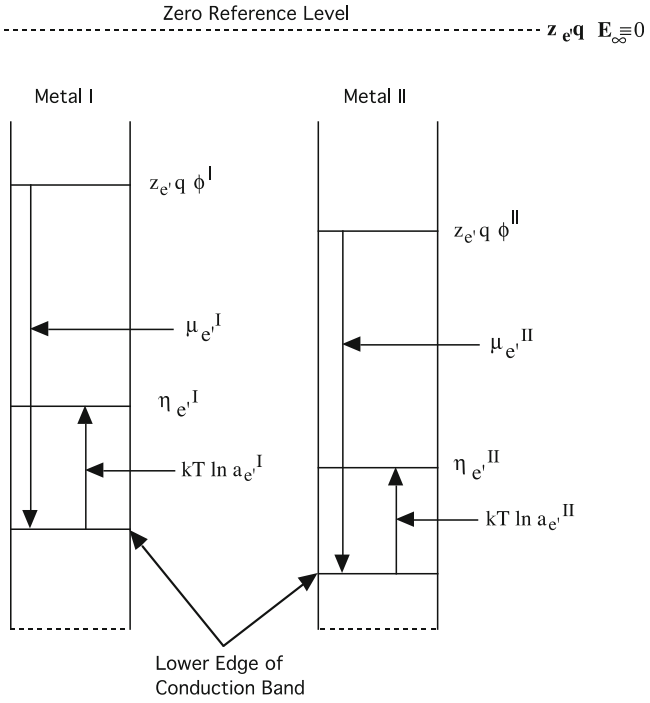

Fig. 13.7 Potentials of two chemically different metals separated by a vacuum, and not in equilibrium with each other. The relative positions of the Fermi levels (electrochemical potentials) is arbitrary, depending upon prior history

Consider two chemically different metals. If they are physically separated and not in equilibrium with each other, their potentials can be portrayed as illustrated in Fig. 13.7.

13.8 Junctions Between Two Metals

If these two metals are brought into contact, so that thermal equilibrium can be established between them, electrons will flow from one to the other until the total energy per electron is the same in both. This means that after equilibrium is attained, $\mu_{e'}^{I}$ must be equal to $\mu_{e'}^{II}$, or in band model language, $E_F^I = E_F^{II}$. The question is how this is achieved. The values of $\mu_{e'}^{\infty I}$ and $\mu_{e'}^{\infty II}$ are chemically binding energies of electrons in the lowest levels of the respective conduction bands. These are thus fixed by the chemical compositions of the two metals. The values of $kT \ln a_e'$ are determined by the electron concentrations in the metals. Since these concentrations are typically very high in metals, the relatively small number of electrons that pass

from one metal to the other upon contact will make relatively small changes in the activities of the electrons. Thus this term will also not change significantly.

This means that the equilibration of the Fermi levels occurs primarily by that adjustment of the electrostatic energy term $z_{e'}q\Phi$ or $z_{e'}q(\Psi + X)$.

Since in each case $\mu_{e'} = \mu_{e'} + z_{e'}q\Phi$, upon equilibration of the $\mu_{e'}$ values (Fermi levels) a fixed value of the difference in the internal electrostatic potentials will be established, directly related to the difference in the chemical potentials of electrons in the two metals. That is

$$z_{e'}q\left(\Phi^{I} - \Phi^{II}\right) = \mu_{e'}^{II} - \mu_{e'}^{I} \tag{13.15}$$

The value of $z_{e'}q\left(\Phi^{I} - \Phi^{II}\right)$ is called the *Galvanic voltage*, or *Galvanic potential difference*, and is characteristic of the two metals in question. It cannot be measured, however, because it is not possible to separate the two contributions to the value of $\Delta\Phi$, the differences in the outer potential $\Delta\Psi$ and in the surface double layer potential ΔX. The transfer of only a relatively few electrons from one metal to the other is expected to modify the X values significantly. As a result, $\left(\Phi^{I} - \Phi^{II}\right)$ is not equal to $\left(\Psi^{I} - \Psi^{II}\right)$.

However, it is possible to measure experimentally $\left(\Psi^{I} - \Psi^{II}\right)$, since these are externally observable values. The energy difference $z_{e'}q\left(\Psi^{I} - \Psi^{II}\right)$ is called the *Volta potential difference*. It is also sometimes called the *contact potential*. The use of this latter term is unfortunate, for it actually relates to a difference in electric potential between two free surfaces that are *not* in physical contact with each other. The relations between the various potentials when two chemically different metals are brought into equilibrium are illustrated in Fig. 13.8.

It is seen that the Volta potential difference is equal to the difference in electron work functions

$$z_{e'}q\left(\Psi^{I} - \Psi^{II}\right) = W_{e'}^{I} - W_{e'}^{II} \tag{13.16}$$

or

$$z_{e'}q\left(\Psi^{I} - \Psi^{II}\right) = z_{e'}q\left[\left(\Psi^{I} - \mu^{I}\right) - \left(\Psi^{II} - \mu^{II}\right)\right] \tag{13.17}$$

13.9 Junctions Between Metals and Semiconductors

Similar considerations are important in the case of equilibration between a metal and a semiconductor. Again, the important feature is that the Fermi levels must be equal under equilibrium conditions. This will not be discussed here, however. The principles are the same as have been elucidated in the lasts few pages, and this topic is addressed in many other places in the literature.

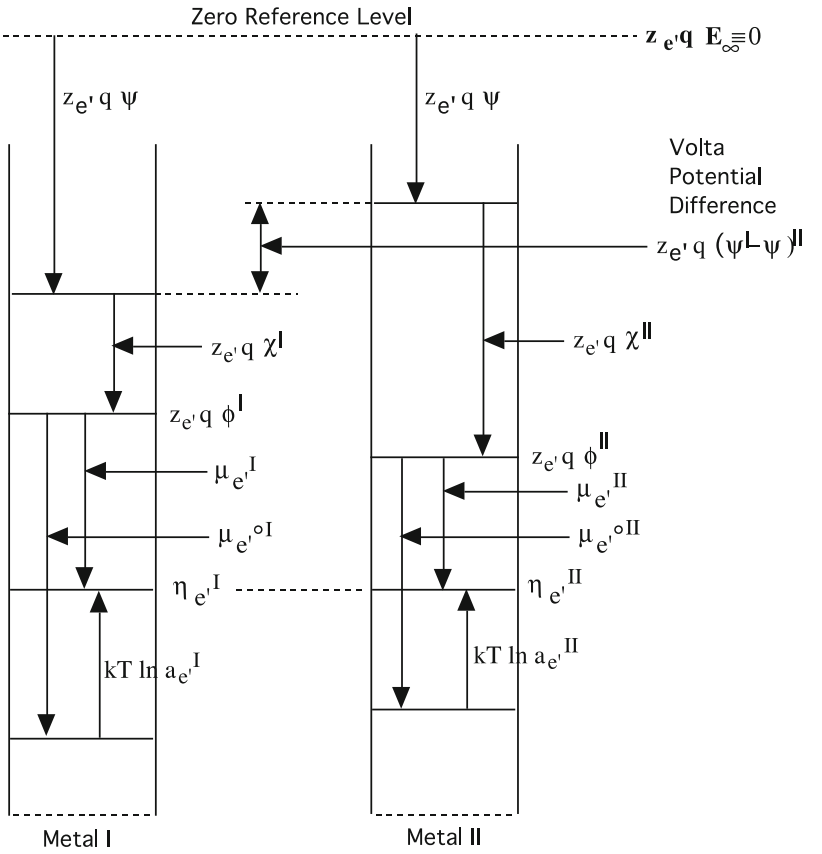

Fig. 13.8 Relationship between various potentials when two chemically different metals are brought into electronic equilibrium, so that their Fermi energies become equal. For purposes of illustration, the two metals are shown physically separated

13.10 Selective Equilibrium

This discussion has assumed that local equilibrium can be maintained within solids. In most practical cases this is reasonable at elevated temperatures. However, it is often not true for all species at lower temperatures. Indeed, it is often found that *selective equilibrium* occurs at low (e.g., ambient) temperatures. The concentrations of less-mobile species can be established during processing at high temperatures, and *frozen in* by cooling to lower temperatures, where they may not be in accord with low temperature equilibria. More mobile species can react to the influence of various forces and reach appropriate equilibria at lower temperatures. The frozen-in less-mobile species do, however, influence the local electrostatic charge balance and thus can play a major role in determining the concentrations of the more mobile defects, as all species participate in the charge balance.

13.11 Reference Electrodes

Reference electrodes play an important role in the study of many aspects of electrochemical systems. Experimental work reported in the literature can involve the use of different reference systems, and it is sometimes difficult to translate between measurements made with one from those made using another.

This situation is made even worse by the fact that reference electrodes that are used in solid-state electrochemical systems are based upon the potentials of electrically neutral chemical species that can be understood by the use of normal chemical thermodynamics. On the other hand, the general practice in aqueous electrochemistry is to use reference electrodes that involve the properties of ions, and the pH of the electrolyte becomes important in some cases, but not in others.

These matters are discussed in terms of the Gibbs Phase Rule, showing the difference between zero-degree-of-freedom (ZDF) electrodes, and those in which an additional parameter, such as the electrolyte pH, must be specified.

The interrelationship between these two types will be illustrated using potential-pH plots, or Pourbaix diagrams. Use of this *thinking tool* provides a simple understanding of the glass electrode systems that are used to measure the pH of electrolytes, for example.

It will also be shown that in electrodes with a mixed-conducting matrix and an internal ZDF reaction, the potential is determined by the internal chemical reaction, rather than the external electrochemical reaction.

13.12 Reference Electrodes in Nonaqueous Lithium Systems

Much of the current interest in batteries involves lithium-based systems with nonaqueous electrolytes. Thus attention should first be directed to the matter of reference electrodes in lithium systems.

13.12.1 Use of Elemental Lithium

Pure metallic lithium is typically used as a reference electrode in experimental activities to investigate the properties of individual electrode components, both those of interest as negative electrodes and those that act as positive electrodes, at ambient and near-ambient temperatures.

Because it is so extremely reactive, it is very difficult to maintain the surface of lithium free of oxide or other layers in even the cleanest gaseous and liquid environments. It is also important to realize that the organic electrolytes that are often used with lithium reference electrodes are typically not stable in the presence

of elemental lithium. Reaction product layers are commonly present on the surface of the lithium, and separate the lithium from the bulk electrolyte. This topic is discussed in Chaps. 14 and 16.

Therefore, the reaction that takes place at the electrochemical interface is typically not really known. It is also important that the identity of the electrolyte is not important, so long as it acts to transport Li ions, and not electrons. Despite these factors, elemental lithium is a widely used and highly reliable primary potential reference in a wide range of lithium-based electrochemical systems.

13.12.2 Use of Two-Phase Lithium Alloys

Some years ago there were substantial efforts to develop elevated temperature lithium-based batteries. Since they operated above its melting point, metallic lithium could not be used. One of the reference electrodes that was often employed was a two-phase mixture of aluminum and the phase LiAl.

In auxiliary experiments the potential of that electrode could be compared to that of pure lithium, which was considered to be the primary reference, and to which all potentials were referred. Because of the entropy change involved in the formation of LiAl by the reaction of lithium with aluminum, this difference is temperature-dependent. Experiments [1] from 375 °C to 600 °C showed that the potential of a two-phase mixture of lithium and LiAl is more positive than that of pure lithium, and that this potential difference ΔE can be expressed by the following relation:

$$\Delta E = 451 - 0.220T(K) \tag{13.18}$$

where ΔE is in millivolts.

This is shown in Fig. 13.9. The reason for the use of a two-phase mixture in this case, and why it is suitable, will become obvious from the discussion below.

Because of their high lithium activity, these 2-phase electrodes also can have reaction product layers on their surfaces in the presence of some electrolytes. As in the case of pure lithium reference electrodes, neither the presence of such layers nor the details of the interfacial reactions have any significant influence upon their potential.

13.13 Reference Electrodes in Elevated Temperature Oxide-Based Systems

Electrochemical systems with solid electrolytes are employed in high temperature fuel cells, oxygen sensors, and related applications. In such cases there are also two general types of reference electrodes used.

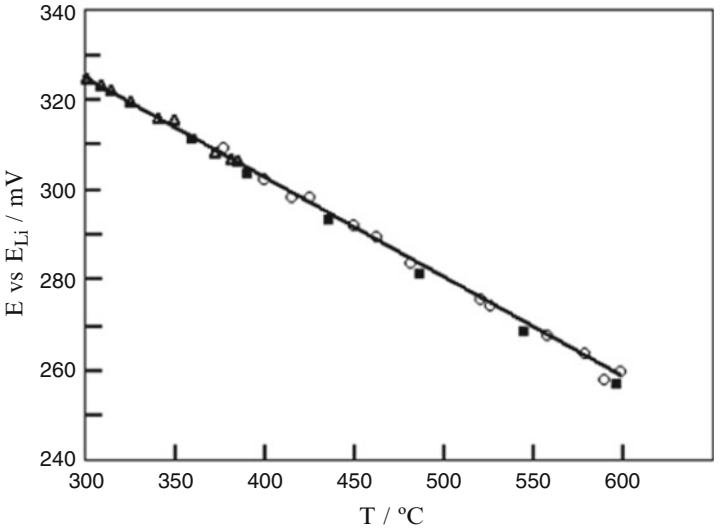

Fig. 13.9 Temperature dependence of the voltage between two-phase Li-LiAl electrode and pure lithium [1]

13.13.1 Gas Electrodes

An inert metal such as platinum in contact with pure oxygen gas is often used as a primary reference in these systems. Alternatively, air or some other gas with a known oxygen activity can be used. Gases with lower oxygen partial pressures will have less positive potentials. The potential difference between pure oxygen and a gas with a lower oxygen partial pressure is typically expressed in terms of the Nernst equation:

$$\Delta E = -\mathrm{RT}/zF\ln p(\mathrm{O}_2) \tag{13.19}$$

where $p(O_2)$ is the oxygen partial pressure of the gas in question. R is the gas constant, z the charge carried by the electrons involved in the assumed reaction (-4), and F the Faraday constant. Air is often used as a reference instead of pure oxygen. Using equation 2 it is possible to compare the potential of an air reference with that of pure oxygen. If it is assumed that air has an oxygen partial pressure of 0.79 atm, ΔE is equal to 6.09 mV at 1200 K, or 927 °C. Thus the air reference potential is 6.09 mV lower than that of pure oxygen at that particular temperature.

13.13.2 Polyphase Solid Reference Electrodes

An alternative to the use of a gas reference electrode is the use of solid electrodes. One example is a 2-phase mixture of Ni and NixO. If conditions are such that an equilibrium between Ni and its oxide can be attained, this combination will have a

fixed value of oxygen activity, equal to that in NixO at its Ni-rich compositional limit. Thus this two-phase mixture can be used as a secondary reference instead of pure oxygen. The oxygen activity and the potential relative to oxygen can be calculated if the Gibbs free energy of formation of NiO is known. The formation reaction is:

$$\mathrm{Ni} + {}^{1}\!/_{2}\mathrm{O_2} = \mathrm{NiO} \tag{13.20}$$

The potential of this materials combination is also less positive than that of pure oxygen. The difference can be calculated from the simple relation:

$$\Delta E = -\left(\Delta G_{r}^{0}/_{zF}\right) \tag{13.21}$$

where $\Delta G_{\mathrm{r}}{}^{0}$ is the Gibbs free energy change involved in the formation reaction. In this case, $z = -2$, as only one oxygen atom is involved. Because the Gibbs free energy contains an entropy term, the value of ΔE will be temperature-dependent. At 925 °C the value of $\Delta G_{\mathrm{r}}{}^{0}$ is −132.16 kJ/mol. Thus the potential of the two-phase Ni, NixO system is 0.685 V less positive than the potential of pure oxygen at that temperature.

One should note that, as was the case in the lithium systems, the potentials and potential differences in these oxide-related cases are independent of the details of the interfacial reactions. The identity of the electrolyte is not important, so long as it effectively transports oxygen ions and has a relatively low electronic conductivity.

The open circuit voltage of an H_2/O_2 fuel cell is also independent of the details of the interfacial electrochemical reactions as well as the identity and detailed properties of the electrolyte. Regardless of whether the electrolyte transports hydrogen ions or oxygen ions, the voltage is always determined by the thermodynamics of the reaction in which water is formed from hydrogen and oxygen. The electrolyte does not need to be solid; it can also be liquid, and either acidic or basic. It can also have a composite structure, such as when a liquid electrolyte is contained within a solid polymer, such as Nafion.

13.14 Relations Between Binary Potential Scales

One can determine the relation between different potential scales if they both refer to a common reference. As an example, consider the relation between a scale based upon the potential of pure lithium, or one based on sodium. Lithium and sodium both react with oxygen to form their respective oxides. If it can be assumed that those reactions were to occur with oxygen at unit activity (1 atm), the difference between the potentials of Li and Na and that of pure oxygen can be calculated from their respective oxide formation reactions.

At 25 °C, the Gibbs free energy of formation values [2] are −562.104 kJ/mol for Li_2O, and −379.090 kJ/mol for Na_2O. Using the relation between the voltages and these Gibbs free energies of formation, it is found that the potential of pure Li is 2.91 volts, and that of sodium 1.96 volts, negative of pure oxygen at 298 K. Those values are the ranges of stability of their respective oxides.

13.15 Potentials in the Ternary Lithium: Hydrogen: Oxygen System

This situation is modified in the case of a ternary system. As an example, if lithium is also present in addition to hydrogen and oxygen, the potential limits of the stability of water are shifted. To understand this, the isothermal Li-H-O ternary phase diagram must be considered.

There are several phases in this system in addition to the elements: Li_2O, LiH, LiOH, $LiOH \cdot H_2O$ and H_2O. The values of the standard Gibbs free energy of formation of these phases are given in Table 13.3.

The locations of these phases are shown in the isothermal ternary Gibbs triangle in Fig. 13.10. Assuming that all of these phases are at unit activity, the potentials of all of the 3-phase sub-triangles can be calculated with respect to each of the elements at the corners of the Gibbs triangle, from thermodynamic information, as discussed earlier. The values shown in that figure are voltages versus pure lithium.

The potential range in which water is stable is bounded by the potentials of two triangles, the three-phase triangles that have H_2O at their corners. It can be seen that their potentials with respect to lithium are 2.23 V and 3.46 V, and 1.23 V apart. The presence of the phases LiOH and $LiOH \cdot H_2O$ caused their potentials to both shift in the positive direction relative to that of Li.

It was pointed out that these calculations relate to a very basic aqueous electrolyte, with a pH value of 14. Conversion of the potential of the triangle that has both hydrogen and water present (2.23 V) to that at pH zero can be done by adding the product of 14 and 0.059 V, the change in potential per pH unit. The result is 3.05 V, which is the value found in electrochemical tables for the potential of the standard hydrogen electrode (SHE).

Table 13.3 Values of the standard Gibbs free energy of formation of phases in the Li-H-O system at 25 °C

Phase	ΔG_f^0/kJ/mol
Li_2O	−562.1
LiOH	−439.0
LiOH . H_2O	−689.5
H_2O	−237.1
LiH	−68.5

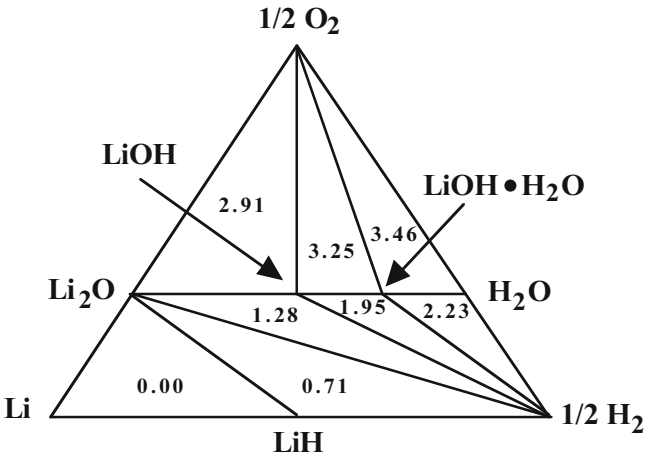

Fig. 13.10 Isothermal Gibbs triangle for the Li-H-O system at 25 °C. The numbers within the sub-triangles are the calculated values of their respective potentials vs. pure lithium

13.16 Lithium Cells in Aqueous Electrolytes

It was pointed out earlier that this relationship between these different potential scales means is that if a material has a potential that is between 2.09 and 3.32 V positive of pure lithium and does not dissolve or otherwise react chemically, it will be stable versus water containing LiOH. Thus one can use electrodes that react with lithium in aqueous electrolytes if Li ions are present in the electrolyte. Lithium-based electrochemical cells can operate in aqueous electrolytes, so long as both electrodes react with lithium and their potentials are within this range. This has been demonstrated experimentally [3–6]. Figure 13.11 shows cyclic voltammograms of VO2(*B*) in two different aqueous electrolytes, one containing Li ions, and the other not. Since the only appreciable reaction occurs when the Li ions are present in the water, it is obvious that the electrode reacts with Li, rather than hydrogen or oxygen.

If the lithium activity is too high in such an electrode, i.e., it has a potential less than 2.23 V versus pure lithium in water of pH 14, it will reduce water, forming H_2 and Li_2O.

13.17 Significance of Electrically Neutral Species

An important feature of the discussion of both nonaqueous and aqueous systems has been that the potentials and thermodynamics of electrically neutral species in the electrodes are important. Potentials and voltages are independent of the identity, or

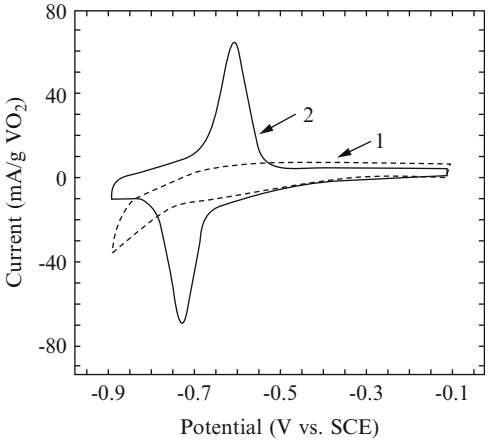

Fig. 13.11 Cyclic voltammograms of VO_2(B) in two different aqueous electrolytes. Scan 1 was made in one without lithium ions, whereas lithium ions were present in the electrolyte of scan 2 [6]

even the character, of the electrolyte. They are directly related to the normal chemical thermodynamic properties of the electrode materials. Reference electrodes are typically elements or thermodynamically-related polyphase mixtures that are electrically neutral.

13.18 Reference Electrodes in Aqueous Electrochemical Systems

The examples discussed above indicate that the reference electrode situation is quite straightforward and is consistent with conventional thermodynamics in nonaqueous systems. However, this is quite different when dealing with aqueous systems, which are within the domain of traditional electrochemistry.

If one looks into the older electrochemical literature, he finds statements such as that reference electrodes were considered somewhat of a "black art" for many years, with information primarily passed on by word of mouth or in brief notes among workers in electrochemistry [7]. A significant step forward was the book entitled *Reference Electrodes* that was edited by Ives and Janz in 1961 [8]. Another source that is often cited is the review article by Butler in 1970 that dealt with reference electrodes in aprotic organic solvents [7].

This general approach to the reference electrode matter is quite different from that described earlier in this chapter. One major difference is that a property of the electrolyte, the hydrogen ion concentration, as expressed in the form of the pH, is generally considered important. This is different from the examples above, in which the electrolyte plays no role other than acting as an ion-pass and electronically-impervious filter.

It is generally accepted in the electrochemical community that the primary reference electrode in aqueous systems should be the so-called standard hydrogen electrode (SHE). It is sometimes also called the "normal hydrogen electrode" (NHE). This electrode involves the use of H_2 gas at a pressure of 1 atmosphere flowing over an inert metallic contact material (generally platinum) in an electrolyte in which the activity of hydrogen ions (not atoms or molecules) is unity. Pains are generally taken to obtain a large gas/metal contact area that is not blocked by the presence of intermediate products.

Pure water dissociates into its component ions H^+ (or more properly, H_3O+, $H_5O_2{}^+$, or $H_9O_4{}^+$) and OH^- only to a small extent, with the degree of dissociation equal to about 1.4×10^{-9}. This means that there are more than 7×108 molecules of water for each H^+ or OH^- ion. As in the case of electrically charged defect pair equilibria in solids, the product of their concentrations is a constant. The ionic product of water, KW, which is defined as:

$$K_W = [H^+][OH^-] \tag{13.22}$$

has been found to be approximately 10^{-14}.

In solutions of acids or bases the relative concentrations of these two ionic species can vary over many orders of magnitude, mostly much less than unity. A logarithmic function, pH, was introduced as a measure of the concentration of one of them, the H^+ ions. Because of the ionic product equilibrium, the value of the other follows. The definition of pH is:

$$\text{pH} = -\log[H^+] \tag{13.23}$$

Thus in neutral water, the concentration of H^+ ions is equal to that of the OH^- ions, and both are 10^{-7} per cm^3, so that the value of the pH is 7.

The assumption is generally made that the activity of H^+ ions is the same as their concentration, $[H^+]$. Thus the value of the pH at the SHE reference electrode where the H^+ ion activity is unity must be 0. In experiments it is often not convenient to actually have an SHE, and the associated pH 0, in an experiment. A number of other types of electrodes are thus generally employed as secondary references. Some of these are listed in Table 13.4.

Table 13.4 Examples of reference electrodes used in aqueous systems

Electrode	Voltage vs. SHE at pH = 0/V
Hg/HgO—0.1 M NaOH	0.926
Hg/Hg_2Cl_2—0.5 M H_2SO_4	0.68
Hg/Hg_2SO_4—sat. K_2SO_4	0.64
Hg/Hg_2Cl_2—0.1 M KCl	0.3337
Hg/Hg_2Cl_2—1 M KCl	0.2801
Hg/Hg_2Cl_2	0.2681
Calomel—sat. KCl	0.2412
Calomel—sat. NaCl	0.2360
Ag/AgCl	0.2223

13.19 Historical Classification of Different Types of Electrodes in Aqueous Systems

In the electrochemical literature one often finds that electrodes used in aqueous systems have been historically classified into three main types, electrodes of the first kind, electrodes of the second kind, and redox, or oxidation-reduction, electrodes.

13.19.1 Electrodes of the First Kind

Some of the common electrodes are sometimes called *cationic electrodes*, although there are also anionic examples. In addition to an inert electrical lead, they commonly consist of a single metal phase that is in contact with an electrolyte containing its cations. Common examples include metallic Ag, Bi, Cd, Hg, or Ni.

Another example is the *reversible hydrogen electrode* (RHE), in which bubbles of gaseous hydrogen at 1 atm pressure flow over a catalytic, but electrochemically inert, metallic surface that is in contact with the electrolyte. The general construction is the same as that of an SHE electrode, except that the pH of the electrolyte is not fixed at 0.

The potential of an electrode M of the first kind is generally given as:

$$E = \text{Constant} + \left(\frac{RT}{zF}\right)\ln[a(M^+)/a(M)] \tag{13.24}$$

where z is the number of electrons per cation in the electrolyte. The constant is called the "standard electrode potential," E^0. If M is an element, its activity is defined as unity, or simply:

$$E = E^0 + \left(\frac{RT}{zF}\right)\ln a(M^+) \tag{13.25}$$

Thus the electrode potential is a function of a property of the electrolyte, the activity, or concentration, of the M^+ ions.

In the case of the reversible hydrogen electrode, $a(H_2)$ is the pressure of the hydrogen gas. If this is 1 atm, this value is unity. Thus the reversible hydrogen electrode potential can be approximately stated as:

$$E = E^0 - 2.303\left(\frac{RT}{F}\right)(\text{pH}) \tag{13.26}$$

If the pH is 0, this is equivalent to the SHE, so that the standard electrode potential E^0 is equal to zero. Thus the difference between the RHE and the SHE is

$$E_{\mathrm{RHE}} = E_{\mathrm{SHE}} = -2.303\left({}^{\mathrm{RT}}/_{F}\right)(\mathrm{pH}) \tag{13.27}$$

The value of the first term on the right-hand side is 0.059 V at 298 K. This difference (in volts) is then:

$$E_{\mathrm{RHE}} - E_{\mathrm{SHE}} = -0.059(\mathrm{pH}) \tag{13.28}$$

There are also analogous "anionic electrodes" of the first kind that contain an elemental gaseous species, such as Cl_2, that enters the electrolyte as anions. In that case, n will have a negative value.

13.19.2 Electrodes of the Second Kind

Electrodes of the second kind have two solid phases in contact with the (liquid) electrolyte, as well as an inert electrical lead. One of the phases is typically a metal, and the other is a *sparingly soluble salt*, or compound, of that metal. Examples of this type are (Ag, AgCl), (Hg, Hg_2Cl_2) (commonly called the *calomel electrode*), (Hg, Hg_2 SO_4), and (Hg/HgO).

These are sometimes called *anionic electrodes*, and generally also are in contact with, or contain, a solution that has a salt of the same anion as that in the second solid phase. As an example, the *standard calomel electrode* (SCE) generally contains solid Hg and solid Hg_2Cl_2 in contact with a saturated solution of KCl. Under these conditions the potential of this electrode is 0.242 V positive of the primary reference SHE potential.

The complication is that experiments are often not performed under the same conditions as those required for the reference electrode. The main issue is the electrolyte. If the experimental and the reference electrode electrolytes are different, they can be connected by use of an additional intermediate electrolyte. Traditionally, this involved the use of a *salt bridge* containing a liquid electrolyte, and care was taken that it did not introduce a significant liquid junction potential. Many modern electrodes use solid electrolytes, such as special ionically-conducting glasses, for this purpose.

If a reference electrode of this type is chemically isolated from the electrolyte, its constitution cannot change, and it will have an electric potential that is independent of the composition of the electrolyte being used in the experiment.

An electrode of the second kind containing solid Hg and solid HgO is often used in alkaline electrolytes, where it is in direct contact with the experimental electrolyte. Under these conditions it behaves differently from the electrodes that contain chloride and sulfate species. In this case the electrode potential is given by:

$$E = E^0 - \left({}^{\mathrm{RT}}/_{F}\right)\ln a(\mathrm{OH}^-) \tag{13.29}$$

or

$$E = E^0 + 2.303\left(^{RT}/_{F}\right)\log[H^+] \tag{13.30}$$

which is also

$$E = E^0 + 2.303\left(^{RT}/_{F}\right)(\text{pH}) \tag{13.31}$$

This means that the potential varies with the pH of the electrolyte in the same way as does the reversible hydrogen electrode (RHE), although they have different values of E^0.

Thus there is a difference between the electrolyte pH dependence of the potentials of these two types of electrodes and those discussed above with isolated chloride or sulfate species. This can be understood by use of *Potential-pH plots*, often called *Pourbaix diagrams*, due to their development by *M*. Pourbaix [9]. These figures are very useful *thinking tools*, as they not only show how the potentials of various reactions vary with the pH of the electrolyte but also indicate domains of stability of the different phases present. The general form of such a diagram is shown in Fig. 13.12.

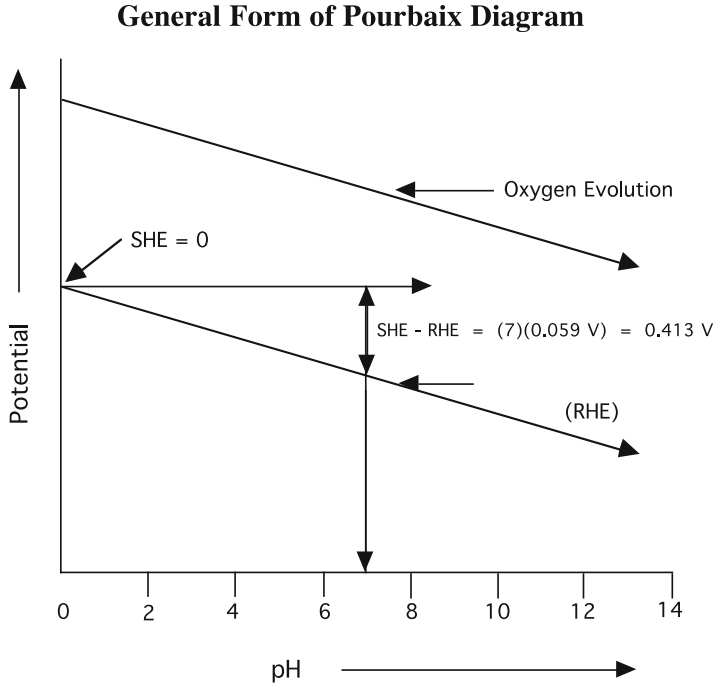

Fig. 13.12 General form of an E vs. pH, or Pourbaix, diagram. The influence of the pH on the potentials at which H_2 and O_2 have unit activity is shown. When the pH is zero, the potentials of the SHE and RHE electrodes are equal

It can be seen that the potential of the SHE, with the requirement that the activity of the H^+ ions is unity, so that it must be physically isolated, is independent of the pH of the electrolyte, whereas the potential of the RHE varies with the pH. As shown above, the potential of the Hg/HgO electrode is pH-dependent as well, whereas the potentials of the Ag/AgCl, Hg,Hg_2Cl_2, and Hg,H_2SO_4 electrodes are not.

The Gibbs Phase Rule can be used to help understand these things, as well as the difference between the treatment of reference electrodes in nonaqueous and aqueous electrochemical systems.

13.20 The Gibbs Phase Rule

The Gibbs Phase Rule [10, 11] plays an important role in the consideration of phase equilibria, and was discussed in Chap. 4. It will be briefly reviewed here, and its application to reference electrodes discussed.

The Gibbs phase rule can be written as:

$$F = C - P + 2 \tag{13.32}$$

where C is the number of components (e.g., elements or electrically neutral stable entities), P is the number of phases present. F is the number of degrees of freedom, or the number of thermodynamic parameters that must be specified in order to define the system and all of its associated electrical and chemical properties.

The eligible thermodynamic parameters are the temperature, the total pressure, and the chemical composition of each phase present. These are all intensive variables, so their values are independent of the amount of any of the materials present.

In binary systems $C = 2$, so that if the temperature and the overall pressure are held constant, and there are two phases present so that $P = 2$, the value of F is zero. This means that all of the intensive variables then have fixed values. These are thus *zero-degree-of-freedom (ZDF) conditions,* and electrodes will have a fixed potential, regardless of the state of charge, and the amounts of the various phases present.

On the other hand, if there is only one phase present in a binary system, $C = 2$, $P = 1$, and thus $F = 1$. This means that the properties are dependent upon the composition within that phase. An example of this is the variation of the potential of an insertion reaction electrode as its composition changes during charge or discharge in a battery.

Similar considerations apply to electrodes containing three components. In this case a useful thinking tool is the *isothermal Gibbs triangle*, or its approximation, the *ternary phase stability diagram*. The electrical potential is independent of the composition within sub-triangles where three phases are in equilibrium. On the other hand, it is composition-dependent in 2-phase and 1-phase regions.

These conclusions have been thoroughly demonstrated experimentally in the case of binary alloy systems [12], and also ternary systems involving the reaction of lithium with binary metal oxides [13–15].

13.21 Application of the Gibbs Phase Rule to Reference Electrodes

13.21.1 Nonaqueous Systems

Application of these principles in nonaqueous systems is straightforward. If the temperature and total pressure are kept constant and there is only one component, e.g., a pure metal, the electrical potential must have a fixed value. On the other hand, if a binary phase, such as a metal oxide, is used as a reference, there must also be another phase in equilibrium with it, so that both C and P equal 2, in order to have a fixed potential. This second phase is often the metal component of the oxide, but it does not have to be. Instead, it could be a gas such as oxygen or air. The important thing is that this second phase should not introduce an additional component, for it would then be a ternary, instead of binary, system.

As mentioned above, if there are three components, i.e., a ternary system, there must be three phases in equilibrium with each other in order for $F = 0$.

13.21.2 Aqueous Systems

Aqueous systems introduce an additional feature. As it is expected that water will equilibrate with the electrode at their interface, the presence of water introduces an additional phase. In addition, it has two components, hydrogen and oxygen. These all have to be included in the consideration of the Gibbs Phase Rule.

In the case of a hydrogen gas electrode in contact with water, there are two components, hydrogen and oxygen, and two phases, water and hydrogen gas. Assuming constant temperature and pressure, $F = 0$, and the system is thermodynamically fixed.

However, experiments show that the electrical potential of such an electrode depends upon the value of the pH. When the pH is zero, the electrode is equivalent to the standard hydrogen electrode, the SHE. However, at other values of electrolyte pH its potential varies, as it is then a reversible hydrogen electrode, an RHE. The electrical potential difference between these two situations was shown above to be:

$$E_{\mathrm{RHE}} - E_{\mathrm{SHE}} = -0.059(\,\mathrm{pH}) \tag{13.33}$$

volts.

This hardly looks like a thermodynamically fixed situation. However, it must be recognized that normal chemical thermodynamics deals with the equilibria of electrically neutral species, and the pH is a measure of the concentration of a charged species, H^+ (or H_3O^+ or $H_5O_2{}^+$).

The chemical potential of a neutral species M, $\mu(M)$, can, in principle, be decomposed into two parts, the chemical potential of its ions, and the chemical potential of its electrons. This can be written as:

$$\mu(\mathrm{M}) = \mu(\mathrm{M}^+) + \mu(\mathrm{e}^-) \tag{13.34}$$

Thus if the value of μ(M) is held constant, as is the case if the system is thermodynamically fixed, the values of the chemical potentials of the ions and the electrons can both vary, but their values will depend upon each other.

In the case of hydrogen:

$$\mu(\mathrm{H}_2) = 2\mu(\mathrm{H}^+) + 2\mu(\mathrm{e}^-) \tag{13.35}$$

which can be rearranged to give

$$\mu(\mathrm{e}^-) = {}^1\!/_2\mu(\mathrm{H}_2) - \mu(\mathrm{H}^+) \tag{13.36}$$

The chemical potential of the electrons, $\mu(e^-)$, is related to the electrically measured quantity E by:

$$\mu(\mathrm{e}^-) = zFE \tag{13.37}$$

Electrons carry a negative charge, so $z = -1$ in this case. Actually, as mentioned already, one always measures differences in E and thus of $\mu(e^-)$, between electrodes, for absolute values of electrical potentials cannot be measured. The activities of individual ionic species also cannot be measured experimentally [16].

The chemical potential of the hydrogen ions can be written in terms of their concentration as:

$$\mu(\mathrm{H}^+) = \mu(\mathrm{H}^+)^0 + \mathrm{RTln}a(\mathrm{H}^+) \tag{13.38}$$

where $\mu(H^+)^\circ$ is a constant. Substituting further,

$$\mu(\mathrm{H}^+) = \mu(\mathrm{H})^0 + 2.303\mathrm{RTlog}\,[\mathrm{H}^+] \tag{13.39}$$

or

$$\mu(\mathrm{H}^+) = \mu(\mathrm{H}^+)^0 - 2.303\mathrm{RT}\,(\mathrm{pH}) \tag{13.40}$$

This can then be put back into the equation for the chemical potential of the electrons, giving:

$$\mu(\mathrm{e}^-) = 1/2\mu(\mathrm{H}_2) - \mu(\mathrm{H}^+)^0 + 2.303(\mathrm{RT})\,(\mathrm{pH}) \tag{13.41}$$

so that the electrical quantity E is related to the pH by

$$E = \text{constant} - 2.303\left({}^{\mathrm{RT}}\!/_{F}\right)(\mathrm{pH}) \tag{13.42}$$

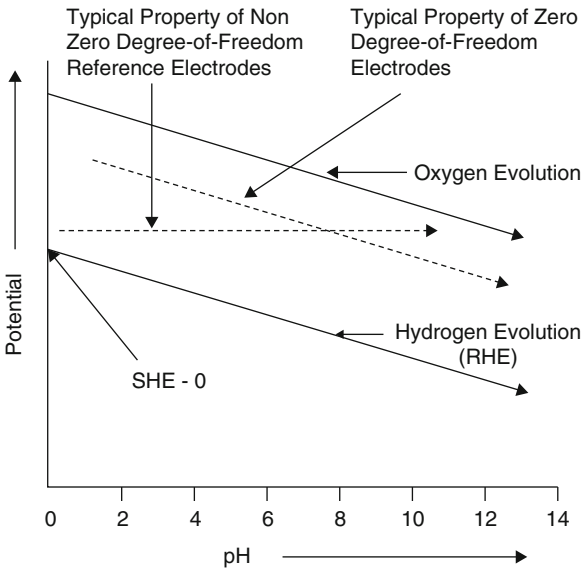

Fig. 13.13 General E vs. pH diagram showing the difference between ZDF and non-ZDF electrodes

where the value of the constant depends upon the identity of the neutral chemical species.

The result is that the potentials of all neutral species with zero degrees of freedom will lie along parallel lines with a slope of −0.059 V per pH unit in a plot of potential vs. pH, i.e., in *Pourbaix diagrams*. Their vertical locations will be determined by their potentials relative to the reversible hydrogen electrode.

Thus there is a clear differentiation between reference electrodes with zero degrees of freedom (ZDF electrodes) and those where this is not true that is readily seen in their dependence upon the pH of an aqueous electrolyte. This is indicated schematically in Fig. 13.13.

The result of this difference is that if one wants to compare electrodes in aqueous systems it is important to know whether they are ZDF electrodes or not, and if one of them is not, additional information, generally the pH of the electrolyte, is needed in order to specify the thermodynamic state.

13.22 Systems Used to Measure the pH of Aqueous Electrolytes

The difference in the potentials of ZDF electrodes and non-ZDF electrodes can be utilized to evaluate the pH of an electrolyte. An electrode to be used for this purpose will typically have a sealed inner compartment with a configuration that provides a

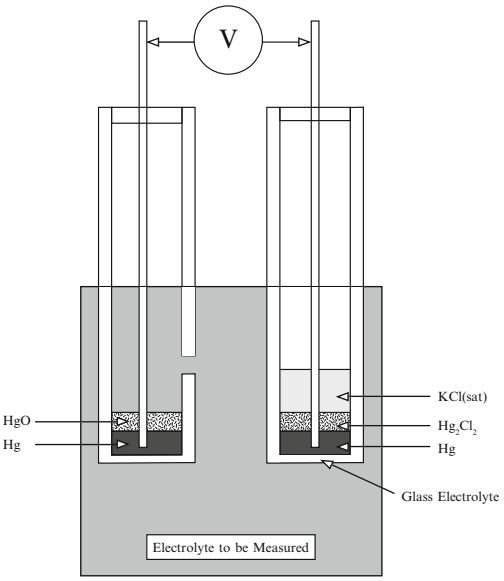

Fig. 13.14 Schematic drawing of the construction of a system that can be used to measure the pH of a liquid electrolyte. A chemically isolated calomel electrode is in contact with the electrolyte through an ionically-conducting glass membrane. A ZDF electrode (Hg/HgO) is in direct contact with the electrolyte

fixed potential relative to the SHE. This is surrounded by a solid electrolyte, generally a glass with a relatively high ionic conductivity, whose exterior is exposed to the electrolyte whose pH is to be evaluated. A second, ZDF, electrode is also present in the electrolyte, and the voltage between the two is measured.

The construction of such a pH-measuring system is shown schematically in Fig. 13.14.

13.23 Electrodes with Mixed-Conducting Matrices

As a final example, consider the use of a mixed-conducting matrix electrode containing a zero-degree-of-freedom (ZDF) reactant. Electrodes of this general class were first discussed some time ago [17, 18]. The microstructure contains a phase that has a high chemical diffusion coefficient for the atoms of the electroactive species and is also an electronic conductor. Although it is not necessary, such a phase will generally have a relatively small compositional width, so that it does not have an appreciable electrochemical capacity. In addition, the microstructure contains phases that can undergo a reconstitution chemical reaction. If the number of such phases is equal to the number of components within them, this reaction will have zero degrees of freedom, and thus a composition-independent potential.

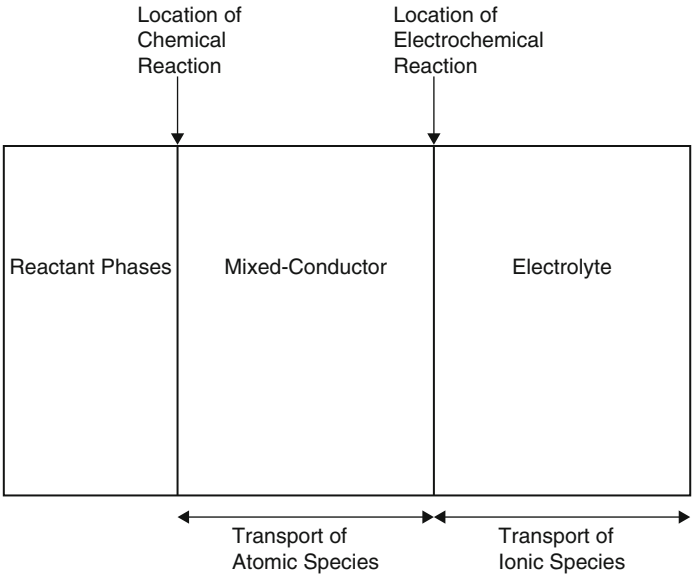

Fig. 13.15 Schematic one-dimensional model of a mixed-conductor matrix electrode. The potential is determined by the electrically neutral chemical reaction in the interior, whereas the electrochemical reaction takes place at the interface between the mixed-conductor and the electrolyte

The result is that this type of electrode has a potential that is determined by the internal ZDF chemical reaction, even though the electrochemical reaction takes place elsewhere, at the electrode/electrolyte interface on the outside of the mixed-conductor material. This is illustrated schematically in Fig.13.15.

Whereas the initial example of this principle involved a Li-Si constant potential reaction inside a Li-Sn alloy mixed conductor at elevated temperatures, it has been demonstrated [19, 20] that this concept also be used at ambient temperature.

Electrodes of this type might be useful as secondary references in cases where one or more of the reactive phases is not stable in contact with the electrolyte. So far as the electrical potential is concerned, the identity of the electrolyte and the details of the interfacial reaction are not important.

13.24 Closing Comments on Reference Electrodes

It is quite evident that the approach to reference electrodes is quite different in the nonaqueous and aqueous electrochemical communities. In the first case neutral chemical species are commonly used as references, and the details of the electrode/electrolyte reaction and the identity and concentrations of the species in the

electrolyte are not considered. Electrical potential differences can be readily calculated from standard chemical thermodynamic data.

In the aqueous electrochemical community potentials are generally discussed in terms of the reactions at the electrode/electrolyte interface and the atomic and ionic species present there. The thermodynamic state of the bulk solid is not generally considered. In some cases the electrode potential depends upon the pH of the electrolyte, whereas in others it does not.

These different approaches can be rationalized by consideration of the Gibbs Phase Rule. When the electrode has zero degrees of freedom (ZDF), all the intensive variables, including the electrical potential, are fixed. On the other hand, if this is not true an additional variable must be specified, and this is commonly the pH in aqueous electrochemistry.

The characteristic dependence of the potential of ZDF electrodes upon the pH has been explained in terms of the two components of the chemical potential of neutral species.

The difference between ZDF electrodes and non-ZDF electrodes can be used to measure the pH, independent of the composition of the electrolyte. In addition, the potential of electrodes with a ZDF internal reaction and a mixed-conducting matrix has nothing to do with phenomena at the electrode/electrolyte interface where the electrochemical reaction takes place.

13.25 Potentials of Chemical Reactions

13.25.1 Introduction

It has been known for some time that ions can be inserted or removed from insertion reaction materials by chemical, as well as electrochemical, means. This is one type of soft chemistry, or *Chemie douce*, as it was initially called in France. Much of the early attention to this possibility was focused upon materials based upon graphite, and reviews of this work can be found in a number of places, e.g., in [21].

An important step in the development of the use of chemical methods to either modify or synthesize advanced battery electrode materials was the work of Armand, who used naphthalene complexes in a polar solvent to insert either sodium or potassium, and n-butyl lithium dissolved in hexane to introduce lithium, into insertion reaction materials [22]. He inserted these alkali metals into layer structures consisting of transition metal salts, such as CrO_3, between graphene planes. The presence of these very covalent species gives these graphite-related materials a very positive potential, so that they are interesting as potential positive electrode reactants.

This is actually quite different from much of the other work on graphite materials in lithium cells, in which the potential is much lower, so that they are

interesting for use as negative electrode materials. Nevertheless, the principles are the same.

The use of *n*-butyl lithium, which is commercially available as a solution in hexane, to insert lithium into a material *M*, forming Li_xM and octane, C_8H_{18}, can be simply written as

$$x\mathrm{LiC_4H_9} + M = \mathrm{Li}_x\mathrm{M} + \frac{x}{2}\mathrm{C_8H_{18}} \tag{13.43}$$

In the sodium-naphthalene case the analogous reaction can be written as

$$x\mathrm{NaC_{10}H_8} + M = \mathrm{Na}_x\mathrm{M} + x\,\mathrm{C_{10}H_8} \tag{13.44}$$

As discussed earlier in this text, the standard Gibbs free energy change in a reaction involving electrically neutral species can be readily converted to an electrical potential difference, or voltage. The Gibbs free energy of formation of n-butyl lithium is about 96.5 kJ/mol, so that the potential that is attained upon its use to add lithium to electrode materials is about 1.0 V vs. elemental lithium. If the potential is greater than that value, it will tend to decompose, providing lithium to react with the material *M*. That is, Eq. (13.43) will tend to go to the right.

Thus it is possible to use such materials as reagents to chemically mimic electrochemical behavior, and thus screen or scan materials that might be considered as potential positive electrode reactants in lithium, or other alkali metal, cells. The amount of alkali metal uptake can be determined by assaying the resultant supernatant solution [23], and a rough indication of the kinetics of their reaction can be obtained by the observation of the temperature rise during the reaction [24]. In a number of cases an indication that a reaction has taken place is provided by a change in the color of the solution.

13.25.2 Relation Between Chemical Redox Equilibria and the Potential and Composition of Insertion Reaction Materials

This situation can be represented schematically, as shown in Fig. 13.16. If the potential of the solid is higher than the redox equilibrium potential, there will be a tendency for lithium to enter it from the adjacent liquid. On the other hand, if the potential of the solid is lower than the redox potential, there will be a tendency for the deletion of lithium, resulting in the potential increasing.

If two different reactants are used that have different redox potentials, the amount of lithium present in the solid can be changed between that characteristic of one of the redox potentials to that corresponding to the other. This is illustrated schematically in Fig. 13.17.

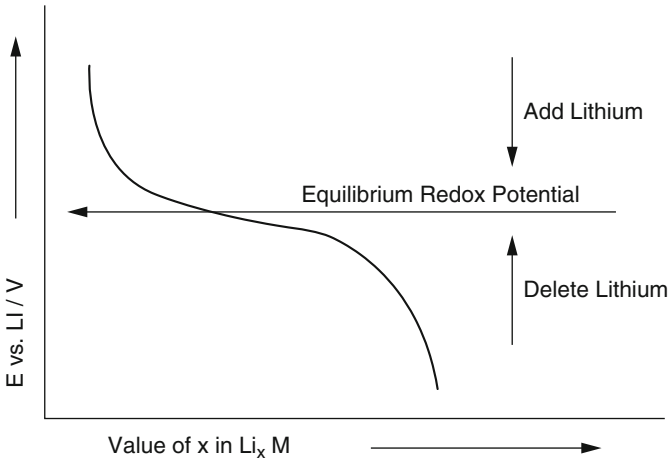

Fig. 13.16 Illustration of the relationship between the potential and the amount of lithium in Li_xM

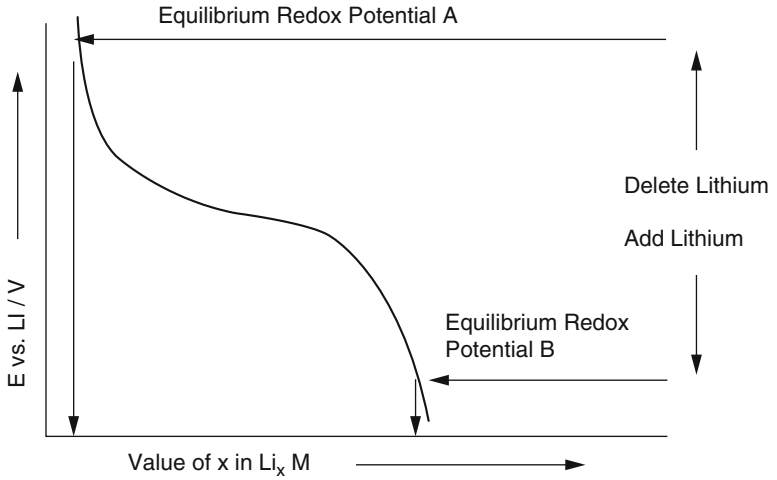

Fig. 13.17 Illustration of the effect of using two different reagents, one at a high potential that causes a reduction in the amount of lithium in the solid, and the other, at a lower potential that increases the lithium content

13.25.3 Other Examples

An example of a chemical reaction that can be used to delete lithium is the reaction of a material containing lithium with iodine to form *LiI*, which was discussed in Chap. 2. The formation and decomposition of *LiI* is potentially reversible. Its standard Gibbs free energy of formation is −269.67 kJ/mol at 25 °C, which converts to 2.8 V. This provides a good approximation for its equilibrium potential

in solutions. However, as in all of the cases discussed here, the actual potential may vary somewhat, depending upon the solvent, reagent concentration, and the amounts and identities of other species present.

This means that if iodine is available and a material Li_xM is present that has a potential lower than about 2.8 V there will be a tendency for iodine to extract lithium from it, forming Li*I*, and raising its potential. This can be represented by the equation

$$\frac{x}{2}I_2 + Li_yM = xLiI + Li_{(y-x)}M \tag{13.45}$$

As an example of the use of this method, solutions of iodine in acetonitrile, CH_3CN, were employed by Murphy et al. [25] to delete lithium from Li_xVS_2 and raise its potential. They also used *n*-butyl lithium to add lithium and reduce its potential [26].

In addition to n-butyl lithium and iodine, there are other oxidation or reducing agents that can be used. Bromine, in a solution of chloroform, $CHCl_3$, has been used to oxidize, and therefore reduce the lithium content of, a number of materials. The standard Gibbs free energy of formation of lithium bromide is −341.6 kJ/mol, so its equilibrium potential is quite high, about 3.54 V. Early examples of the use of bromine were the deletion of lithium from $LiVO_2$ [27], and from the more positive electrode material $LiCoO_2$ [28].

Other, more highly oxidizing, reagents were discussed by [29] and [30]. One example is the hexafluorophosphate salt NO_2PF_6, which can be dissolved in acetonitrile and has a potential about 4.45 V above that of lithium. Its reaction with a lithium transition metal dioxide can be written as

$$LiMO_2 + xNO_2PF_6 = Li_{1-x}MO_2 + xNO_2 + xLiPF_6 \tag{13.46}$$

A number of chemical reagents that have been used to modify mixed-conducting electrode materials in lithium systems are included in Table 13.5. Some of these chemical reagents are reversible, whereas others are not. More information about organolithium materials can be found in [31].

Table 13.5 Examples of lithium reaction materials and their approximate potentials vs. elemental lithium

Reagent	Solvent	E vs. Li Volts	Color, higher E	Color, lower E
MoF_6	Acetonitrile	4.75	None	None
NO_2PF_6	Acetonitrile	4.45	None	None
Bromine	Acetonitrile	3.54	Brown	None
DDQ	Acetonitrile	3.5	None	Red
Iodine	Acetonitrile	2.8	Purple	None
Benzophenone	Tetrahydrofuran	1.5	None	Blue
n-butyl lithium	Hexane	1.0	None	None
Benzophenone	Tetrahydrofuran	0.8	Blue	Purple
Naphthalene	Tetrahydrofuran	0.5	None	Green

Note: DDQ is 2,3-dichloro-4,5-dicyanobenzoquinone

13.25.4 Summary

There are a number of chemical equilibria that can act to influence the amount of inserted material; i.e., lithium, present in a mixed conductor in a manner analogous to the application of an electrochemical potential by the use of an electrochemical cell. Equilibria at low potentials are typically used to add lithium, and those with higher potentials are more commonly used to delete lithium from potential electrode materials.

13.26 Potential and Composition Distributions Within Components of Electrochemical Cells

13.26.1 Introduction

The electrostatic, chemical and electrochemical potentials inside condensed phases depend upon the nature and concentrations of the species that are present. These, in turn, vary with the local values of the relevant thermodynamic potentials, which are typically not uniform inside electrochemical cells.

A number of examples will be discussed in this chapter, including ionic conductors and mixed conductors between different types of non-blocking and selectively-blocking electrodes under the imposition of either electrical or chemical potential differences.

Under charge transport conditions the *transference numbers* of individual species vary with position if a gradient in thermodynamic potentials is present. This can be readily understood by use of *Defect Equilibrium Diagrams* as *thinking tools*.

These parameters can be experimentally evaluated by the use of proper sensors. One type measures the local value of the Fermi level of the electrons, and the other can be used to evaluate the local chemical potential or activity of neutral chemical species.

This is an important topic for several reasons. Local potentials, and their gradients, determine both the potentials and the kinetic behavior of electrodes in batteries. They also play critical roles in the properties of fuel cells.

13.26.2 Relevant Energy Quantities

The energy of species inside solids is the sum of their chemical and electrical energies. The chemical energy is expressed as the chemical potential, and for species i,

$$E_{\text{chem}} = \mu_i \tag{13.47}$$

The electrical energy is the product of the charge and the local value of the inner potential.

$$E_{\text{elect}} = z_i q \phi \tag{13.48}$$

The electrochemical potential η_i is the sum of the chemical and electrical energies

$$\eta_i = \mu_i + z_i q \phi \tag{13.49}$$

13.26.3 What Is Different About the Interior of Solids?

Chemical potentials outside of solids always are referenced to electrically neutral chemical species. But chemical species inside solids are typically electrically charged ions. In order to achieve internal charge balance, their charges must be balanced by the presence of either other charged ions or excess electrons or holes (a deficiency of electrons).

For equilibrium between an electrically neutral species M on the outside and the corresponding combination of an ionic species M^+ and an electron on the inside:

$$\mu_{\text{M}} = \mu_{\text{M}^+} + \mu_{\text{e}^-} \tag{13.50}$$

Each of these species has a corresponding electrochemical potential, the combination of chemical and electrostatic potentials, or potential energies

$$\eta_{\text{M}^+} = \mu_{\text{M}^+} + z_{\text{M}^+} q \phi \tag{13.51}$$

$$\eta_{\text{e}^-} = \mu_{\text{e}^-} + z_{\text{e}^-} q \phi \tag{13.52}$$

Here z is the charge number, q the electronic charge, and ϕ the local inner electrical potential. Since $Z_{\text{M}^+} = 1$ and $Z_{\text{e}^-} = -1$, if we add these equations the terms containing the inner potential cancel each other, giving

$$\eta_{\text{M}^+} + \eta_{\text{e}^-} = \mu_{\text{M}^+} + \mu_{\text{e}^-} \tag{13.53}$$

This can be simply rearranged to become

$$\mu_{\text{M}} = \eta_{\text{M}^+} + \mu_{\text{e}^-} \tag{13.54}$$

The external chemical potential of a neutral species M is equal to the sum of the electrochemical potentials of its two related internal species, M^+ and e^-.

The sum of the gradients of the electrochemical potentials of the charged species inside a solid can be observed as an externally measurable gradient in the chemical potential of the neutral species. In the case of a one-dimensional physical system with a distance parameter x this can be written as

$$\frac{d\mu_{\mathrm{M}}}{dx} = \frac{d\eta_{\mathrm{M}^+}}{dx} + \frac{d\eta_{\mathrm{e}^-}}{dx} \tag{13.55}$$

Gradients in their respective electrochemical potentials constitute the driving forces for the transport of species.

13.26.4 Relations Between Inside and Outside Quantities

Information about potentials inside solids is typically obtained by use of external measurements. In the case of electronic species, this involves equilibration of the internal Fermi level with the Fermi level of an external metal probe. In the case of chemical species it is necessary to use an electrochemical cell and to balance chemical force with an equivalent electrical force

$$\Delta\mu_i = -z_i q E \tag{13.56}$$

where $\Delta\mu_i$ is the difference in chemical potential between neutral chemical species, z_i is the charge number of the ionic species under consideration, q is the elementary charge, and E is the voltage across the electrochemical cell

13.26.5 Basic Flux Relations Inside Phases

The particle flux density of any species i, J_i, is the number of particles of that type that cross a transverse area of 1 cm^2 per second.

This can be expressed in terms of the concentration $[i]$ (particles/cm^3) and the macroscopic drift velocity v_i (cm/s).

$$J_i = [i] v_i \tag{13.57}$$

The general mobility of species i, B_i, is defined as the ratio of the drift velocity and the negative gradient in the electrochemical potential, which is the force causing that drift.

$$B_i = -v_i \Big/ \frac{d\eta_i}{dx} \tag{13.58}$$

Note that the general mobility B_i is different from the electrical mobility b_i, which is defined as the drift velocity of species i per unit internal electrical field

$$b_i = -v_i \Big/ \frac{d\phi}{dx} \tag{13.59}$$

Thus the particle flux density of any species i can be written as

$$J_i = -[i]B_i \frac{d\eta_i}{dx} \tag{13.60}$$

Introducing the general definition of the electrochemical potential

$$J_i = -[i]B_i \left[\frac{d\mu_i}{dx} + z_i q \frac{d\phi}{dx}\right] \tag{13.61}$$

13.26.6 Two Simple Limiting Cases

To understand these matters, two types of materials as simple limiting cases can be considered,

1. A metal, in which there is no internal electrical field, and therefore

$$J_i = -[i]B_i \left[\frac{d\mu_i}{dx}\right] \tag{13.62}$$

2. A chemically homogeneous material in which $d\mu_i/dx$ is zero, so that

$$J_i = -[i]B_i \left[\frac{d\phi}{dx}\right] \tag{13.63}$$

13.26.7 Three Configurations

As examples, three simple configurations will be explored.

1. A solid electrolyte in which the transport of ionic species is blocked by the electrodes.
2. A mixed conductor in which the transport of electronic species is blocked by the electrodes.
3. A composite structure with a mixed conductor in series with a solid electrolyte.

13.26.8 Variation of the Composition with Potential

As mentioned above, ionic and electronic species are present inside a solid, and their respective concentrations vary with the values of the relevant electrochemical potentials.

The chemical compositions of solids also depend upon the chemical potentials of the species present.

These features can be readily understood for simple cases, and as an example, the concentrations of both ionic and electronic defects will be calculated here as a function of the overall composition and the electrical potential for a simple binary phase MX. This is an approach that was pioneered by workers in Philips Laboratories [32–34]. It is useful to express the results in a *Defect Equilibrium Diagram* (*DED*). It will be seen that such a graphical presentation of these matters can act as a very useful *thinking tool*.

13.26.9 Calculation of the Concentrations of the Relevant Defects in a Binary Solid MX That Is Predominantly an Ionic Conductor

In a binary solid, four defects have to be considered: two electronic defects, electrons and holes, as well as two ionic defects, which might be interstitials and vacancies of one of the components.

Since there are four unknowns, there must be four relevant equations.

Two of these are mass action relations, one for the formation of electron–hole pairs

$$K_{\mathrm{e}} = [\mathrm{e}^{-}]\,[h^{o}] \tag{13.64}$$

in which the brackets indicate concentrations (number of particles/cm^3), and one for the formation of ionic defect pairs

$$K_i = [D_{\mathrm{M}^{\circ}}]\,[D_{\mathrm{X}'}] \tag{13.65}$$

The notation that is used here is a modification of that generally referred to as *Kröger-Vink notation*. Instead of the common practice of using a dot to indicate a positive relative charge, a degree sign is used in this text, for that is a symbol that is readily available in typewriters and computers. In addition the symbol D is used here as a general symbol for an ionic defect. $D_{\mathrm{M}^{\circ}}$ is an M-rich ionic defect, and $D_{\mathrm{X}'}$ is a defect whose presence makes the material more X-rich.

In addition to Eqs. (13.64) and (13.65), an expression is needed that relates to the overall chemical composition, and thus to the concentration of at least one of the ionic defects, in the phase *MX*. There are various ways in which this might be done. One is to assume that the *MX* is in equilibrium with its chemical environment, so that the chemical potentials of the species within it are the same as those in the environment. Consider the case in which it is assumed that the material is in equilibrium with a surrounding phase containing the species *X*.

The equilibrium between *X* species in the surrounding phase (assume that it is a gas and contains diatomic *X*2 molecules) and singly charged *X* or *M* defect species inside the *MX* can be written as

$$X_{(g)} = 1/2\, X_{2(g)} = D_{X'} + h^o \tag{13.66}$$

in which the X-rich defect species DX' could be either an interstitial X ion or a vacancy on the M lattice. Either one of these has a negative effective charge, and as mentioned above, it makes no difference which one is actually present in the material in this calculation. In either case, a positively charged electron hole would also have to be present in order to achieve charge balance.

An additional equation can be the law of mass action relation that corresponds to the incorporation of one of the chemical species, and its charge-balancing electronic species, into the nominally MX phase. An example is the X-incorporation relation

$$K_X = \frac{\left[D_{X'}\right]\left[h^o\right]}{(aX_2)^{1/2}} \tag{13.67}$$

It would have been possible to use a relation that involves M-rich defects instead. In that case, however, an electron would have to be present in order to maintain charge balance.

In addition to these law-of-mass-action type relations, there must also be an expression that reflects the requirement for overall electrostatic charge balance. This is sometimes called the *electroneutrality condition*. The number of negative charges introduced by the presence of the defects carrying negative effective charges must be balanced by the positive charge due to the presence of species carrying positive charges. This can be written as

$$\left[e'\right] + \left[D_{X'}\right] = \left[h^o\right] + \left[D_{M^o}\right] \tag{13.68}$$

Simultaneous solution of these four equations can be used to obtain expressions to use to evaluate the four defect concentrations.

Because of the composition dependence in the incorporation Eq. (13.20), the concentrations of all of the defects depend upon the composition of the phase, and thus upon the electrical potential.

To simplify matters it is useful to introduce a composition parameter F

$$F = K_X[a(X_2)]^{1/2} \tag{13.69}$$

By substitution into the electroneutrality condition, the concentrations of the various defects can then be calculated in terms of the values of the equilibrium constants and the composition parameter F.

$$\left[e'\right] = K_e\left[\frac{K_i + F}{F(K_e + F)}\right]^{1/2} \tag{13.70}$$

$$[h^{o}] = \left[\frac{F(K_{\mathrm{e}} + F)}{K_i + F}\right]^{1/2} \tag{13.71}$$

$$\left[D_{X'}\right] = \left[\frac{F(K_i + F)}{K_{\mathrm{e}} + F}\right]^{1/2} \tag{13.72}$$

$$[D_{M^{o}}] = K_i \left[\frac{K_{\mathrm{e}} + F}{F(K_i + F)}\right]^{1/2} \tag{13.73}$$

These relations specify the concentrations of the four pertinent defects as functions of the overall composition of the *MX* phase, as expressed in terms of the value of the composition parameter F. They will each vary with temperature, as the values of the constants are temperature-dependent.

13.27 Defect Equilibrium Diagrams

The form of these relations is illustrated in the *Defect Equilibrium Diagram* shown in Fig. 13.18. The concentrations of the four types of defects are plotted on a logarithmic scale against the logarithm of the parameter F. It has been assumed in this example that the material MX is primarily an ionic conductor. This will be the case if the Gibbs free energy necessary to form the ionic defect pair is less than that necessary to form the electronic defect pair. Thus the value of K_i is significantly greater than the value of K_{e}. The constants used in this illustration are: $K_{\mathrm{e}} = 10^{10}$, $\mathrm{K}_i = 10^{40}$, and $\mathrm{K}_X = 10^{20}$. It can be seen that there are three general regions of behavior, labeled as Region I at low values of F when the material will be relatively M-rich, Region II at intermediate values of F, and Region III at high values of F, when the material will be relatively X-rich.

13.27.1 Approximations Relevant in Specific Ranges of Composition or Activity

It is often useful to work with approximations to the general relations that are applicable over these three different ranges of composition or activity. As mentioned above, the important criterion for the determination of useful approximations is the value of the composition parameter F. In Region *I* the X activity is very small and the M activity correspondingly large, and F is very small, less than both K_{e} and K_i. In the central Region II, the value of F is between K_i and K_{e}. Likewise, when the value of the X activity is large and the M activity small, F will be larger than both K_{e} and K_i.

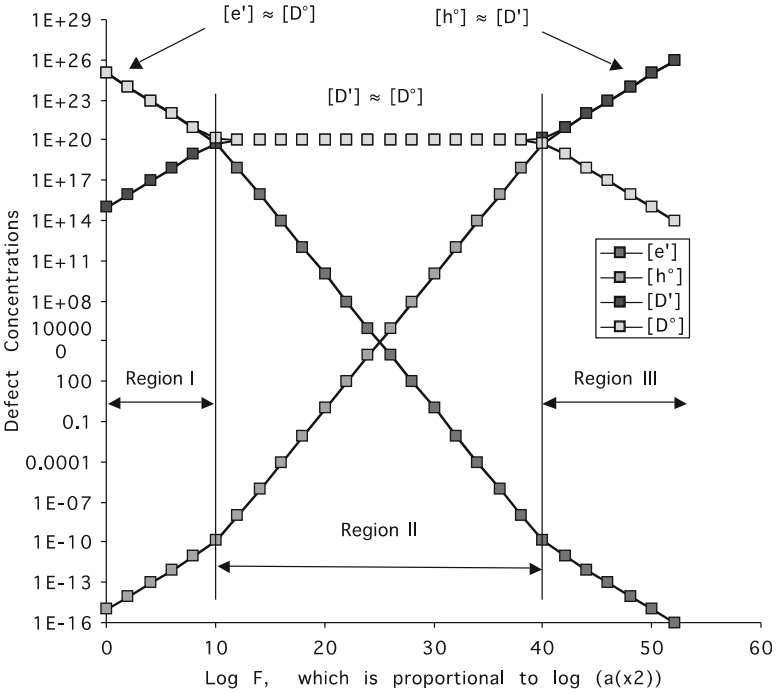

Fig. 13.18 Defect Equilibrium Diagram showing concentrations of defect species inside solid MX as functions of the composition parameter F

At very low values of X activity F will be smaller than both K_e and K_i, giving the following approximations for the defect concentrations.

$$\left[e'\right] = K_e\left(\frac{K_i}{FK_e}\right)^{1/2} \tag{13.74}$$

$$[h^o] = \left(\frac{FK_e}{K_i}\right)^{1/2} \tag{13.75}$$

$$\left[D_{X'}\right] = \left(\frac{FK_i}{K_e}\right)^{1/2} \tag{13.76}$$

$$[D_{M^o}] = K_i\left(\frac{K_e}{FK_i}\right)^{1/2} \tag{13.77}$$

Likewise, at intermediate values of X activity $K_i > F > K_e$, and the defect concentrations can be approximated by:

$$\left[e'\right] = \frac{K_e K_i^{1/2}}{F} \tag{13.78}$$

$$[h^o] = F K_i^{-1/2} \tag{13.79}$$

$$\left[D_{X'}\right] = K_i^{1/2} \tag{13.80}$$

$$[D^o] = K_i^{1/2} \tag{13.81}$$

When the X activity is very large, F becomes much greater than both K_e and K_i. The defect concentrations can be approximated by:

$$\left[e'\right] = K_e F^{-1/2} \tag{13.82}$$

$$[h^o] = F^{1/2} \tag{13.83}$$

$$\left[D_{X'}\right] = F^{1/2} \tag{13.84}$$

$$[D_{M^o}] = K_i F^{-1/2} \tag{13.85}$$

It can be seen from observation of the example Defect Equilibrium Diagram shown in Fig. 13.18 that the transition between Regions I and II occurs when $F = K_e$, and the transition between Regions II and III is where $F = K_i$. The slopes in Region II are $\pm$ 1, and in Regions I and III are $\pm$ 1/2. Thus it is very easy to draw the general form of such a figure, even without knowing the values of the relevant constants.

Figure 13.18 shows that the defects that have the greatest concentrations, and which therefore play the dominant role in the electroneutrality relation and in determining the properties, are different in the three Regions. The species with the highest concentrations in the central Region II are both ionic defects. This indicates that the material may be primarily an ionic conductor in this range of composition. This is not true in the other Regions, where the composition has more extreme values, either relatively M-rich in Region I, or relatively X-rich in Region III. In those cases, the dominant defect concentrations include one ionic defect and one electronic defect, and it is likely that there is important, if not dominant, electronic conductivity.

Since the mobilities of the electronic defects are generally much higher than those of ionic defects, this material will be an n-type conductor at higher

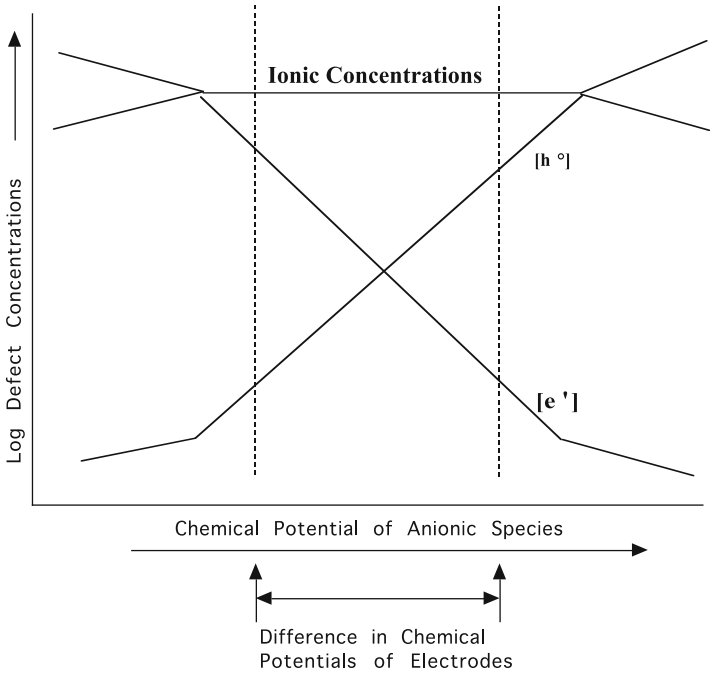

Fig. 13.19 Schematic Defect Equilibrium Diagram Showing Central Region of Solid Electrolyte Behavior

values of F, and a p-type conductor at lower values of F than the transitions between the respective regions in Fig. 13.1. Therefore it is obvious that if it is desired that a material act as a solid electrolyte in an electrochemical cell it is important that the potentials of the two electrodes both be well within the central region of the *Defect Equilibrium Diagram* for the material in question. This is shown schematically in Fig. 13.19.

It will be shown in a later chapter that if this is not true, the measured voltage across the cell will be different from (less than) that expected from the difference in the chemical potentials at the electrodes.

13.27.2 Situation in Which an Electrical Potential Difference Is Applied Across a Solid Electrolyte Using Electrodes That Block the Entry and Exit of Ionic Species

As discussed in a later chapter, electrical measurement methods are often used in order to determine the ionic conduction properties of materials that are being considered as solid electrolytes. There are two general strategies. One is to utilize

electrodes that are essentially transparent to the ionic species, so that the overall impedance is dominated by what happens within the solid being measured. This often involves *DC measurements*. The other strategy is to use electrodes that are deliberately blocking to the ionic species, and to measure the system response to the application of alternating potential differences. Such AC measurement methods are often called *impedance spectroscopy*. The blocking-electrode case will be discussed here.

The flux of any species i is proportional to the gradient of its electrochemical potential.

$$J_i = -[i]B_i \frac{d\eta_i}{dx} \tag{13.86}$$

If one, or both, of the electrodes block the passage of the ionic species, there can be no ionic flux in the solid electrolyte material being investigated. Therefore, the gradient in the electrochemical potential of the ions inside the material must be zero.

$$\frac{d\eta_i}{dx} = \frac{d\mu_i}{dx} + z_i q \frac{d\phi}{dx} = 0 \tag{13.87}$$

And if the potentials of both electrodes fall within the central region of the Defect Equilibrium Diagram for the electrolyte, there is no gradient in the concentrations of the ionic species, so that

$$\frac{d\mu_i}{dx} = 0 \tag{13.88}$$

And thus

$$\frac{d\phi}{dx} = 0 \tag{13.89}$$

So there is no internal electrical field inside the solid, despite the imposition of an external electrical potential difference.

There will be gradients in the chemical potentials, and thus of the concentrations, of the electrons and holes, however. The result is that there is an electronic current across the cell, but it is due to the composition gradients of the holes and electrons in the interior of the electrolyte, not the presence of an electrical field.

Experimental observation of the magnitude and the voltage dependence of this current provide information about the separate contributions of the holes and electrons. This is known as the Hebb-Wagner experiment, and is discussed elsewhere in this text.

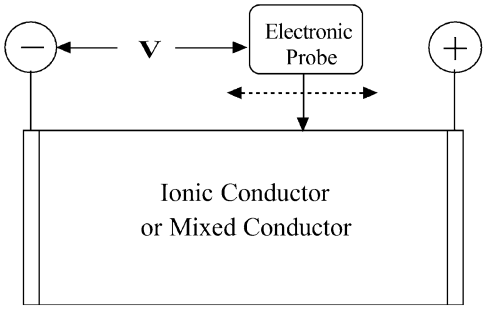

Fig. 13.20 Use of an electronic probe (e.g., a metal wire) to measure the variation of the electrochemical potential of the electrons with position

13.27.3 The Use of External Sensors to Evaluate Internal Quantities in Solids

Electronic probes can be used to evaluate the electrochemical potential (Fermi level) of the electrons at specific locations. If there is no passage of current between the probe and the solid, their Fermi levels must be equal. Such measurements can be made as a function of position, and referenced to one of the electrodes of the cell, in order to provide information about the spatial variation of the electronic Fermi level along the material being investigated. This is shown schematically in Fig. 13.20.

But information about the potential of the ionic species within the solid requires a different approach. As mentioned earlier, it is not possible to independently measure the properties of ions. Chemical potentials and forces within solids always relate to neutral species or combinations of species. The way to acquire this information is to use a probe that employs a suitable ionic conductor as electrolyte and an electronically-conducting chemical reference electrode. By measurement of the voltage across this ionically-conducting probe the difference in the chemical potential of the reference and the material being investigated can be obtained. If this is done as a function of position, information can be obtained about the chemical potential of the neutral chemical species present. This is shown schematically in Fig. 13.21.

13.27.4 Another Case, A Mixed Conductor in Which the Transport of Electronic Species Is Blocked

Instead of the electrodes acting to block the transport of ionic species, it is possible to block the passage of electrons into and out of a mixed conductor or ionic conductor. This can be accomplished by putting an ionic conductor in the system,

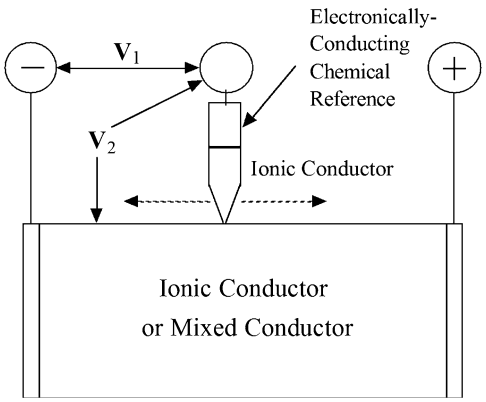

Fig. 13.21 Use of an ionically conducting probe and reference electrode in order to obtain information about the variation of the chemical potential of the neutral chemical species present with position

so that if current is passed between the electrodes there will be an ionic flux, but no electronic flux.

Even though there may be current flow through the system, external measurement of the Fermi Level with an electronic probe will show that there is no internal electrical field.

Instead of the relation

$$\frac{d\mu_{\mathrm{M}}}{dx} = \frac{d\eta_{\mathrm{M}^+}}{dx} + \frac{d\eta_{\mathrm{e}^-}}{dx} \tag{13.90}$$

if there is no gradient in the electrochemical potential of the electrons, this simplifies to

$$\frac{d\mu_{\mathrm{M}}}{dx} = \frac{d\eta_{\mathrm{M}^+}}{dx} \tag{13.91}$$

An experimental example is shown in Fig. 13.22 [35]. In that case, an ionic probe was used to evaluate the electrochemical potential of silver ions within the mixed conductor Ag_2S, which was placed between two slabs of AgI, which is a pure silver ionic conductor. Thus current flow resulted in the gradient within the Ag_2S when silver ions were transported from one silver metal electrode to the other.

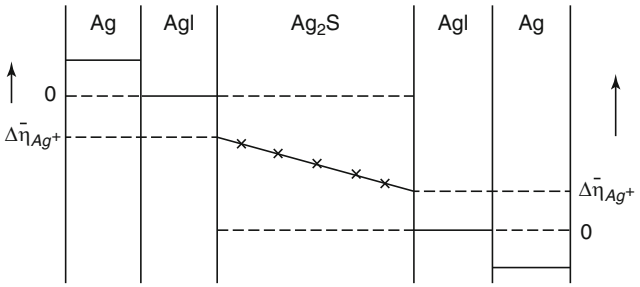

Fig. 13.22 Variation of the chemical potential of silver with position within Ag_2S, a mixed conductor, during current passage, evaluated by the use of an ionic probe [4]

13.27.5 Further Comments on Composite Electrochemical Cells Containing a Mixed Conductor in Series with a Solid Electrolyte

One of the concepts that has been proposed for use in fuel cells involves the use of a *monolithic structure* that is a composite of an ionic conductor and a mixed conductor that both have the same crystal structure. The mixed conductor can then act as an electrode. The potential advantage of this approach is that it would minimize the generation of stresses due to local differences in thermal expansion.

Assuming that these two components have the same crystal structure and are of approximately the same composition, there are two general ways to do this.

One is by the use of localized doping of an ionic conductor to produce mixed conductor regions at the surface with increased electronic conductivity. These doped regions can then act as mixed-conducting electrodes in series with the adjacent solid electrolyte region.

An alternative might be possible in some cases that would not require doping. This can be understood by consideration of the *Defect Equilibrium Diagrams* discussed earlier. It can be seen that if the local electrical potential is sufficiently negative, there is the tendency for the presence of excess electrons, making the material an n-type mixed conductor. Alternatively, it may be possible to induce the local presence of holes at very positive potentials to make the material a p-type electronic conductor. The first of these is shown schematically in Fig. 13.23.

When this is the case, the measured voltage is reduced below that which would be the case if the chemical potential difference were placed upon a purely ionic conductor. This is illustrated in Fig. 13.24. Unfortunately, this means that the use of this monolithic concept in a solid electrolyte fuel cell necessarily means that the output voltage is reduced.

The spatial distribution of the chemical potential of the neutral chemical species M is shown in Fig. 13.25.

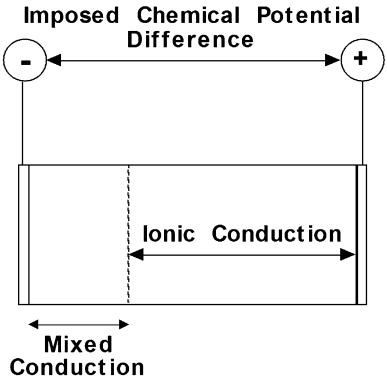

Fig. 13.23 Schematic illustration of the case of an electrochemical cell in which an imposed chemical (or electrical) potential difference is such that the potential of the negative electrode is in the region of the DED in which the concentration of electrons is large enough to cause local mixed-conduction

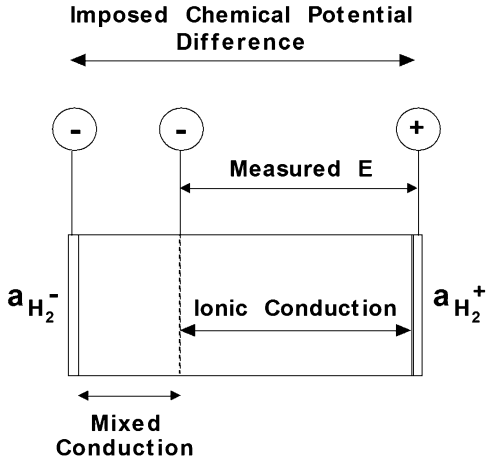

Fig. 13.24 Schematic illustration showing that the electrical voltage is less than that corresponding to the imposed chemical potential difference if a portion of the material is mixed-conducting

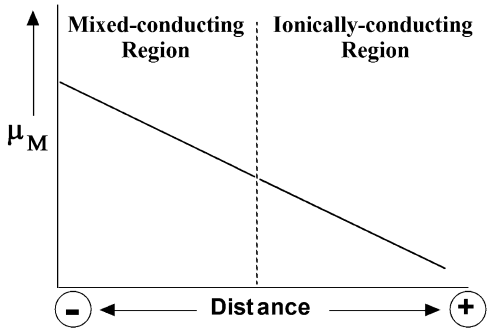

Fig. 13.25 Spatial distribution of the chemical potential of the neutral chemical species *M* across the cell illustrated in Figs 13.23 and 13.24

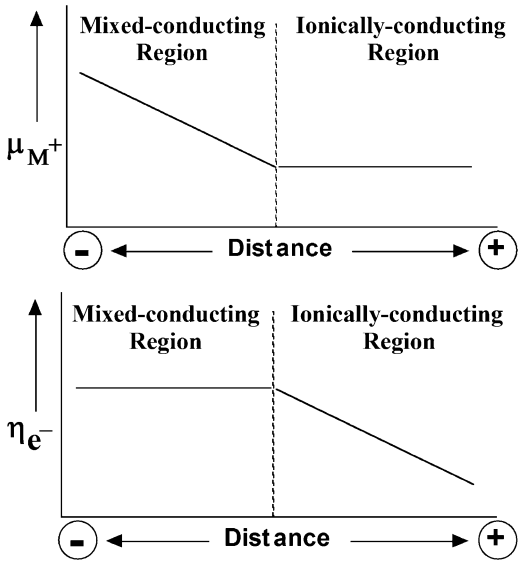

Fig. 13.26 Spatial distribution of the chemical potential of the M+ ions and the electrochemical potential of the electrons (Fermi level) is illustrated for the cell illustrated in Figs. 13.23 and 13.24

The corresponding distributions of the chemical potentials of the M^+ ions and the electrochemical potential of the electrons are illustrated in Fig. 13.26 for this situation.

It is seen that, although the chemical potential of the neutral chemical species, an externally measurable quantity, is a linear function of distance across the cell, the positional variations of the internal potentials of the two types of species are quite different.

13.28 Transference Numbers of Particular Species

The several situations that have been discussed here clearly indicate that the charge transport properties of a given material can vary significantly, depending upon the potentials imposed by its electrodes, as well as whether the electrodes—and other phases present—limit the passage of either ionic or electronic species.

A term used in this connection is the *Hittorf transference number* of a particular species. It indicates the fraction of the total charge current that is transported by that species.

Consideration of the Defect Equilibrium Diagram shows that the concentrations of the various charged species present vary with the potentials applied by the electrodes, and the relation between chemical potentials and electrical potentials. Variation of these concentrations means that there is a variation in the transference

numbers of the different species. Transference numbers can thus also vary with position within a solid.

But in addition, it is obvious that transference numbers also depend upon the experimental conditions—e.g., the properties of the electrodes used in a given experiment.

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