

Interfacial Electrochemistry

WOLFGANG SCHMICKLER

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Wolfgang Schmickler

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Foreword

When I started working in electrochemistry the textbooks used for University courses dealt predominantly with the properties of electrolyte solutions, with only a brief attempt at discussing the processes occurring at electrodes. Things began to change with the pioneering books of Delahay and of Frumkin which discussed kinetics in a way that a chemical engineer or a physical chemist might appreciate. Very little was said about interfacial structure, despite Butler's remarkable "Electrocapilarity", which was really premature as it appeared before the research needed to support this view had developed sufficiently. This was done in the subsequent years, to a large extent for mercury electrodes, but only from a macroscopic viewpoint using electrical measurements and predominantly thermodynamic analysis. In the last two decades the possibilities of obtaining atomic scale information and of analysing it have widened to an unprecedented extent. This has been reflected in some of the recent textbooks which have appeared, but none has embraced this modern point of view more wholeheartedly than Professor Schmickler's. Coming originally from a theoretical physics background and having already collaborated in an excellent (pre-molecular) electrochemistry textbook, he is well able to expound these developments and integrate them with the earlier studies of electrode kinetics in a way which brings out the key physical chemistry in a lucid way. His own extensive contributions to modern electrochemistry ensures that the exposition is based on a detailed knowledge of the subject. I have found the book a pleasure to read and I hope that it will not only be widely used by electrochemists, but also those physical chemists, biochemists and others who need to be convinced that electrochemistry is not a "mystery best left to the professional". I hope that this book will convince them that it is a major part of physical science.

Roger Parsons

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Preface

Electrochemistry has undergone significant changes during the last two decades, which are marked by four developments:

The use of single crystal electrodes. While the polycrystalline electrodes that were used in older works gave reproducible results in studies of reactions, they did not possess a definite structure. Only recently have electrochemists learned to prepare and characterize single crystal electrodes. This has greatly extended the study of the structure of the electrochemical interface.

The development of surface-sensitive techniques. The classical electrochemical methods involve the measurement of potential and current. While these are extremely useful in the study of reaction rates and mechanisms, they give no information on the structure of the interface. A variety of surface-sensitive techniques has now been adapted to the electrochemical situation and applied to the investigation of electrode surface structure.

An increase in theoretical activity. Any exact science requires a healthy balance between experiment and theory. The wealth of structural information that has become available requires models and theories for its interpretation, and has thus spurred increased activity both in proper theory and in computer simulations.

An increasing overlap with surface science. Electrochemistry and surface science have similar problems and share a number of techniques. This has led to a fruitful dialogue between these two fields, as is evidenced by a series of joint meetings.

These changes must be reflected in the teaching of electrochemistry, particularly at the more advanced level. I therefore saw the need for a textbook aimed at students who have already taken an elementary course at the early undergraduate level and who want an introduction into modern electrochemistry. Typically, they would be at the graduate or late undergraduate level and thinking about specializing in electrochemistry or a related subject. In addition, I hope that this book will be useful for colleagues from neighboring disciplines, particularly to surface scientists, and last, but not least, to my fellow electrochemists.

This book is divided into three parts: the first part covers the fundamental aspects, which should form the backbone of any course. As is evident from the title I consider electrochemistry to be a science of interfaces – the definition is given in the introduction –, so I have treated the interfaces between a metal or a semiconductor and an electrolyte solution, and liquid-liquid interfaces. I have not considered solid

electrolytes or molten salts, mainly because little is known about the electrochemical interfaces that they form.

The experimental section which follows has been kept fairly short. I have tried to convey the essence of each method and have provided at least one example for its application. Ideally, a lecture course based on this book should be followed by a laboratory course in which the students learn some of the details and tricks.

The last part covers a few theoretical issues. I expect that theory will play an increasingly role in electrochemistry, so every student should be introduced into the basic ideas behind current models and theories. I have tried to keep this section simple and in several cases have provided simplified versions of more complex theories. Only the last chapter, which covers the quantum theory of electron transfer reactions, requires some knowledge of quantum mechanics and of more advanced mathematical techniques, but no more than is covered in a course on quantum chemistry.

At the end of each chapter I have provided a set of problems which illustrate and extend the subject. Since none of the textbooks that I know contain any problems, I have personally made up a special set of problems for this text. Solving problems is the best way to obtain a working knowledge of a subject.

I would like to conclude by thanking those who helped and advised me. Above all I am grateful to Dr. Roger Parsons, FRS, who read both the draft and the final version, and made numerous suggestions for improvement; I accepted almost all of them. I also wish to thank Dr. Elizabeth Santos, who read the first draft, for her good advice on many points, and Olaf Pecina, who corrected the pre-final version and solved all the problems. Last but not least I thank Margrit Lingner for encouragement, technical support, and for persuading me to include problems.

Ulm, Germany
October 1995

W. S.

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List of Main Symbols

a	activity	α	anodic transfer coefficient
C	differential capacity per unit area	β	cathodic transfer coefficient
C_{GC}	Gouy-Chapman or space charge capacity	Γ	surface excess
C_H	Helmholtz capacity	γ	surface tension
c	concentration	δ_N	diffusion-layer thickness
E	electric field	ϵ	dielectric constant
E_F	Fermi energy, Fermi-level	ϵ_0	permittivity of vacuum
e_0	unit of charge	η	overpotential
F	Faraday's constant	Θ	coverage
G	Gibbs energy	κ	Debye inverse length
I	electric current	λ	energy of reorganization
j	current density	μ	chemical potential
k	Boltzmann's constant	$\tilde{\mu}$	electrochemical potential
k	rate constant	ν	frequency
l	electrosorption valency	σ	surface-charge density
m	dipole moment	Φ	work function
m	mass	ϕ	inner potential
n	particle density		electrode potential
R	gas constant	χ	surface dipole potential
R	resistance	ψ	outer potential
T	temperature	ω	circular frequency
Z	impedance		
z	charge number		

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Part I

Fundamentals of Electrochemistry

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Introduction

Electrochemistry is an old science: There is good archaeological evidence that an electrolytic cell was used by the Parthians (250 *B.C.* to 250 *A.D.*), probably for electroplating, though a proper scientific investigation of electrochemical phenomena did not start before the experiments of Volta and Galvani [1,2]. The meaning and scope of electrochemical science has varied throughout the ages: For a long time it was little more than a special branch of thermodynamics; later attention turned to electrochemical kinetics. During recent decades, with the application of various surface-sensitive techniques to electrochemical systems, it has become a science of interfaces, and this, we think, is where its future lies. So in this book we use as a working definition:

Electrochemistry is the study of structures and processes at the interface between an electronic conductor (the electrode) and an ionic conductor (the electrolyte) or at the interface between two electrolytes.

This definition requires some explanation. (1) By *interface* we denote those regions of the two adjoining phases whose properties differ significantly from those of the bulk. These interfacial regions can be quite extended, particularly in those cases where a metal or semiconducting electrode is covered by a thin film. Sometimes the term *interphase* is used to indicate the spatial extension. (2) It would have been more natural to restrict the definition to the interface between an electronic and an ionic conductor only, and, indeed, this is generally what we mean by the term *electrochemical interface*. However, the study of the interface between two immiscible electrolyte solutions is so similar that it is natural to include it under the scope of electrochemistry.

Metals and semiconductors are common examples of electronic conductors, and under certain circumstances even insulators can be made electronically conducting, for example by photoexcitation. Electrolyte solutions, molten salts, and solid electrolytes are ionic conductors. Some materials have appreciable electronic *and* ionic conductivities,

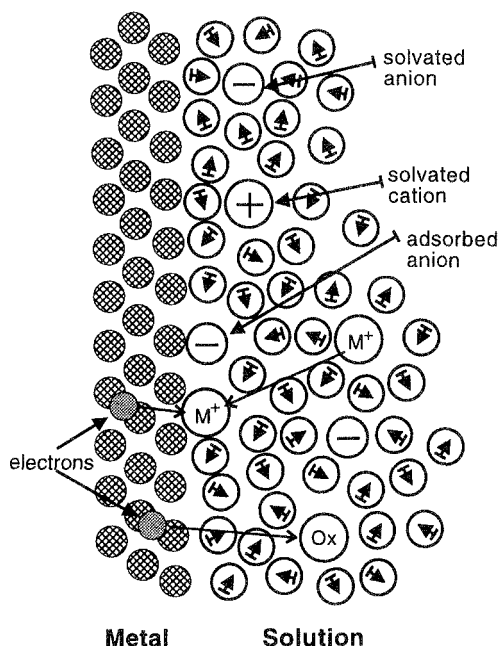


Figure 1.1 Structure and processes at the metal-solution interface.

and depending on the circumstances one or the other or both may be important.

With metals, semiconductors, and insulators as possible electrode materials, and solutions, molten salts, and solid electrolytes as ionic conductors, there is a fair number of different classes of electrochemical interfaces. However, not all of these are equally important: The majority of contemporary electrochemical investigations is carried out at metal-solution or at semiconductor-solution interfaces. We shall focus on these two cases, and consider some of the others briefly.

1.1 A typical system: the metal-solution interface

To gain an impression of the structures and reactions that occur in electrochemical systems, we consider the interface between a metal and an electrolyte solution. Figure 1.1 shows a schematic diagram of its structure. Nowadays most structural investigations are carried out on single crystal surfaces; so the metal atoms, indicated by the hatched circles

on the left, are arranged in a lattice. Solvent molecules generally carry a dipole moment, and are hence represented as spheres with a dipole moment at the center. Ions are indicated by spheres with a charge at the center. Near the top of the picture we observe an anion and a cation, which are close to the electrode surface but not in contact with it. They are separated from the metal by their solvation sheaths. A little below is an anion in contact with the metal; we say it is *specifically adsorbed* if it is held there by chemical interactions. Usually anions are less strongly solvated than cations; therefore their solvation sheaths are easier to break up, and they are more often specifically adsorbed, particularly on positively charged metal surfaces. Adsorption occurs on specific sites; the depicted anion is adsorbed on top of a metal atom, in the *atop* position. The two types of reactions shown near the bottom of the figure will be discussed below.

Generally the interface is charged: the metal surface carries an excess charge, which is balanced by a charge of equal magnitude and opposite sign on the solution side of the interface. Figure 1.2 shows the charge distribution for the case in which the metal carries a positive excess charge, and the solution a negative one – there is a deficit of electrons on the metal surface, and more anions than cations on the solution side of the interface. Since a metal electrode is an excellent conductor, its excess charge is restricted to a surface region about 1 Å thick. Usually one works with fairly concentrated (0.1 to 1 M) solutions of strong electrolytes. Such solutions also conduct electric currents well, though their conductivities are several orders of magnitude smaller than those of metals. For example, at room temperature the conductivity of silver is $0.66 \times 10^6 \Omega^{-1}\text{cm}$; that of a 1 M aqueous solution of KCl is $0.11 \Omega^{-1}\text{cm}$. The greater conductivity of metals is caused both by a greater concentration of charge carriers and by their higher mobilities. Thus silver has an electron concentration of $5.86 \times 10^{22} \text{cm}^{-3}$, while a 1 M solution of KCl has about $1.2 \times 10^{21} \text{ions cm}^{-3}$. The difference in the mobilities of the charge carriers is thus much greater than the difference in their concentrations. Because of the lower carrier concentration, the charge in the solution extends over a larger region of space, typically 5 to 20 Å thick. The resulting charge distribution – two narrow regions of equal and opposite charge – is known as *the electric double layer*. It can be viewed as a capacitor with an extremely small effective plate separation, and therefore has a very high capacitance.

The voltage drop between the metal and the solution is typically of the order of 1 V. If the voltage is substantially higher, the solution is

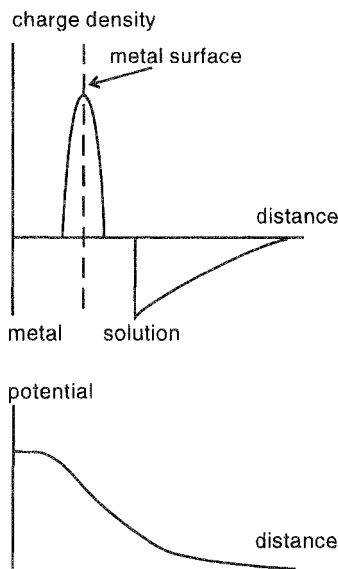


Figure 1.2 Distribution of charge and potential at the metal-solution interface (schematic).

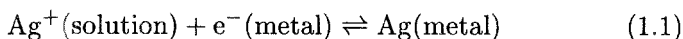
decomposed – in aqueous solutions either oxygen or hydrogen evolution sets in. Since this potential drop extends over such a narrow region, it creates extremely high fields of up to 10^9 V m^{-1} . Such a high field is one of the characteristics of electrochemical interfaces. In vacuum fields of this magnitude can only be generated at sharp tips and are therefore strongly inhomogeneous. Electrochemical experiments on metals and semiconductors are usually performed with a time resolution of $1 \mu\text{s}$ or longer¹ – a few milliseconds is typical for transient measurements (details will be given in Chapter 13). If one looks at the interface over this time range, the positions of the ions are smeared out, and one only sees a homogeneous charge distribution and hence a homogeneous electrostatic field. Inhomogeneities may exist near steps, kinks, or similar features on the metal surface.

The structure of the interface is of obvious interest to electrochemists. However, the interface forms only a small part of the two ad-

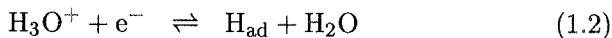
¹For the following reason: electrochemical experiments involve a change of the electrode potential, and hence charging or discharging the capacitor formed by the double layer. Since the double-layer capacity is large, and the resistance of the solution is not negligible, it has a long time constant associated with it, and the response at short times is dominated by this charging of the double layer.

joining phases, and spectroscopic methods which generate signals both from the bulk and from the interface are not suitable for studying the interface, unless one finds a way of separating the usually dominant bulk signal from the small contribution of the interface. Techniques employing electron beams, which have provided a wealth of data for surfaces in the vacuum, cannot be used since electrons are absorbed by solutions. Indeed, a lack of spectroscopic methods that are sensitive to the interfacial structure has for a long time delayed the development of electrochemistry, and only the past 10–15 years have brought substantial progress.

Reactions involving charge transfer through the interface, and hence the flow of a current, are called *electrochemical reactions*. Two types of such reactions are indicated in Fig. 1.1. The upper one is an instance of *metal deposition*. It involves the transfer of a metal ion from the solution onto the metal surface, where it is discharged by taking up electrons. Metal deposition takes place at specific sites; in the case shown it is a *hollow site* between the atoms of the metal electrode. The deposited metal ion may belong to the same species as those on the metal electrode, as in the deposition of a Ag^+ ion on a silver electrode, or it can be different as in the deposition of a Ag^+ ion on platinum. In any case the reaction is formally written as:



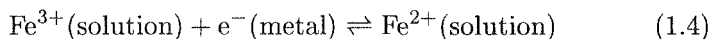
Metal deposition is an example of a more general class of electrochemical reactions, *ion transfer reactions*. In these an ion, e.g. a proton or a chloride ion, is transferred from the solution to the electrode surface, where it is subsequently discharged. Many ion-transfer reactions involve two steps. The hydrogen-evolution reaction, for example, sometimes proceeds in the following way:



where H_{ad} refers to an adsorbed proton. Only the first step is an electrochemical reaction; the second step is a purely chemical recombination and desorption reaction.

Another type of electrochemical reaction, an *electron-transfer reaction*, is indicated near the bottom of Fig. 1.1. In the example shown an oxidized species is reduced by taking up an electron from the metal. Since electrons are very light particles, they can tunnel over a distance of 10 Å or more, and the reacting species need not be in contact with

the metal surface. The oxidized and the reduced forms of the reactants can be either ions or uncharged species. A typical example for an electron-transfer reaction is:



Both ion and electron transfer reactions entail the transfer of charge through the interface, which can be measured as the electric current. If only one charge transfer reaction takes place in the system, its rate is directly proportional to the current density, i.e. the current per unit area. This makes it possible to measure the rates of electrochemical reactions with greater ease and precision than the rates of chemical reactions occurring in the bulk of a phase. On the other hand, electrochemical reactions are usually quite sensitive to the state of the electrode surface. Impurities have an unfortunate tendency to aggregate at the interface. Therefore electrochemical studies require extremely pure system components.

Since in the course of an electrochemical reaction electrons or ions are transferred over some distance, the difference in the electrostatic potential enters into the Gibbs energy of the reaction. Consider the reaction of Eq. (1.4), for example. For simplicity we assume that the potential in the solution, at the position of the reacting ion, is kept constant. When the electrode potential is changed by an amount $\Delta\phi$, the Gibbs energy of the electron is lowered by an amount $-e_0 \Delta\phi$, and hence the Gibbs energy of the reaction is raised by $\Delta G = e_0 \Delta\phi$. Varying the electrode potential offers a convenient way of controlling the reaction rate, or even reversing the direction of a reaction, again an advantage unique to electrochemistry.

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1. A. Galvani, *De Viribus Electricitatis in Motu Musculari Commentarius, ex Typ. Instituti Scientiarum Bononiae*, 1791; see also: S. Trasatti, *J. Electroanal. Chem.* **197** (1986) 1.
2. A. Volta, *Phil. Trans.* II (1800) pp. 405-431; *Gilbert's Ann.* **112** (1800) 497.

Problems

1. Consider the surface of a silver electrode with a square arrangement of atoms (this is a so-called Ag(100) surface, as will be explained in Chapter 4) and a lattice constant of 2.9 Å. (a) What is the excess charge

density if each Ag atom carries an excess electron? (b) How large is the resulting electrostatic field if the solution consists of pure water with a dielectric constant of 80? (c) In real systems the excess charge densities are of the order of $\pm 0.1 \text{ C m}^{-2}$. What is the corresponding number of excess or defect electrons per surface atom? (d) If a current density of 0.1 A cm^{-2} flows through the interface, how many electrons are exchanged per second and per silver atom?

2. Consider a plane metal electrode situated at $z = 0$, with the metal occupying the half-space $z \leq 0$, the solution the region $z > 0$. In a simple model the excess surface charge density σ in the metal is balanced by a space charge density $\rho(z)$ in the solution, which takes the form: $\rho(z) = A \exp(-\kappa z)$, where κ depends on the properties of the solution. Determine the constant A from the charge balance condition. Calculate the interfacial capacity assuming that κ is independent of σ .
3. In a simple model a water molecule is represented as a hard sphere with a diameter $d = 3 \text{ \AA}$ and a dipole moment $m = 6.24 \times 10^{-30} \text{ C m}$ at its center. Calculate the energy of interaction E_{int} of a water molecule with an ion of radius a for the most favorable configuration. When an ion is adsorbed, it loses at least one water molecule from its solvation shell. If the ion keeps its charge it gains the image energy E_{im} . Compare the magnitudes of E_{int} and E_{im} for $a = 1$ and 2 \AA . Ignore the presence of the water when calculating the image interaction.

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Preliminaries

In this chapter we introduce and discuss a number of concepts that are commonly used in the electrochemical literature and in the remainder of this book. In particular we will illuminate the relation of electrochemical concepts to those used in related disciplines. Electrochemistry has much in common with *surface science*, which is the study of solid surfaces in contact with a gas phase or, more commonly, with ultra-high vacuum (uhv). A number of surface science techniques has been applied to electrochemical interfaces with great success. Conversely, surface scientists have become attracted to electrochemistry because the electrode charge (or equivalently the potential) is a useful variable which cannot be well controlled for surfaces in uhv. This has led to a laudable attempt to use similar terminologies for these two related sciences, and to introduce the concepts of the *absolute scale of electrochemical potentials* and the *Fermi level of a redox reaction* into electrochemistry. Unfortunately, there is some confusion of these terms in the literature, even though they are quite simple.

2.1 Inner, outer, and surface potentials

Electrochemical interfaces are sometimes referred to as *electrified interfaces*, meaning that potential differences, charge densities, dipole moments, and electric currents occur. It is obviously important to have a precise definition of the electrostatic potential of a phase. There are two different concepts. The *outer* or *Volta potential* ψ_α of the phase α is the work required to bring a unit point charge from infinity to a point just outside the surface of the phase. By “just outside” we mean a position very close to the surface, but so far away that the image interaction with the phase can be ignored; in practice, that means a distance of about $10^{-5} - 10^{-3}$ cm from the surface. Obviously, the outer potential ψ_α is a measurable quantity.

In contrast, the *inner* or *Galvani potential* ϕ_α is defined as the work required to bring a unit point charge from infinity to a point *inside* the phase α ; so this is the electrostatic potential which is actually

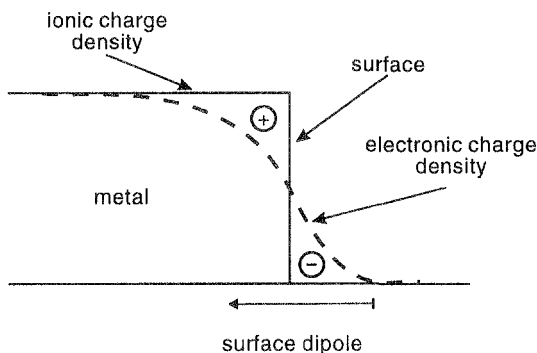


Figure 2.1 Charge distribution and surface dipole at a metal surface. For simplicity the positive charge residing on the metal ions has been smeared out into a constant background charge.

experienced by a charged particle inside the phase. Unfortunately, the inner potential cannot be measured: If one brings a real charged particle – as opposed to a point charge – into the phase, additional work is required due to the chemical interaction of this particle with other particles in the phase. For example, if one brings an electron into a metal, one has to do not only electrostatic work, but also work against the exchange and correlation energies.

The inner and outer potential differ by the *surface potential* $\chi_\alpha = \phi_\alpha - \psi_\alpha$. This is caused by an inhomogeneous charge distribution at the surface. At a metal surface the positive charge resides on the ions which sit at particular lattice sites, while the electronic density decays over a distance of about 1 \AA from its bulk value to zero (see Fig. 2.1). The resulting dipole potential is of the order of a few volts and is thus by no means negligible. Smaller surface potentials exist at the surfaces of polar liquids such as water, whose molecules have a dipole moment. Intermolecular interactions often lead to a small net orientation of the dipoles at the liquid surface, which gives rise to a corresponding dipole potential.

The inner potential ϕ_α is a bulk property. Even though it cannot be measured, it is still a useful concept, particularly for model calculations. Differences in the inner potential of two phases can be measured, if they have the same chemical composition. The surface potential χ_α is a surface property, and may hence differ at different surfaces of a

single crystal. The same is then also true of the outer potential ψ ; thus different surface planes of a single crystal of a metal generally have different outer potentials. We will return to these topics below.

2.2 The electrochemical potential

In ordinary thermodynamics the chemical potential of a species i is defined as:

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{p,T} \quad (2.1)$$

where G is the Gibbs energy of the phase under consideration, p denotes the pressure, T the temperature, and N_i the number of particles of species i . So the chemical potential is the work required to add a particle to the system at constant pressure and temperature. Alternatively, one may define μ_i by taking the derivative with respect to m_i , the number of moles of species i . The two definitions differ by a multiplicative constant, Avogadro's constant; we shall use the former definition.

If the particles of species i in Eq. (2.1) are charged, one speaks of an *electrochemical potential* instead, and writes $\tilde{\mu}_i$. The usual thermodynamic equilibrium conditions are now in terms of the $\tilde{\mu}_i$. For example, if a species i is present both in a phase α and in a phase β , and the interface between α and β is permeable to i , then $\tilde{\mu}_{i,\alpha} = \tilde{\mu}_{i,\beta}$ at equilibrium.

In adding a charged particle work is done against the inner potential ϕ , and it may be useful to separate this out and write:

$$\tilde{\mu}_i = \left(\frac{\partial G}{\partial N_i} \right)_{p,T} = \mu_i + z_i e_0 \phi \quad (2.2)$$

where z_i is the charge number of species i , e_0 is the unit of charge, and μ_i is again called the *chemical potential* since it contains the work done against chemical interactions. For an uncharged species chemical and electrochemical potential are the same.

At zero temperature the electrons in a solid occupy the lowest energy levels compatible with the Pauli exclusion principle. The highest energy level occupied at $T = 0$ is the Fermi level, E_F . For metals the Fermi level and the electrochemical potential are identical at $T = 0$, since any electron that is added to the system must occupy the Fermi level. At finite temperatures E_F and the electrochemical potential $\tilde{\mu}$ of the electrons differ by terms of the order of $(kT)^2$, which are typically

a fraction of a percent and are hence negligible for most purposes. Numerical values of E_F or $\tilde{\mu}$ must refer to a reference point, or energy zero. Common choices are a band edge or the vacuum level, i.e. a reference point in the vacuum at infinity. Obviously, one has to be consistent in the choice of the reference point when comparing the Fermi levels of different systems.

For electrons in a metal the *work function* Φ is defined as the minimum work required to take an electron from inside the metal to a place just outside (c.f. the preceding definition of the outer potential). In taking the electron across the metal surface, work is done against the surface dipole potential χ . So the work function contains a surface term, and it may hence be different for different surfaces of a single crystal. The work function is the negative of the Fermi level, provided the reference point for the latter is chosen just outside the metal surface. If the reference point for the Fermi level is taken to be the vacuum level instead, then $E_F = -\Phi - e_0\psi$, since an extra work $-e_0\psi$ is required to take the electron from the vacuum level to the surface of the metal. The relations of the electrochemical potential to the work function and the Fermi level are important because one may want to relate electrochemical and solid-state properties.

2.3 Absolute electrode potential

The standard electrode potential [1] of an electrochemical reaction is commonly measured with respect to the standard hydrogen electrode (SHE) [2], and the corresponding values have been compiled in tables. The choice of this reference is completely arbitrary, and it is natural to look for an absolute standard such as the vacuum level, which is commonly used in other branches of physics and chemistry. To see how this can be done, let us first consider two metals, I and II, of different chemical composition and different work functions Φ_I and Φ_{II} . When the two metals are brought into contact, their Fermi levels must become equal. Hence electrons flow from the metal with the lower work function to that with the higher one, so that a small dipole layer is established at the contact, which gives rise to a difference in the outer potentials of the two phases (see Fig. 2.2). No work is required to transfer an electron from metal I to metal II, since the two systems are in equilibrium. This enables us calculate the outer potential difference between the two metals in the following way. We first take an electron from the Fermi level E_F of metal I to a point in the vacuum just outside metal I. The work required for this is the work function Φ_I of metal I.

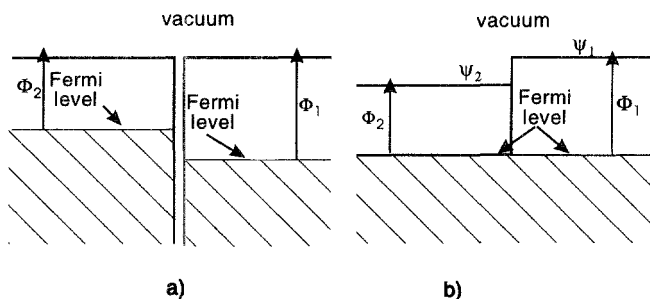


Figure 2.2 Two metals of different work functions before (a) and after (b) contact (schematic).

We then take the electron in the vacuum to a point just above metal II; this requires the work $-e_0(\psi_{II} - \psi_I)$. We then take the electron to the Fermi level of metal II, and gain the energy $-\Phi_{II}$. Since the total work for this process must be zero, we obtain:

$$\psi_I - \psi_{II} = \frac{-(\Phi_I - \Phi_{II})}{e_0} \quad (2.3)$$

so that the outer potential difference can be calculated from the metal work function. By the same reasoning different faces of a single metal crystal have different outer potentials if their work functions are not equal.

We should like to define a “work function” of an electrochemical reaction which enables us to calculate outer potential differences in the same way for a metal-solution interface, and this work function should also refer to the vacuum. For this purpose we consider a solution containing equal amounts of Fe^{3+} and Fe^{2+} ions in contact with a metal M , and suppose that the reaction is at equilibrium. We now transfer an electron from the solution via the vacuum to the metal in the following way:

1. Take an Fe^{2+} ion from the solution into the vacuum above the solution; the work required is the negative of $\Delta G_{\text{sol}}^r(\text{Fe}^{2+})$, the *real Gibbs energy of solvation* of the Fe^{2+} ion. Real Gibbs energies of solvation are measurable; they include the work done against the surface potential of the solution. In contrast, tabulated values of conventional solvation energies usually do not contain this contribution; they are not measurable, but are obtained by assigning a certain value to the solvation energy of a reference ion.

2. Take an electron from the Fe^{2+} ion: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$; the work required is the third ionization energy I_3 of Fe.
3. Put the Fe^{3+} back into the solution, and gain $\Delta G_{\text{sol}}^r(\text{Fe}^{3+})$.
4. Take the electron from just outside the solution across to a position just outside the metal; the work required is $-e_0(\psi_m - \psi_s)$; the index m denotes the metal, s the solution.
5. Take the electron to the Fermi level of the metal, and gain $-\Phi_m$ in energy.

Adding up all the energies, we obtain:

$$-\Delta G_{\text{sol}}^r(\text{Fe}^{2+}) + I_3 + \Delta G_{\text{sol}}^r(\text{Fe}^{3+}) - e_0(\psi_m - \psi_s) - \Phi_m = 0 \quad (2.4)$$

or

$$e_0(\psi_m - \psi_s) = [\Delta G_{\text{sol}}^r(\text{Fe}^{3+}) - \Delta G_{\text{sol}}^r(\text{Fe}^{2+}) + I_3] - \Phi_m \quad (2.5)$$

Comparison with Eq. (2.3) suggests that we identify the expression in the square brackets, which depends only on the properties of the redox couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the solution, with the work function of this couple and define:

$$\Phi(\text{Fe}^{3+}/\text{Fe}^{2+}) = \Delta G_{\text{sol}}^r(\text{Fe}^{3+}) - \Delta G_{\text{sol}}^r(\text{Fe}^{2+}) + I_3 \quad (2.6)$$

All the quantities on the right-hand side of this equation are measurable; so this work function is well defined. Fortunately, it is not necessary to calculate the work function for every electrode reaction: The difference between the work functions of two electrode reactions (measured in eV) equals the difference between their standard potentials on the conventional hydrogen scale (measured in V) – this can be easily seen by constructing electrochemical cells with the SHE (standard hydrogen electrode) as a counter electrode. So it is sufficient to know the work function of one particular reaction in a given solvent. For the SHE (i.e. the couple H_2/H^+), the work function is currently estimated as 4.5 ± 0.2 eV; so one obtains the work function of any electrochemical reaction by simply adding this number to the standard potential (in volts) on the SHE scale. By dividing the resulting scale of work functions by the unit charge (or expressing quantities in volts instead of electron volts) one obtains the *absolute scale of electrochemical potentials*.