Electrochemistry at Metal and Semiconductor Electrodes

By Norio Sato

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PREFACE

Electrochemistry at Electrodes is concerned with the structure of electrical double layers and the characteristic of charge transfer reactions across the electrode/electrolyte interface. The purpose of this text is to integrate modern electrochemistry with semiconductor physics; this approach provides a quantitative basis for understanding electrochemistry at metal and semiconductor electrodes.

Electrons and ions are the principal particles that play the main role in electrochemistry. This text, hence, emphasizes the *energy level concepts* of electrons and ions rather than the phenomenological thermodynamic and kinetic concepts on which most of the classical electrochemistry texts are based. This rationalization of the phenomenological concepts in terms of the physics of semiconductors should enable readers to develop more *atomistic* and *quantitative* insights into processes that occur at electrodes.

This book incorporates into many traditional disciplines of science and engineering such as interfacial chemistry, biochemistry, enzyme chemistry, membrane chemistry, metallurgy, modification of solid interfaces, and materials corrosion.

This text is intended to serve as an introduction for the study of advanced electrochemistry at electrodes and is aimed towards *graduates* and *senior undergraduates* studying materials and interfacial chemistry or those beginning research work in the field of electrochemistry.

Chapter 1 introduces a concept of energy levels of particles in physicochemical ensembles. Electrons are *Fermi particles* whose energy levels are given by the Fermi levels, while ions are *Boltzmann particles* whose energy is distributed in an exponential Boltzmann function. In Chapter 2 the energy levels of electrons in solid metals, solid semiconductors, and aqueous solutions are discussed. Electrons in metals are in *delocalized energy bands*; electrons in semiconductors are in delocalized energy bands as well as in localized levels; and *redox electrons* associated with redox particles in aqueous solutions are in *localized levels* which are split into occupied (reductant) and vacant (oxidant) electron levels due to the Franck-Condon principle. Chapter 3 introduces the energy levels of ions in gas, liquid, and solid phases. In aqueous solution, the acidic and basic proton levels in water molecules interrelate with proton levels in solute particles such as acetic acid.

In Chapter 4 the physical basis for the *electrode potential* is presented based on the electron and ion levels in the electrodes, and discussion is made on the electronic and ionic electrode potentials. Chapter 5 deals with the structure of

the electrical double layer at the electrode/electrolyte interfaces. The *potential of zero charge* of metal electrodes and the *flat band potential* of semiconductor electrodes are shown to be characteristic of individual electrodes. The interface of semiconductor electrodes is described as either in the state of *band edge level pinning* or in the state of *Fermi level pinning*. Chapter 6 introduces electrochemical cells for producing electric energy (chemical cells) and chemical substances (electrolytic cells).

In Chapter 7 general kinetics of electrode reactions is presented with kinetic parameters such as stoichiometric number, reaction order, and activation energy. In most cases the affinity of reactions is distributed in multiple steps rather than in a single particular rate step. Chapter 8 discusses the kinetics of electron transfer reactions across the electrode interfaces. Electron transfer proceeds through a *quantum mechanical tunneling* from an occupied electron level to a vacant electron level. Complexation and adsorption of redox particles influence the rate of electron transfer by shifting the electron level of redox particles. Chapter 9 discusses the kinetics of ion transfer reactions which are based upon *activation processes* of Boltzmann particles.

Chapter 10 deals with photoelectrode reactions at semiconductor electrodes in which the concentration of minority carriers is increased by photoexcitation, thereby enabling the transfer of electrons to occur that can not proceed in the dark. The concept of *quasi-Fermi level* is introduced to account for photoenergy gain in semiconductor electrodes. Chapter 11 discusses the coupled electrode (*mixed electrode*) at which anodic and cathodic reactions occur at the same rate on a single electrode; this concept is illustrated by corroding metal electrodes in aqueous solutions.

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<div align="right">Norio Sato.</div>

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CHAPTER 1

THE ENERGY LEVEL OF PARTICLES

1.1 Particles and Particle Ensembles

Materials and substances are composed of particles such as molecules, atoms and ions, which in turn consist of much smaller particles of electrons, positrons and neutrons. In electrochemistry, we deal primarily with charged particles of ions and electrons in addition to neutral particles. The sizes and masses of ions are the same as those of atoms: for relatively light lithium ions the radius is 6×10^{-11} m and the mass is 1.1×10^{-26} kg. In contrast, electrons are much smaller and much lighter than ions, being $1/1,000$ to $1/10,000$ times smaller (classical electron radius $= 2.8 \times 10^{-15}$ m, electron mass $= 9.1 \times 10^{-31}$ kg). Due to the extremely small size and mass of electrons, the quantization of electrons is more pronounced than that of ions. Note that the electric charge carried by an electron ($e = -1.602 \times 10^{-19}$ C) is conventionally used to define the elemental unit of electric charge.

In general, a single particle has unitary properties of its own. In addition, a large number of particles constitutes a statistical ensemble that obeys ensemble properties based on the statistics that apply to the particles. According to quantum statistical mechanics, particles with half an odd integer spin such as electron and positron follow the *Fermi statistics*, and particles with an even integer spin such as photon and phonon follow the *Bose-Einstein statistics*. For heavy particles of ions and atoms, which also follow either the Fermi or the Bose-Einstein statistics, both Fermi and Bose-Einstein statistics become indistinguishable from each other and may be represented approximately by the *Boltzmann statistics* in the temperature range of general interest.

Particles that obey Fermi statistics are called *Fermi particles* or *fermions*. The probability density of Fermi particles in their energy levels is thus represented by the Fermi function, $f(\varepsilon)$, that gives the probability of fermion occupation in an energy level, ε, as shown in Eqn. 1–1:

$$f(\varepsilon) = \cfrac{1}{\exp\left(\cfrac{\varepsilon - \varepsilon_F}{k\,T}\right) + 1} \; , \qquad\qquad\qquad (1\text{--}1)$$

where k is the Boltzmann constant, T is the absolute temperature, and ε_F is the thermodynamic potential of Fermi particle called the *Fermi level* or *Fermi energy*. Fermi statistics permits only one energy eigenstate to be occupied by one particle.

Particles that obey Bose-Einstein statistics are called *Bose particles* or *bosons*. The probability density of bosons in their energy levels is represented by the Bose-Einstein function as shown in Eqn. 1–2:

$$f(\varepsilon) = \cfrac{1}{\exp\left(\cfrac{\varepsilon - \varepsilon_B}{k\,T}\right) - 1} \; , \qquad\qquad\qquad (1\text{--}2)$$

where ε_B is the thermodynamic potential of Bose particles, called the *Bose-Einstein level* or *Bose-Einstein condensation level*. In Bose-Einstein statistics one energy eigenstate may be occupied by more than one particle.

Figure 1–1 shows the two probability density functions. In Fermi statistics, the probability of particle occupation (Fermi function) becomes equal to unity at energy levels slightly lower than the Fermi level ($f(\varepsilon) \doteq 1$ at $\varepsilon < \varepsilon_F$) and to zero at energy levels slightly higher than the Fermi level ($f(\varepsilon) \doteq 0$ at $\varepsilon > \varepsilon_F$), apparently decreasing from one to zero in a narrow energy range around the Fermi level, ε_F,
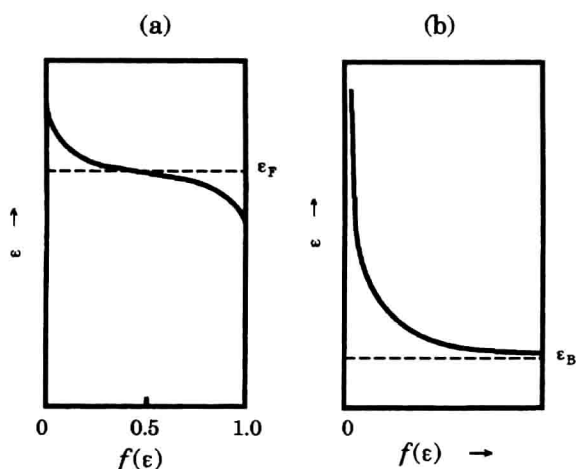
Fig. 1–1. Probability density functions of particle energy distribution: (a) Fermi function, (b) Bose-Einstein function. ε = particle energy; $f(\varepsilon)$ = probability density function; ε_F = Fermi level; ε_B = Bose-Einstein condensation level.

with increasing particle energy. On the other hand, in Bose-Einstein statistics the particle occupation probability decreases nearly exponentially with increasing particle energy above the Bose-Einstein level, ε_B. At high energy levels ($\varepsilon \gg \varepsilon_F$, $\varepsilon \gg \varepsilon_B$), both Fermi and Bose statistics may be approximated by the classical Boltzmann distribution function shown in Eqn. 1–3:

$$f(\varepsilon) = C \exp\left(\frac{-\varepsilon}{kT} \right) , \tag{1–3}$$

where C is a normalization constant, and the exponential factor of $\exp(-\varepsilon/kT)$ is called the *Boltzmann factor*. The Boltzmann function is valid for particle ensembles of low density at relatively high temperature.

According to quantum statistics, a particle is in a state of *degeneracy* if the particle ensemble follows either the Fermi or the Bose-Einstein statistics. We may assume that a particle is in the state of degeneracy at low temperatures and in the state of nondegeneracy at high temperatures. The transition temperature, T_c, (*degeneracy temperature*) between the two states is proportional to the 2/3 power of particle density, n, and inversely proportional to the particle mass, m. The degeneracy temperature for Fermi particles, that is called the *Fermi temperature*, is given by $T_c = \varepsilon_F/k = (h^2/8\,m\,k) \times (3\,n/\pi)^{2/3}$, where h is the Planck constant. The transition temperature from degeneracy to nondegeneracy is estimated to be about 10,000 K for free electrons in metals and about 1 K for ions and atoms in condensed phases. Electrons in metal crystals, then, are degenerated Fermi particles, while ions and atoms in condensed phases are nondegenerated Boltzmann particles in the temperature range of general interest.

In quantum mechanics, the energy of particles is quantized into a series of allowed energy levels, $\varepsilon_n = n^2 h^2/(8\,m\,a^2)$; where a is the space size for a particle, m is the particle mass, and n ($n = 1, 2, 3, \cdots$) is the quantum number. The interval of allowed energy levels is then given by $\Delta\varepsilon = \varepsilon_{n+1} - \varepsilon_n = (2n+1)h^2/(8\,m\,a^2)$, indicating that the greater the particle mass and the greater the particle space size, the smaller are the energy level intervals and, hence, the less are the quantization effects. The transition from the quantized energy levels to the continuous energy levels corresponds to the degeneracy–nondegeneracy transition of particle ensembles.

The particles we will deal with in this textbook are mainly electrons and ions in condensed solid and liquid phases. In condensed phases ions are the classical Boltzmann particles and electrons are the degenerated Fermi particles.

1.2 Chemical Potential and Electrochemical Potential

According to classical thermodynamics, the energy of particles may be represented in terms of entropy, internal energy, enthalpy, free energy, and free enthalpy, depending on the independent variables we choose to describe the state of particle ensemble system. We use in this textbook the free enthalpy, G, (also called the Gibbs free energy or Gibbs energy) with independent variables of temperature, T, and pressure, p; and the free energy, F, (also called the Helmholtz free energy) with independent variables of temperature, T, and volume, V.

The differential energy of a substance particle, i, in a particle ensemble is called the *chemical potential*, μ_i, when the particle is electrically neutral (atoms and molecules),

$$\mu_i = \left(\frac{\partial G}{\partial x_i} \right)_{p,T,x} = \left(\frac{\partial F}{\partial x_i} \right)_{V,T,x} ; \tag{1-4}$$

and the differential energy is called the *electrochemical potential*, $\bar{\mu}_i$, when the particle is electrically charged (ions and electrons),

$$\bar{\mu}_i = \left(\frac{\partial G}{\partial x_i} \right)_{p,T,x,\phi} = \left(\frac{\partial F}{\partial x_i} \right)_{V,T,x,\phi} ; \tag{1-5}$$

where x_i is the *molar fraction* of particle i and ϕ is the *inner potential* (electrostatic potential) of the particle ensemble. In Eqns. 1–4 and 1–5 we may use, instead of the molar fraction, x_i, the particle concentration, n_i, in terms of the number of particles in unit volume of the particle ensemble. For an ensemble comprising only the same particles of pure substance, the chemical potential becomes equal to the free enthalpy or free energy divided by the total number of particles in the ensemble $(\mu_i = G/N_i = F/N_i)$, and so does the electrochemical potential $(\bar{\mu}_i = G/N_i = F/N_i)$. The chemical potential may be defined not only for non-charged neutral particles but it can also be defined for charged particles by subtracting the electrostatic energy from the electrochemical potential of a charged particle, as is shown in Eqn. 1–9.

For an ensemble comprising a mixture of different kinds of substance particles, chemical thermodynamics introduces the *absolute activity*, λ_i, to represent the chemical potential, μ_i, of component i as shown in Eqn. 1–6:

$$\mu_i = k\,T \ln \lambda_i . \tag{1-6}$$

Further, introducing a standard state (reference state) where the chemical potential of component i is μ_i^* and the absolute activity is λ_i^*, we obtain from Eqn. 1–6 the following equation:

$$\mu_i - \mu_i^* = k\,T \ln \frac{\lambda_i}{\lambda_i^*}. \tag{1-7}$$

The ratio $\lambda_i / \lambda_i^* = a_i$ is called the *relative activity* or simply the *activity*, which of course depends on the standard state chosen. In general, the standard state of substances is chosen either in the state of pure substance $(x_i \to 1)$ based on the Raoult's law $[\,\mu_i^* = (\partial G / \partial x)_{x \to 1}\,]$ or in the state of infinite dilution $(x_i \to 0)$ based on the Henry's law $[\,\mu_i^* = (\partial G / \partial x)_{x \to 0}\,]$.

The ratio of the activity, a_i, to the molar fraction, x_i, or to the concentration, n_i, is the *activity coefficient*, $\gamma_i = a_i / x_i$ or $\gamma_i = a_i / n_i$. Then, Eqn. 1–7 yields Eqn. 1–8:

$$\mu_i = \mu_i^* + k\,T \ln a_i = \mu_i^* + k\,T \ln \gamma_i + k\,T \ln x_i. \tag{1-8}$$

The chemical potential, μ_i^*, in the standard state defines the *"unitary energy level"* of component i in a particle ensemble, and the term $k\,T \ln(\gamma_i x_i)$ is the *communal energy*, in which the term $k\,T \ln x_i$ is called the *cratic energy* representing the energy of mixing due to the indistinguishability of identical particles in an ensemble of particles [Gurney, 1953].

For charged particles an electrostatic energy of $z_i e \phi$ has to be added to the chemical potential, μ_i, to obtain the electrochemical potential, $\bar\mu_i$, as shown in Eqn. 1–9:

$$\bar\mu_i = \mu_i + z_i e \phi = \mu_i^* + k\,T \ln a_i + z_i e \phi, \tag{1-9}$$

where z_i is the charge number of component i, e is the elemental charge, and ϕ is the electrostatic inner potential of the ensemble.

1.3 Electrochemical Potential of Electrons

For high density electron ensembles such as free valence electrons in solid metals where electrons are in the state of degeneracy, the distribution of electron energy follows the Fermi function of Eqn. 1–1. According to quantum statistical dynamics [Davidson, 1962], the *electrochemical potential*, $\bar\mu_e$, of electrons is represented by the Fermi level, ε_F, as shown in Eqn. 1–10:

$$\bar\mu_e = \left(\frac{\partial G}{\partial n_e} \right)_{p,T,x,\phi} = \left(\frac{\partial F}{\partial n_e} \right)_{V,T,x,\phi} = \varepsilon_F, \tag{1-10}$$

where n_e is the electron concentration in the electron ensemble.

The *"state density"*, $D(\varepsilon)$, of electrons is defined as the number of energy eigenstates, each capable of containing one electron, for unit energy interval (energy differential) for unit volume of the electron ensemble. According to the electron theory of metals [Blakemore, 1985], the state density of free electrons in metals is given by a parabolic function of electron energy ε as shown in Eqn. 1–11:

$$D(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2\,m_e}{\hbar^2} \right)^{\frac{2}{3}} (\varepsilon - \varepsilon_0)^{\frac{1}{2}}, \qquad (1\text{--}11)$$

where ε_0 is the potential energy of electrons (the Hartree potential) in metals. The concentration, $n_e(\varepsilon)$, of electrons that occupy the eigenstates at an energy level of ε is given by the product of the state density and the probability density of Fermi function as in Eqn. 1–12:

$$n_e(\varepsilon) = D(\varepsilon) \cdot f(\varepsilon) = \frac{D(\varepsilon)}{\exp\left(\dfrac{\varepsilon - \varepsilon_F}{k\,T} \right) + 1}. \qquad (1\text{--}12)$$

Similarly, the concentration of eigenstates vacant of electrons is given by Eqn. 1–13:

$$D(\varepsilon) - n_e(\varepsilon) = D(\varepsilon)\{\, 1 - f(\varepsilon)\,\} = \frac{D(\varepsilon)}{\exp\left(\dfrac{\varepsilon_F - \varepsilon}{k\,T} \right) + 1}. \qquad (1\text{--}13)$$

It follows from Eqns. 1–12 and 1–13 that the state density is *half occupied* by electrons with the remaining half vacant for electrons at the Fermi level, ε_F, as shown in Fig. 1–2. Since the Fermi temperature of electrons ($T_c = \varepsilon_F / k$) in electron
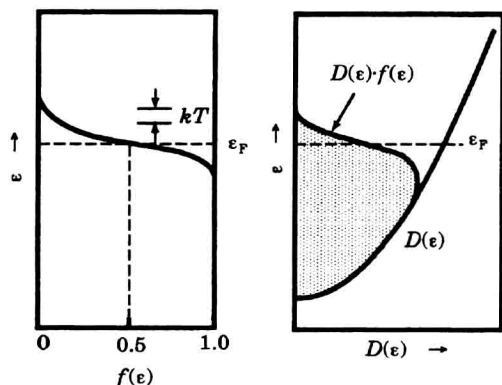

Fig. 1–2. Energy distribution of electrons near the Fermi level, ε_F, in metal crystals: ε = electron energy; $f(\varepsilon)$ = distribution function (probability density); $D(\varepsilon)$ = electron state density; $D(\varepsilon) \cdot f(\varepsilon)$ = occupied electron state density.