TECHNIQUES

OF ELECTROCHEMISTRY

Volume 1

Edited by

ERNEST YEAGER   **ALVIN J. SALKIND**

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PREFACE

Electrochemistry and electrochemical techniques are generally regarded as a specialty, rather than a basic discipline. Most of the researchers and practitioners using electrochemical techniques were trained in some other field, usually chemistry, biology, physics, electrical engineering, or chemical engineering. As a result, there has existed for some time a need for a compilation of the various standard techniques.

The chapters in this book, and in other volumes in the series, are all written by authors recognized for their work with electrochemical techniques. The material is directed to the nonelectrochemist as well as to the electrochemist who wishes to gain insight into techniques with which he is not very familiar. The background knowledge required of the reader is that ordinarily obtained in undergraduate courses in physical chemistry and instrument analysis. The emphasis here differs substantially from that in the Advances in Electrochemistry and Electrochemical Engineering series, edited by Paul Delahay and Charles Tobias. We refer the reader to this excellent series for reviews of a rather sophisticated nature, principally directed to the advanced technical student and the experienced electrochemist.

This volume is devoted mainly to techniques relating to electrode processes. In subsequent volumes those concerned with electrolytes, industrial and applied techniques, and biology and medicine will be covered.

We thank the contributors to this volume, who gave generously of their time in helping to make this first document of the techniques of electrochemistry. We hope that our colleagues will bring to our attention any errors of omission or commission that have occurred.

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I. MEASUREMENT OF REVERSIBLE ELECTRODE POTENTIALS*

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I. INTRODUCTION. VOLTA AND GALVANI POTENTIALS

   This chapter is devoted to a discussion of the measure-
ment of certain useful quantities known as electrode
potentials. There are many types of electrode. All
share one common property: they function as sites for
the transfer of electrical charge (electrons or ions)
across a phase boundary. In one of the contiguous phases
charge moves by electronic conductive processes, whereas
in the other it moves by an electrolytic mechanism
through the transport of charged particles (ions).
   The concept of electrode potential therefore involves
the notion of a difference in charge density or energy of
electrons in the two phases. This may be regarded as the
work required to move a unit charge or a standard number
of electrons from one phase across the boundary into the
other phase. It is here that fundamental difficulties
are encountered.
   Let us imagine an isolated homogeneous solid or liquid
phase. An excess of ions or electrons in the surface
imparts an electric potential ψ to that phase. This
potential, called the external potential or Volta poten-
tial of the phase, is defined (1) as the work necessary
to bring a unit point charge infinitely slowly from an
infinite distance up to the surface of the phase (or
rather to a distance of about 10^{-4} cm, below which image
forces become appreciable). The inner potential or Gal-
vani potential ϕ of the phase, however, is defined as the
work necessary to move a unit charge from infinity to the
interior of the phase. The two quantities evidently
differ by the surface potential χ:

$$\phi = \psi + \chi \tag{1}$$

The surface potential is independent of the excess charge
on the phase; it may arise from a double layer of
oriented dipoles in the surface.
   In principle, the Volta potential ψ can be measured,
since it is essentially a measure of the work required to
transfer charge within a single phase. On the contrary,
the surface potential and the Galvani potential are not
directly measurable. Galvani potential differences for
single electrodes represent differences in the inner
electric potential between two points in different phases
and therefore cannot be obtained experimentally. On the
contrary, differences of Galvani potential corresponding
to the transfer of ions between the internal parts of the
same phase can be measured readily. Although only rela-
tive values for the Galvani potentials of single

electrode processes are obtained, these can nonetheless
be of considerable utility.

A closer examination of interphase equilibrium is
appropriate here. If a neutral substance i is capable of
passing freely from one phase to another, a condition of
equilibrium will be reached when the chemical potential
of this component μ_i is the same in the two phases. In
an electrochemical system, however, in which only one
type of charge carrier can cross the boundary, equality
of the electrochemical potential μ_i^* must be achieved
before the phases are at equilibrium. This potential
depends not only on the chemical potential μ_i but on the
Galvani electric potential ϕ of the phase:

$$\mu_i^* = \mu_i + z_i F \phi \tag{2}$$

where F is the faraday and z_i is the number of charges
borne by the charge carrier.

For a simple metallic electrode system of the type
$M^+(1);M(s)$, where 1 represents the liquid (solution)
phase and s the solid phase, the ion M^+ is the charge
carrier and the electrochemical process can be written

$$M^+(1) + e = M(s) \tag{3}$$

Hence the Galvani potential difference at equilibrium $\Delta\phi$
becomes

$$\Delta\phi = \phi_s - \phi_1 = \frac{\mu_1 - \mu_s}{z_i F} \tag{4}$$

where μ is the chemical potential of the charge-bearing
ions in the two phases at equilibrium. Fundamentally, $\Delta\phi$
cannot be measured for reasons already indicated. At the
same time, it is evident from Eqs. 2 and 4 that the dif-
ference of chemical potential of a single charge species
in two different phases is also indeterminate. These
difficulties have led to the conventional definition of
"single electrode potentials" in terms of Galvani poten-
tial differences within a single phase rather than in
terms of $\phi_s - \phi_1$.

II. CELL REACTION AND ELECTROMOTIVE FORCE

It is clear that all electrode processes involve a
transfer of charge from one phase to another. One
example of such an electrochemical process is set forth
in Eq. 3. Such processes can be regarded as oxidation
half-reactions or reduction half-reactions, as electrons
are produced or consumed, respectively, in the reaction

as written.

Complete oxidation-reduction (redox) reactions consist of two half-reactions, one consuming the electrons that are produced in the other. Inasmuch as electrons can be moved from place to place through metallic conductors when a potential gradient exists, it is possible to isolate the oxidation half-reaction from the reduction half-reaction. The complete reaction can then proceed only when the connection is made; it will continue until the connection is broken or equilibrium is reached.

Many oxidation or reduction half-reactions can be made to occur as electrode processes and are characterized by high electrochemical reversibility. Examples of such reactions and the electrodes corresponding to them are as follows:

Half-reaction	Electrode
$2H^+ \quad + 2e = H_2(g)$	$Pt; H_2(g), H^+$
$Zn^{2+} \quad + 2e = An(s)$	$Zn^{2+}; Zn$
$Fe^{3+} \quad + \ e = Fe^{2+}$	$Fe^{3+}, Fe^{2+}; Pt$
$AgCl(s) + \ e = Ag(s) + Cl^-$	$Cl^-, AgCl; Ag$

When no metal is involved in the reaction, the transfer of electrons takes place by means of some chemically inert metal such as gold or platinum.

For example, consider a cell composed of a zinc electrode, a silver-silver chloride electrode, and a solution of zinc chloride:

$$Zn; \ Zn^{2+}, \ Cl^-, \ AgCl; \ Ag$$
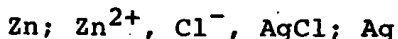
The two half-reactions (given above) are added to obtain the complete cell reaction. When the zinc and silver terminals are connected through a resistance, an electric current is found to flow through the external conduit because of the potential difference between the electrodes. The direction of flow is from the more negative electrode (where oxidation takes place spontaneously when the electrodes are connected) to the positive electrode (where reduction takes place). At the same time, an ionic current flows through the zinc chloride solution to maintain electrical neutrality; all of the cations and anions present contribute to this current according to their individual mobilities and charges.

The difference of potential between the zinc and silver electrodes is measured by balancing it with an equal and opposite voltage from a potentiometer, so that no current flows through the external circuit. In order not to include unwanted metal-to-metal potentials in the

measured potential difference, the terminal pieces at each electrode must be of the same metal. The simplest way to accomplish this would be to add a piece of zinc to the silver electrode or a piece of silver to the zinc electrode. The same objective is achieved by the use of two copper wires connecting the cell to the measuring instrument. The measured potential difference is then actually the driving force of the cell reaction and hence is termed the electromotive force (emf). It is a measure of the tendency toward reaction.

The measured emf is thus regarded as the difference of the inner electric potentials (Galvani potential ϕ) of the two identical metallic terminals attached to the electrodes. Although the emf of the whole cell is the only measurable quantity, it is actually composed of two or more Galvani potential differences arising at the individual phase boundaries. In the zinc-silver chloride cell just outlined (provided with terminals of the same metal), there are three phase boundaries and three ϕ terms to be considered. In many cells a liquid-liquid junction adds a fourth. Unfortunately, these individual Galvani potential differences cannot be evaluated separately.

III. CONVENTIONS FOR ELECTROMOTIVE FORCE AND ELECTRODE POTENTIALS

The complete cell reaction, formed by adding the two half-reactions in the preceding example, could be written to signify either the spontaneous reduction of zinc ions by silver metal or the spontaneous reduction of silver chloride by zinc metal. Although either process may occur, given the proper conditions of temperature, pressure, and concentration, by convention the cell reaction is written as if the oxidation process is occurring at the electrode on the left of the written cell scheme. Hence

$$Zn + 2AgCl = ZnCl_2 + 2Ag \tag{5}$$
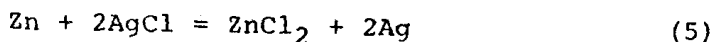
To bring about uniformity in relating the sign of the emf to the direction of the spontaneous chemical reaction that can occur in the cell, it has been necessary to adopt a sign convention. Furthermore, a convention for the sign and magnitude of the potential of single electrodes is made necessary by the impossibility of measuring Galvani potential differences for single electrode processes.

The Stockholm convention drafted by the International

Union of Pure and Applied Chemistry (IUPAC) in 1953 went far toward bringing about the desired uniform practice in the treatment of electrochemical data throughout the world. This statement, with minor revisions made in 1968 (2), is concise and useful and is repeated here in its entirety:

"The electric potential difference for a galvanic cell. The cell should be represented by a diagram, for example:

$$Zn \mid Zn^{2+} \mid Cu^{2+} \mid Cu$$

The electric potential difference ΔV is equal in sign and magnitude to the electric potential of a metallic conducting lead on the right minus that of an identical lead on the left.
   "When the reaction of the cell is written as:

$$\frac{1}{2\ Zn} + \frac{1}{2\ Cu^{2+}} \rightarrow \frac{1}{2\ Zn^{2+}} + \frac{1}{2\ Cu}$$
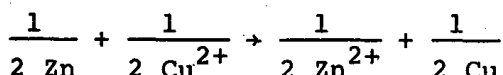
this implies a diagram so drawn that this reaction takes place when positive electricity flows through the cell from left to right. If this is the direction of the current when the cell is short-circuited, as it will be in the present example (unless the ratio $[Cu^{2+}]/[Zn^{2+}]$ is extremely small), the electric potential difference will be positive.
   "If, however, the reaction is written as:

$$\frac{1}{2\ Cu} + \frac{1}{2\ Zn^{2+}} \rightarrow \frac{1}{2\ Cu^{2+}} + \frac{1}{2\ Zn}$$
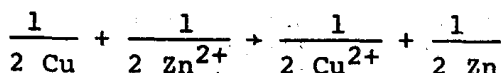
this implies the diagram

$$Cu \mid Cu^{2+} \mid Zn^{2+} \mid Zn$$

and the electric potential difference of the cell so specified will be negative (unless the ratio $[Cu^{2+}]/[Zn^{2+}]$ is extremely small).
   "The limiting value of the electric potential difference for zero current through the cell is called the electromotive force and denoted by E.
   "Electrode potential. The so-called electrode potential of an electrode (half-cell) is defined as the electromotive force of a cell in which the electrode on the left is a standard hydrogen electrode and that on the right is the electrode in question. For example, for the

zinc electrode (written as Zn^{2+} | Zn) the cell in question is:

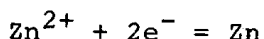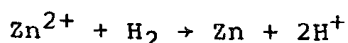$$Pt \mid H_2 \mid H+ \mid Zn^{2+} \mid Zn$$
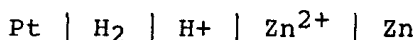
The reaction taking place at the zinc electrode is:

$$Zn^{2+} + 2e^- = Zn$$

The latter is to be regarded as an abbreviation for the reaction in the mentioned cell:

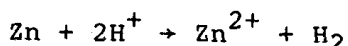$$Zn^{2+} + H_2 \rightarrow Zn + 2H^+$$

In the standard state the electromotive force of this cell has a negative sign and a value of -0.763 V. The electrode potential of the zinc electrode is therefore -0.763 V.

"The symbol $Zn \mid Zn^{2+}$ on the other hand implies the cell:

$$Zn \mid Zn^{2+} \mid H^+ \mid H_2 \mid Pt$$
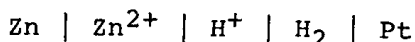
in which the reaction is:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

The electromotive force of this cell should <u>not</u> be called an electrode potential."

A somewhat different formulation of conventions has been drafted by the International Commission of Electrochemical Thermodynamics and Kinetics (CITCE) (3). The measured quantity is termed the <u>electric tension</u> U of a cell and is defined by $\phi l - \phi r$, where l and r refer to the leads (of the same metal) attached to the left and right electrodes, respectively, of the cell as written. The <u>chemical tension</u> or emf E is equal in magnitude and opposite in sign to the reversible cell tension U_{rev} measured under conditions of electrochemical equilibrium, that is, when no current is flowing. These definitions lead to the same sign for E as does the IUPAC convention. The electrode potential, or <u>relative electrode tension</u> in the CITCE nomenclature, is defined as the reversible cell tension of the cell in which the electrode in question (on the left of the cell scheme) is combined with a standard hydrogen electrode (on the right). This arrangement of electrodes is opposite to that specified

by the IUPAC convention, but the CITCE definition fortun-
ately leads again to a result consistent with the IUPAC
convention.

The CITCE formulation is more general than that of the
IUPAC in that it recognizes nonequilibrium conditions
existing during current flow as well as the state of
electrochemical equilibrium (no current flow). When a
current passes through a galvanic cell, the cell tension
is altered, but U_{rev} and E remain invariant in magnitude
and sign. In this chapter we deal almost entirely with
equilibrium electrode states and have no use for the
nomenclature of tensions.

IV.   THERMODYNAMICS OF REVERSIBLE CELLS

A galvanic cell is said to be reversible when the cell
reaction can be reversed at will by raising or lowering
the balancing voltage by an infinitesimal amount above or
below the cell emf. In cells which are incapable of
reversible operation, a change in direction of the cur-
rent flowing through the cell may produce a reaction
entirely different from that occurring on spontaneous
discharge. Furthermore, reversible cells can be operated
under irreversible conditions. Only when the spontaneous
process is allowed to proceed at an infinitely slow rate
is the measured emf a true indication of the reversible
free energy change or maximum attainable work of the cell
reaction.

A.   Gibbs Energy of the Cell Reaction

The usefulness of emf measurements of reversible cells
derived from the fundamental thermodynamic relationship

$$\Delta G = -nFE \tag{6}$$

according to which ΔG, the molar change in Gibbs energy
(free energy) when the cell reaction takes place rever-
sibly, is simply related to the emf E and to n, the
number of faradays of electricity that must pass through
the cell to produce the amount of reaction in question.
The Gibbs energy is, of course, an extensive quantity in
contrast to the intensive quantities ϕ and E.

As we have stated, cell reactions are formulated as if
oxidation were taking place at the left electrode and
reduction at the right electrode of the cell scheme as
written. If this is indeed the actual situation and the
polarity of the cell is - +, the emf will be given a
positive sign in accord with the IUPAC convention, sig-

nifying that the cell reaction takes place spontaneously
in the direction as formulated (ΔG negative). When, on
the contrary, the polarity is found to be + -, the emf is
negative, signifying that ΔG is positive and that the
reaction proceeds from right to left.

These principles apply with equal force to the elec-
trode potential, which is, as already seen, the emf of
the complete cell in which the electrode in question (on
the right) is combined with the standard hydrogen elec-
trode (on the left). The term "standard" signifies that
all species participating in the half-reaction are in
their thermodynamic standard states; for ionic species
this is the hypothetical state in which the ionic activ-
ity is 1. The standard emf is denoted E°. As a conse-
quence of these conventions, half-reactions at single
electrodes are written as reductions; the sign of the
electrode potential then indicates the actual direction
of the spontaneous cell reaction when the electrode is
combined with the standard hydrogen electrode.

A positive electrode potential thus means that when
the electrode is combined with the standard hydrogen
electrode, oxidation takes place spontaneously at the
site of the standard electrode while reduction takes
place at the first electrode. The most noble metals have
positive electrode potentials because hydrogen is able to
reduce their ions to the elemental state. Similarly, the
most electroactive elements (the alkali metals, zinc,
etc.) have negative electrode potentials because these
elements are able to reduce hydrogen ions to hydrogen
gas.

B. Chemical Equilibrium and Electromotive Force

To demonstrate the relationships between the emf and
chemical equilibrium, it is helpful to write a cell reac-
tion in general terms, as follows:

$$aA + bB + \cdots = uU + vV + \cdots \tag{7}$$
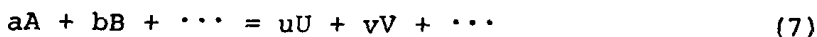
and to introduce the relative activity (or activity) a
of each reactant and product i. The activity in modern
definition is a dimensionless quantity that derives its
numerical magnitude from the difference between the chem-
ical potential μ_i and the chemical potential in a refer-
ence standard state μ_i^o:

$$\mu_i - \mu_i^o = RT \ln a_i = RT \ln (m_i \gamma_i) \tag{8}$$

where m_i is molality and γ_i is the activity coefficient

on the molal scale of concentration. Activities based on
other concentration scales differ numerically from $m_i \gamma_i$,
but interconversion of values is not difficult (4).

The value of ΔG for the general reaction 7 is given by

$$\Delta G = u\mu_U + v\mu_V + \ldots - a\mu_A - b\mu_B - \cdots \qquad (9)$$

from which are obtained, by combination with Eqs. 6 and
8,

$$\Delta G = \Delta G° + RT \ln \frac{a_U^u \, a_V^v \cdots}{a_A^a \, a_B^b \cdots} \qquad (10)$$

and

$$E = E° - \frac{RT}{nF} \ln \frac{a_U^u \, a_V^v \cdots}{a_A^a \, a_B^b} \qquad (11)$$

The standard free energy change $\Delta G°$ has been written for
its equivalent $u\mu_U° + v\mu_V° + \ldots - a\mu_A° - b\mu_B° - \cdots$.

Equation 11 is sometimes called the Nernst equation.
Inasmuch as the standard emf $E°$ is a function only of
temperature, pressure, and the standard states chosen,
this equation describes the effect of the concentrations
(activities) of the reactants and products on the elec-
trode potential. A tenfold change in the activity quo-
tient is seen to alter the electrode potential by about
0.06 V when $n = 1$. It is not uncommon for changes of
polarity to be observed when conditions are such that the
concentrations of reactants and products vary widely.
Values of the Nernst slope $(RT \ln 10)/F$ from 0 to 100°C
are listed in Table I (5).

Another important conclusion emerges from Eq. 10. When
the cell reaction is at equilibrium, there is no driving
force to produce further reaction and both E and ΔG are
zero. The activity quotient is then equal to the
equilibrium constant K. Hence

$$E° = - \frac{\Delta G°}{nf} = \frac{RT}{nF} \ln K \qquad (12)$$

Since each electrochemical half-reaction (compare Eq. 3)
may be regarded as a variation of the prototype reaction

$$\text{oxidant} + n\text{e} = \text{reductant} \qquad (13)$$

the electrode potential measures the strength of the oxi-

TABLE I

Values of $(RT \ln 10)/F$ from 0 to 100°C

t (°C)	$(RT \ln 10)/F$ (V)
0	0.054197
5	0.055189
10	0.056181
15	0.057173
20	0.058165
25	0.059157
30	0.060149
35	0.061141
40	0.062133
45	0.063126
50	0.064118
55	0.065110
60	0.066102
65	0.067094
70	0.068086
75	0.069078
80	0.070070
85	0.071062
90	0.072054
95	0.073046
100	0.074038

dant with respect to the oxidizing power of hydrogen ions at unit activity. In other words, it reflects the equilibrium constant for the reaction

$$\text{oxidant} + \frac{1}{2} H_2(g) = \text{reductant} + H^+ \quad (a = 1) \qquad (14)$$
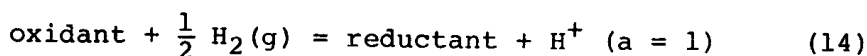
The standard electrode potential E° similarly reflects the magnitude of the equilibrium constant of this reaction when all the substances are at unit activity.

The variation of the single electrode potential E with the concentrations of oxidant, reductant, and other species participating in the electrode half-reaction is expressed in terms of the standard electrode potential E° by the Nernst equation (Eq. 11). When this formula is applied to the electrode potential, the activities of hydrogen and hydrogen ion, being unity, disappear.