Standard Potentials in Aqueous Solution

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Preface

Standard electrode potentials (variously called redox potentials, oxidation-reduction potentials, etc.) are widely used by the scientific community because they provide predictive power about the course of chemical reactions and the behavior of metal/solution interfaces. They represent crucial reference data for diversified disciplines, ranging from the physical sciences to geology, oceanography and biology. Thus, standard potentials are of general interest to all practicing chemists and of special relevance in such widely disparate areas as corrosion research, biochemistry, chemical engineering, physical chemistry, analytical chemistry, electrochemistry, and inorganic synthesis. The need for a reliable compilation has been admirably filled by the classic monograph of Wendell M. Latimer, *Oxidation Potentials* (or *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*) first published in 1938 and last revised in 1952. Although this widely used work was later supplemented by numerous other compilations, Latimer has remained the authoritative reference in this field. A desire to incorporate a wealth of new data and to bring notations and conventions into accord with current usage has led Commissions I.3 (Electrochemistry) and V.5 (Electroanalytical Chemistry) of the International Union of Pure and Applied Chemistry (IUPAC) to undertake the preparation of this book.

Latimer had admirable features of consistency throughout the book. This is an unmatched advantage of single authorship. However, Latimer himself recognized the corollary limitation: "Much...should have been recalculated by modern methods *but the labor involved is beyond the capacity of a single author*" (quoted from the Preface of the first edition, Prentice-Hall, Inc., New York, 1938; emphasis added). That constraint has since become genuinely insurmountable: no single individual could currently undertake such a Herculean task. In view of this situation we have opted for multiple authorship. Chapters were prepared by knowledgeable specialized experts and reviewed by referees whose names are included in this book. It is hoped that the potentials given here represent the *critically selected* values or at least the best estimates now available. To keep this book to a manageable size, discretion was exercised as to which half-reactions would be included for a given element. For similar reasons, data have been limited to a single temperature, 25°C. Furthermore, no attempt was made to give complete citations to all pertinent original publications. The bibliography has been restricted to previous important compilations and "key papers." This monograph is intended as a convenient aid to the reader and the bibliography is *not* meant to be a pantheon of all contributions in the field.

The book is organized in the following way. The first two chapters deal with units, conventions, methods of determination, and the concept of the single electrode potential. These are followed by standard potentials and thermodynamic data for the elements grouped according to their positions in the periodic table.

The editors gratefully acknowledge the assistance and support of the members of the IUPAC Commissions I.3 and V.5, and sincerely thank all those involved (authors and reviewers), who contributed to this effort without financial remuneration to ensure that the book could be produced at a price affordable to students and the rest of the scientific community.

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1

Standard Electrode Potentials: Units, Conventions, and Methods of Determination*

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I. SYMBOLS

The standard electrode potential is a physical quantity and, like all physical quantities, it is the product of a numerical value (a pure number) and a unit (volt). It is represented by the symbol $E°$, the superscript indicating the standard nature of the quantity. More precisely, $E°$ in the context of this book is the standard potential of a cell reaction when that reaction involves the oxidation of molecular hydrogen to solvated protons. When necessary the reaction will be indicated in parentheses or brackets after the symbol $E°$, for example,

$$E°(\mathrm{Zn}^{2+}(\mathrm{aq}) + \mathrm{H}_2(\mathrm{g}) \rightarrow 2\mathrm{H}^+(\mathrm{aq}) + \mathrm{Zn}(\mathrm{s})) \qquad (1.1)$$

which may be abbreviated [assuming that the reaction $\mathrm{H}_2(\mathrm{g}) \rightarrow 2\mathrm{H}^+(\mathrm{aq}) + 2\mathrm{e}^-$ is always present]

$$E°(\mathrm{Zn}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \rightarrow \mathrm{Zn}) \qquad (1.2)$$

or

$$E°(\mathrm{Zn}^{2+}/\mathrm{Zn}) \qquad (1.3)$$

Other important physical quantities to be used in this work are:

T	Thermodynamic temperature
G	Molar Gibbs energy
S	Molar entropy
C_p	Molar heat capacity
H	Molar enthalpy
x_A	Mole fraction of species A

---

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m_A	Molality of species A (number of moles of A dissolved in 1 kg of solvent	
c_A	Concentration of species A, also indicated as [A] (number of moles of A contained in 1 liter of solution, formerly called molarity)	
p_A	Partial pressure of species A	
p_A^*	Fugacity of species A	
a_A	Activity of species A	
f_A	Activity coefficients	Mole fraction basis
γ_A		Molality basis
y_A		Concentration basis
K	Thermodynamic equilibrium constant of a reaction	
n	Charge number of a cell reaction [see Section III, following (1.8)]	

II. UNITS AND CONSTANTS

The units of energy and potential employed are those adopted by the Conférence Générale des Poids et Mesures and known as SI (Système International) units. The primary energy unit is the joule, defined in terms of the SI base units, the kilogram, meter, and second:

$$1 \text{ joule} \equiv 1 \text{ J} \equiv 1 \text{ kg m}^2 \text{ s}^{-2} \tag{1.4}$$

Many data in the literature are quoted in calories. They have been converted into joules using the conversion factor 4.1840 J cal^{-1}. Also, 1 eV = $1.6021892 \times 10^{-19}$ J. The unit of electrical potential difference is the volt, defined in terms of these SI base units together with the ampere:

$$1 \text{ volt} \equiv 1 \text{ V} \equiv 1 \text{ kg m}^2 \text{ s}^{-3} \text{ A}^{-1} \equiv 1 \text{ J A}^{-1} \text{ s}^{-1} \tag{1.5}$$

Pressure, molality, and concentration units have most usually been

$$1 \text{ atmosphere} \equiv 101\,325 \text{ N m}^{-2} \text{ (Pa)}$$

$$1 \text{ mol kg}^{-1} \text{ (mass of solvent)}$$

$$1 \text{ mol L}^{-1} = 1 \text{ mol dm}^{-3} \text{ (volume of solution)}$$

and these will continue to be used here. Conversion of pressure or concentration units to the coherent SI units of 1 N m^{-2} and 1 mol m^{-3} involves recalculation of the values of standard thermodynamic quantities [see (1.4) and (1.5)]. Since no measure of international agreement has been reached on this awkward problem, the traditional units have been retained here.

Important fundamental constants used in this work are [1]:

Celsius temperature defined by

$$t = T - T_0 \quad \text{where } T_0 = 273.15 \text{ K}$$

Faraday constant: $F = 9.648456 \times 10^{4}\ \mathrm{C\ mol^{-1}}$

Gas constant: $R = 8.31441\ \mathrm{J\ mol^{-1}\ K^{-1}}$

The combination of fundamental constants RT/F is frequently used. At 25°C it has the value

$RT/F = 0.0256926\ \mathrm{V}$

$(RT/F)\ \ln 10 = 0.0591594\ \mathrm{V}$

III. CONVENTIONS

The galvanic cell is represented by a diagram. For example, the chemical cell consisting of an aqueous solution of hydrogen chloride of concentration 1 mol $\mathrm{L^{-1}}$, a platinum-hydrogen electrode with hydrogen at a partial pressure of 1 atm, and a silver-silver chloride electrode is represented by the diagram

$$\mathrm{Cu(s)} \;\vdots\; \mathrm{Pt(s)} \mid \mathrm{H_2(g)} \mid \mathrm{HCl(aq)} \mid \mathrm{AgCl(s)} \mid \mathrm{Ag(s)} \;\vdots\; \mathrm{Cu(s)}$$

$$p = 1\ \mathrm{atm} \qquad c = 1\ \mathrm{mol\ L^{-1}} \tag{1.6}$$

in which the Cu(s) at either end of the cell represent the terminals of the cell, which must be of the same material (although not necessarily copper). A single vertical bar represents a phase boundary; a dashed vertical bar (⋮) represents a junction between miscible liquids, and double dashed vertical bars (⋮⋮) represent a liquid junction in which the liquid junction potential has been eliminated by some more or less accurate extrapolation or other procedure.

The electric potential difference E of a cell written in this way is always taken as the potential of the right-hand terminal with respect to that of the left-hand terminal. Thus if the cell is written down in the opposite direction, the sign of E must be reversed.

The reaction occurring in the cell is written down in the direction that corresponds to the flow of electrons in the external circuit from the left-hand terminal to the right-hand terminal. Thus for the cell (1.6), the reaction is

$$\mathrm{H_2(g) + 2AgCl(s) \rightarrow 2H^{+}(aq) + 2Cl^{-}(aq) + 2\ Ag(s)} \tag{1.7}$$

Again, if the cell is written in the opposite direction, the reaction must also be reversed.

The potential difference measured becomes of thermodynamic significance when the current through the external circuit becomes zero, all local charge transfer equilibria across phase boundaries represented in the cell diagram (except at electrolyte-electrolyte junctions) and local chemical equilibria being established. The resulting value of E is termed the electromotive force (emf) of the cell, a name that no longer represents the reality of the concept but which is so well established that it seems impossible to replace (the same is true for the equivalent terms in other languages).

When all species in the cell reaction are in their standard states (pure solids, unit standard concentrations, etc.), the measured emf of the cell is, to a good approximation, equal to the standard potential of the reaction in the cell $E°$, which is also given by

$$E^\circ = -\Delta G^\circ/nF = (RT/nF)\ \ln K \tag{1.8}$$

where ΔG° is the standard Gibbs energy change in the cell reaction and K is the thermodynamic equilibrium constant of this reaction. n, the charge number of the reaction, is the number of electrons passing around the external circuit when one unit of the cell reaction occurs as written [e.g., for (1.7), $n = 2$].

The *standard electrode potential* of an electrode reaction $E^\circ(Zn^{2+}/Zn)$ is the standard potential of a reaction in a cell whose left-hand electrode is a hydrogen electrode. [Note that this is the point at which the present (IUPAC) convention differs from that used in Latimer's book, where the hydrogen electrode is on the right of the cell in its standard format. Clearly, the standard electrode potentials consequently have the opposite sign.] For example, in the IUPAC convention

$$E^\circ(Zn^{2+}/Zn) = -0.763\ V$$

At the end of the section on each element a summary of the principal standard electrode potentials for that element at 298.15 K is given in the form of a potential diagram. This summarizes the oxidation states of the element with the highest oxidation state on the left. The numbers between each state give E°/V.

IV. STANDARD STATES IN SOLUTION

For many phases in galvanic cells the standard state is the pure element or pure compound at unit pressure and at the temperature of the experiment, frequently 25°C. For mixtures that are miscible in all proportions these standard states may be retained by expressing the composition of the mixture in terms of mole fraction (= pure component). This means, of course, that all components in a mixture miscible in all proportions cannot be simultaneously in their standard states.

The chemical potential of a species A is then written

$$\mu_A = \mu^\circ(p,T) + RT\ \ln a_A \tag{1.9}$$

where the activity

$$a_A = f_A x_A \tag{1.10}$$

Note that μ° is the chemical potential in the standard state when $x_A \rightarrow 1$, $f_A \rightarrow 1$, so that the standard state is also the reference state (the state where the activity coefficient goes to a defined limit, i.e., unity).

For many electrolytes the symmetrical system described above is inconvenient, partly because salts and solvents are often not completely miscible. It is therefore more common to use systems based on molality or concentration. The former has the advantage that it is independent of temperature. Equation (1.9) remains valid for the solute but the activity is given by

$$a_A = \gamma_A(m_A/m^\circ) \tag{1.11}$$

or

$$a_A = y_A(c_A/c^\circ) \tag{1.12}$$

where $m^\circ(c^\circ)$ is the standard molality (concentration) 1 mol kg^{-1} (1 mol dm^{-3}). Thus the standard state is at a composition in the region of 1 mol kg^{-1} or 1 mol L^{-1} but is significantly different from unit molality or unit concentration because electrolytes are substantially nonideal. This is sometimes expressed by saying that the standard state is "a hypothetical ideal state of unit molality or unit concentration."

In this book the standard state in solution is the hypothetical ideal state of unit concentration measured in mol L^{-1} (unless otherwise stated). Thus equilibrium constants are dimensionless, being products of activities, and c° is taken as 1 mol L^{-1} for all species in solution.

As the solute becomes more and more dilute its mutual interactions decrease and vanish as m_A or $c_A \rightarrow 0$. In this reference state γ_A or $y_A = 1$. Thus the reference state is defined as

$$m_A \rightarrow 0 \quad \gamma_A \rightarrow 1 \tag{1.13}$$

or

$$c_A \rightarrow 0 \quad y_A \rightarrow 1 \tag{1.14}$$

while the standard state is defined by

$$a_A^\circ = 1 \tag{1.15}$$

In this standard state the Gibbs energy of the solvent in aqueous solutions is not very different from that in the pure state. Hence the solvent may be regarded as being approximately in its standard state, too (if that is taken as the pure substance). However, the approximation may in fact be rather poor, and this difficulty is avoided by omitting the solvent from the cell reaction in most of the examples given in this book.

V. STANDARD STATE IN THE GAS PHASE

Up to the present time the generally used standard state pressure (p°) has been 1 standard atmosphere (101 325 Pa). During the time that this book was prepared, a recommendation for a change in this standard state was proposed [2]. The new recommendation for the standard state pressure made by IUPAC is 10^5 Pa (1 bar). In view of the fact that all the data collected in this book are referred to the standard pressure of 1 atm, it has been decided to retain this as the standard state pressure, at which the standard electrode potential is specified.

At the same time, it should be noted that the change to the standard state of 10^5 Pa would affect very few of the data presented here. The major effect for most standard potentials would be that the standard hydrogen electrode potential shifts 0.169 mV in the positive direction, that is, 0.169 mV would have to be subtracted from the quoted standard electrode potentials on this account. For cell reactions that otherwise involve only condensed

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