

Comprehensive Treatise of Electrochemistry

1

The Double Layer

Edited by

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Volume 1: The Double Layer

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Preface to Comprehensive Treatise of Electrochemistry

Electrochemistry is one of the oldest defined areas in physical science, and there was a time, less than 50 years ago, when one saw "Institute of Electrochemistry and Physical Chemistry" in the chemistry buildings of European universities. But, after early brilliant developments in electrode processes at the beginning of the twentieth century and in solution chemistry during the 1930s, electrochemistry fell into a period of decline which lasted for several decades. The systems were too complex for the theoretical concepts of the quantum theory, which was too little understood at a phenomenological level to allow its ubiquity in applications in so many fields to be comprehended.

However, a new growth began faintly in the late 1940s, and clearly in the 1950s. This growth was exemplified by the formation in 1949 of what is now called The International Society for Electrochemistry. The usefulness of electrochemistry as a basis for understanding conservation was the focal point in the founding of this Society. Another very important event was the choice by NASA in 1958 of fuel cells to provide the auxiliary power for space vehicles.

With the new era of diminishing usefulness of the fossil fuels upon us, the role of electrochemical technology is widened (energy storage, conversion, enhanced attention to conservation, direct use of electricity from nuclear-solar plants, finding materials which interface well with hydrogen). This strong new interest is not only in the technological applications of electrochemistry. Quantum chemists have taken great interest in redox processes. Organic chemists are interested in situations where the energy of electrons is as easily controlled as it is at electrodes. Some biological processes are now seen in electrodic terms, with electron transfer to and from materials which would earlier have been considered to be insulators.

It is now time for a comprehensive treatise to look at the whole field of electrochemistry.

The present treatise was conceived in 1974, and the earliest invitations to authors for contributions were made in 1975. The completion of the early volumes has been delayed by various factors.

There has been no attempt to make each article emphasize the most recent situation at the expense of an overall statement of the modern view. This treatise is not a collection of articles from *Recent Advances in Electrochemistry* or *Modern Aspects of Electrochemistry*. It is an attempt at making a mature statement about the present position in the vast area of what is best looked at as a new interdisciplinary field.

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Preface to Volume 1

The present volume is the first in the Comprehensive Treatise series and deals with the double layer at the electrode-solution interface. This seems to be an appropriate place to begin, and the authors, whom the editors have carefully chosen to describe the present position in this field, are those who have contributed greatly to the field of electrochemistry in the last quarter of a century or so.

We must admit that there are some fundamental uncertainties with respect to the double layer. For one thing, the present theory is a mixture of continuum and particle concepts. The present theory of the double layer depends greatly on dielectric constant concepts, which are concepts more typical of nineteenth- than twentieth-century thinking. There are no theories in the double layer that are entirely particulate.

Again, it is remarkable that although the concepts of the double layer deal with the interplay between various layers of electronic charges, there has been no quantum mechanical contribution made to this area of study. A quantum statistical theory of the double layer is what is most needed at the present time.

Thus, this volume must be regarded as presenting a picture of the state of a field which is probably on the plateau of further development and which stands before a substantial change.

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Notation

a_{\pm}	mean activity; a_i , a_j activities of species i, j	E_H	measured potential on the hydrogen scale in the same solution
c	concentration (molar); velocity of light (cm s^{-1})	E_{NHE}	measured potential on the scale of the normal hydrogen electrode
C_1, C_2 , etc.	differential capacities of regions 1, 2, etc.	E_{SS}	energy of surface states
cn	coordination number	E_{VB}	energy of valence band
d	thickness, e.g., of a film, or of a dielectric	\mathcal{E}	electrostatic field
D	diffusion coefficient	f_{\pm}	rational activity coefficient (mean)
$D_{x_{\psi}}$	dissociation energy for molecule x_{ψ}	F	Faraday constant
D	dielectric displacement	g	interaction parameter, in non-Langmuir isotherms
e	electron charge	$g_{ij}(r_{ij})$	radial distribution function (of distance r_{ij}); pair correlation function
E	potential (cf. electrode, on metal-solution potential difference, in kinetics)	G, H, S	Free energy, enthalpy, and entropy (per mole)
E_{cal}	measured potential on the scale of the normal calomel electrode	h	Planck's constant
E_{CB}	energy of conduction band	i	current density
E_F	Fermi level	I_0	intensity of light

I	current moment of inertia	P	pressure (Pa), e.g., P_{O_2} , presence of a gas, O_2 ; momentum
J	flux; quantum number for rotation	$P(E)$	probability (for state of energy E)
k	with subscript, rate constants	q, Q	partition function
k_s	salting out (Setschenow) coefficient	Q_i	charge for some species, i , e.g., on a surface
k	Boltzmann constant	r_i	radius of an ion
K	thermodynamic equilibrium constant	r_{ij}	distance between particles i, j
K_1, K_2 , etc.	integral capacities of regions 1, 2, etc.	R	molar gas constant; resistance
m	concentration (molal); mass of particle	t	time
M	molarity; N no longer used; number of particles	T	absolute temperature (K); with subscript, nmr relaxation times (T_1, T_2)
n	solvation number; quantum number for vibration	U	internal energy
n_{CB}	density of electronic states in the conduction band	v	velocity (usually of a reaction); mobility of ion under 1 V cm^{-1} charge
n_e	concentration of electrons	V	volume; partial molar volume
n_e^s	concentration of electrons at the surface	x, y, z	coordinate system; distances
n_e^0	concentration of electrons in bulk	y_{\pm}	stoichiometric activity coefficient (mean, molar)
n_p	concentration of holes	\neq	activated state (used as superscript)
n_p^s	concentration of holes at the surface	Greek Symbols	
n_p^0	concentration of holes in bulk	α	light absorption coefficient; transfer coefficient; specific expansibility
N_A	concentration of charge acceptors	β	charge-transfer symmetry factor; specific compressibility
N_D	concentration of charge donors	γ	surface tension
N_{ss}	concentration of surface states		

γ_{\pm}	stoichiometric activity coefficient (mean) molal	μ_e	mobility of electrons
δ	diffusion-layer thickness; barrier thickness	μ_p	mobility of holes
$\Delta_i^{i,b}\varphi$	potential inside a metal ($i = m$), semiconductor ($i = sc$), or insulator ($i = ins$)	μ^0	standard chemical potential
$\Delta_1^i\varphi$	potential drop at the inner Helmholtz plane φ ($i = M, sc, ins, etc.$)	$\bar{\mu}$	electrochemical potential
$\Delta_0^2\varphi$	potential in the diffuse (Gouy) double layer	ν	stoichiometric number; frequency of vibration (s^{-1})
$\Delta_2^i\varphi$	potential in the Helmholtz layer ($i = M, sc, or ins$)	$\bar{\nu}$	wave number (cm^{-1})
Γ_i	surface excess of species i	ρ	density of space charge; resistivity
ε	permittivity; quantum efficiency	$\rho(E)$	volume charge density
ζ	zeta potential	$\rho_i(E)$	density of states ($i = M, sc, or ins$)
η	overpotential; viscosity	σ	surface charge density in distribution; charge in double-layer region (subscripted) divided by area
θ	fractional surface coverage; relative permittivity; dielectric constant	σ_e	capture cross section of electrons
κ	conductivity; Debye-Hückel parameter	σ_m	charge on metal surface, divided by area
$\Lambda_{\pm,c}$	molar ionic conductivity at concentration c	σ_p	capture cross section of holes
Λ_c	molar conductivity at concentration c	τ	relaxation time
Λ_{∞}	molar conductivity at infinite dilution	ϕ	double-layer potential (subscripted for indication of region)
$\Lambda_{\pm,\infty}$	molar ionic conductivity at infinite dilution	ϕ_x	apparent molar function of x ; with subscript \bar{x} , partial molar function of x
μ	electric dipole moment; or chemical potential	φ	inner potential
		$\Delta\varphi$	Galvani potential
		χ	surface potential
		$\Delta\chi$	surface potential difference
		ψ	outer potential
		$\Delta\psi$	Volta potential
		ω	angular frequency

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1

Thermodynamic Methods for the Study of Interfacial Regions in Electrochemical Systems

ROGER PARSONS

1. Introduction

Thermodynamics is concerned with the relations between the observable properties of macroscopic pieces of matter. It is essentially an empirical science based on accumulated experience of the behavior of real systems. Its great utility is due to the fact that it enables information derived from experiment to be presented in a form which may be more readily understandable than the experimental results themselves. This transformation of information may be done without a detailed knowledge of the structure of the system being studied. Conversely, if no information about structure is contained in the original experimental data, no such information can be obtained by the operation of thermodynamic transformations on these data.

This chapter is concerned with the deduction of information about the composition of interfacial regions from a property such as the interfacial tension in a liquid system together with a knowledge of the equilibrium properties of the adjoining bulk phases. This particular transformation of information may be claimed as the most remarkable of the applications of classical thermodynamics. The technique by which this may be carried out was developed

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