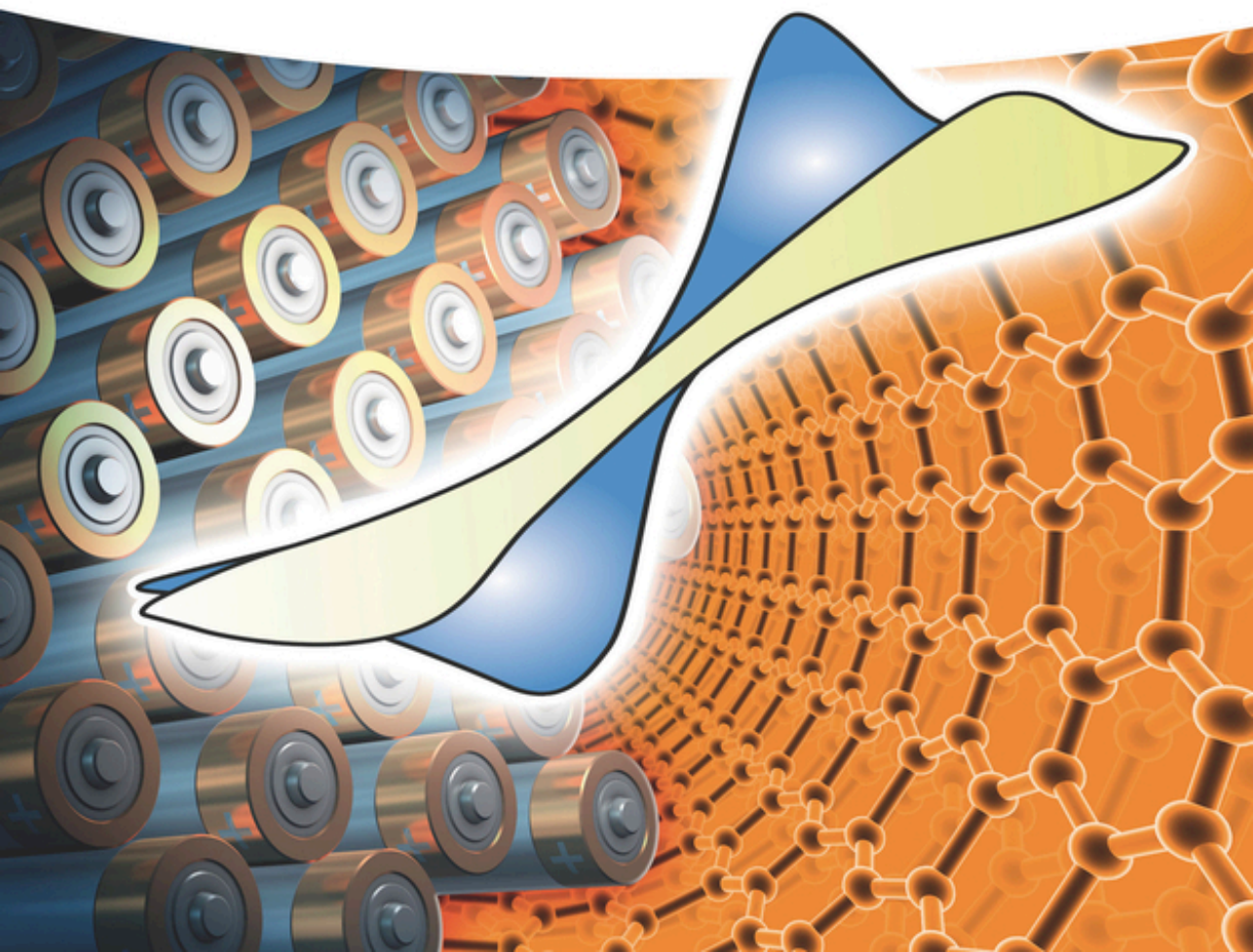


Noam Eliaz and Eliezer Gileadi

Physical Electrochemistry

Fundamentals, Techniques, and Applications
Second, Completely Revised and Updated Edition



Physical Electrochemistry

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Fundamentals, Techniques, and Applications

Noam Eliaz and Eliezer Gileadi

Second Edition

WILEY-VCH

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Dedicated to our beloved wives, Dalia Papouchado and Billie Eliaz, for their love, continued support, encouragement, and patience. Without them, our scientific careers would not be what they have been, and this book would not have been written.

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Preface

Physical electrochemistry deals with the theory of the double layer at the metal/solution interphase, the thermodynamics and kinetics (rates and mechanisms) of reactions and processes that involve electron transfer. It is important in many aspects of fundamental chemistry, physics, biology, and engineering. There are many applications of electrochemistry, including corrosion, electrochemical deposition, electroforming, electromachining and electropolishing, electro-organic synthesis, biosensors, batteries, fuel cells, and supercapacitors.

In spite of its importance, physical electrochemistry is rarely included in the undergraduate curriculum of chemistry and engineering in universities around the world. This book aims to serve as a key textbook in undergraduate courses that deal with electrochemistry, and also as a reference source for graduate students, researchers, and engineers who have interest in the field. Admittedly, the book contains more than what could be taught in one semester. This is deliberate in order to allow some choice for the teacher to concentrate on aspects of the field that best fit the needs of the particular class. However, even covering one half or two thirds of the material in this book should provide students with some understanding of physical electrochemistry, the techniques applied, and at least one of the applications in which electrochemistry is involved, and facilitate the learning and understanding of some specific subject that may be needed later in his or her professional life. This book is also recommended as a text suitable for self-learning, which could be used to introduce scientists and engineers who have not had an opportunity to participate in a formal course on electrochemistry to aspects of this field needed for their research and development.

The book can be divided into three parts: (i) *the fundamentals of electrochemistry*: the potentials of phases, the electrical double layer (EDL), electrode kinetics, single-step and multistep electrode reactions, electrocapillarity, electrosorption, underpotential deposition (UPD), and single-crystal electrochemistry; (ii) the most important *electrochemical measurement techniques*: cyclic voltammetry (CV), rotating-disk electrodes, microelectrodes and nanoelectrodes, electrochemical impedance spectroscopy (EIS), and electrochemical quartz crystal microbalance (EQCM); and (iii) *applications of electrochemistry in materials science and engineering, nanoscience and nanotechnology, and industry*: corrosion, electrochemical deposition (electroplating of metals and alloys, electroless and electrophoretic deposition), nanoparticles and surfaces,

electrocatalysis, electrochemical printing, and energy conversion and storage (batteries, fuel cells, supercapacitors, and hydrogen storage).

The first edition of this book was published by Wiley-VCH in 2011. Following its success, we made our best efforts to revise and improve this book significantly by (i) shortening certain sections that we find less needed for students nowadays; (ii) updating and extending some chapters according to the state-of-the-art in the field, for example, electrochemical printing, batteries, fuels cells, supercapacitors, and hydrogen storage; (iii) adding key illustrations (figures and tables); (iv) adding recommended references at the end of each chapter; etc. Thus, we believe that the second edition will be valuable also to those of you who have read the first edition.

When writing this book we took advantage of our long experience in teaching courses such as physical electrochemistry, corrosion engineering, and materials science and engineering. There are different criteria by which the quality of a textbook could be judged. From our point of view, the success or failure of this book will be judged by its ability to enhance and spread the teaching and use of physical electrochemistry, and establish it as the basis for graduate courses offered widely in universities around the world. We hope you enjoy reading our book and find it easy to follow and enriching!

July 2018

Noam Eliaz and Eliezer Gileadi
Tel Aviv, Israel

Symbols and Abbreviations

Symbols

a	empirical Tafel constant	V
a_i	activity of substance i	mol m^{-3} , mol kg^{-1} , or mole fraction
A	affinity of a reaction	J mol^{-1}
A	exposed surface area	cm^2
A_p	area of the drop during the application of pulse in normal-pulse polarography	m^2
b	Tafel slope	V decade^{-1}
b_a	Tafel slope of the anodic (oxidation) reaction	V decade^{-1}
b_c	Tafel slope of the cathodic (reduction) reaction	V decade^{-1}
B_o	Bond number	dimensionless
c_i	concentration of substance i	mol m^{-3}
c_b	concentration of the electroactive species in the bulk of the solution	mol m^{-3}
c_s	concentration of the electroactive species at the surface ($x = 0$)	mol m^{-3}
c_{\ddagger}	concentration of the activated complex	mol m^{-3}
C_{dl}	double-layer capacitance	$\mu\text{F cm}^{-2}$
C_H	the Helmholtz capacitance	$\mu\text{F cm}^{-2}$
C_L	the adsorption pseudocapacitance derived from the Langmuir isotherm	$\mu\text{F cm}^{-2}$
C_0	subsurface concentration of atomic hydrogen	mol m^{-3}
C_{0R}	summation of the subsurface concentration of hydrogen in interstitial lattice sites and reversible trap sites on the charging side of the sample	mol m^{-3}
C_ϕ	adsorption pseudocapacitance	$\mu\text{F cm}^{-2}$
d	distance between the tip of the Luggin capillary and the working electrode	m
d	distance between the two plates of a capacitor	m
D	diffusion coefficient	$\text{m}^2 \text{s}^{-1}$

D_{eff}	effective diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
D_0	nozzle diameter	m
E	electrical potential	V
E^0	standard potential	V
E_{app}	applied potential	V
E_{b}	breakdown potential	V
E_{corr}	corrosion potential	V
E_{max}	the potential where the pseudocapacitance reaches its maximum value	V
E_{mp}	mixed potential	V
E_{p}	protection potential	V
E_{pp}	primary passivation potential	V
E_{pzc}	potential of zero charge	V
E_{rev}	reversible potential according to the Nernst equation	V
$E_{1/2}$	polarographic half-wave potential	V
f	fugacity	atm
f	Frumkin parameter	dimensionless
f_0	resonance frequency	Hz
G	Gibbs free energy	J mol^{-1}
ΔG	change in the Gibbs free energy	J mol^{-1}
ΔG_{solv}	energy of hydration of a metal ion	J mol^{-1}
ΔG^0	change in the standard Gibbs free energy	J mol^{-1}
$\Delta G^{0\ddagger}$	the standard electrochemical Gibbs free energy of activation	J mol^{-1}
$\overline{\Delta G}^0$	the change in the standard electrochemical Gibbs free energy	J mol^{-1}
ΔG_{θ}^0	the standard Gibbs free energy of adsorption for a chosen value of θ	J mol^{-1}
I	current	A
I	ionic strength	m or M
I_{d}	diffusion-limited current in dropping mercury electrode	A
I_{D}	current at the disk of a rotating ring disk electrode	A
I_{L}	mass-transport-limited current	A
I_{R}	current at the ring of a rotating ring disk electrode	A
j	current density	A m^{-2}
j_{a}	net anodic current density	A m^{-2}
j_{avg}	average current density in pulse plating	A m^{-2}
j_{c}	net cathodic current density	A m^{-2}
$j_{\text{ac}}/j_{\text{ct}}$	activation-controlled current density/charge-transfer current density	A m^{-2}
j_{cc}	critical current density	A m^{-2}

j_{corr}	corrosion current density	A m^{-2}
j_{dep}	deposition current density	A m^{-2}
j_{dl}	double-layer charging current	A m^{-2}
j_{L}	limiting current density	A m^{-2}
$j_{\text{L,chem}}$	chemically-controlled limiting current density	A m^{-2}
j_{max}	the final steady-state current density	A m^{-2}
j_{p}	applied peak current density	A m^{-2}
j_{pas}	passive current density	A m^{-2}
j_0	exchange current density	A m^{-2}
J_{ss}	permeation flux of hydrogen at steady state	$\text{mol m}^{-2} \text{ s}^{-1}$
k	rate constant for a homogenous reaction	depends on order
k_{b}	homogeneous rate constant for “backward” reaction	depends on order
k_{f}	homogeneous rate constant for “forward” reaction	depends on order
k^0	chemical (heterogeneous) rate constant at the reversible potential $\Delta\phi = 0$	m s^{-1}
$k_{\text{s,h}}$	heterogeneous rate constant at standard potential	m s^{-1}
K	equilibrium constant	dimensionless
K^\ddagger	equilibrium constant for formation of the activated complex	dimensionless
l	characteristic length of rotating disk electrode	m
L	membrane thickness in electrochemical permeation test	m
L	characteristic length of a capillary surface	m
m	flow rate in dropping mercury electrode	kg s^{-1}
M	atomic mass	g mol^{-1}
n	number of electrons transferred per molecule	dimensionless
nF	charge transferred per mole of species	C mol^{-1}
N	rotation rate	rpm
N	collection efficiency of a rotating ring disk electrode	dimensionless
N	total number of atoms in a particle	dimensionless
p_i	partial pressure of the i th components	atm
p_r	vapor pressure of a drop of radius r	atm
q_{M}	excess charge density on the metal surface	C cm^{-2}
q_{S}	excess charge density on the solution side of the interphase	C cm^{-2}
r	radius of the working electrode	m
r	the rate of change of the standard Gibbs free energy of adsorption with coverage	J mol^{-1}
r_{cyl}	radius of the RCE	m
$R_{\text{F}}/R_{\text{ct}}$	faradaic resistance/charge-transfer resistance	$\Omega \text{ m}^2$
R_{p}	polarization resistance	$\Omega \text{ m}^2$
R_{S}	uncompensated solution resistance	$\Omega \text{ m}^2$
Re	Reynolds number	dimensionless

R_{film}	resistance of a nonconductive surface film	$\Omega \text{ m}^2$
t	time	s
t	drop time in polarography	s
$t_{\text{lag}_{63\%}}$	time during charging transient when the current density reaches 63% of the final steady-state current density	s
t_{p}	pulse duration in normal-pulse polarography	s
t^*	dimensionless pulse time in electroplating	dimensionless
T	thermodynamic (absolute) temperature	K
U	bond energy	J mol^{-1}
U_{cyl}	linear surface (peripheral) velocity of RCE	cm s^{-1}
U_{hyd}	hydration energy of ions in solution	eV
V	voltage drop	V
V_{t}	thermal voltage	V
v	potential sweep rate	V s^{-1}
v	heterogeneous reaction rate	$\text{mol m}^{-2} \text{ s}^{-1}$
v	characteristic velocity of rotating disk electrode	m s^{-1}
v	stoichiometric coefficient	dimensionless
v	number of occurrences of the rate-determining step in the electrode reaction	dimensionless
v_{eq}	reaction exchange rate at equilibrium	$\text{mol m}^{-2} \text{ s}^{-1}$
Wa	Wagner number	dimensionless
w	mass of a corroded metal	g
x	distance	m
X^{\ddagger}	activated complex	
z	charge number, valence	dimensionless
$Z(\omega)$	impedance	Ω
Z_{W}	Warburg impedance	Ω
α	transfer coefficient	dimensionless
$\alpha_{\text{a}}, \alpha_{\text{c}}$	anodic/cathodic transfer coefficient	dimensionless
β	symmetry factor	dimensionless
$\beta_{\text{a}}, \beta_{\text{c}}$	anodic/cathodic symmetry factor	dimensionless
γ	surface energy	J m^{-2}
γ_i	the activity coefficient of substance i	dimensionless
γ_{\pm}	mean activity coefficient	dimensionless
Γ	surface excess	mol m^{-2}
Γ	surface concentration	mol cm^{-2}
Γ_{max}	maximum surface concentration	mol cm^{-2}
δ	thickness of the Nernst diffusion layer	m
${}^{\alpha}\Delta^{\beta}\phi$	the difference between the inner potentials between two different phases, α and β	V
∇	del, the gradient operator	dimensionless

ϵ	absolute permittivity (dielectric constant) of the medium	F m^{-1}
ϵ_r	relative permittivity of the medium	dimensionless
ζ	zeta potential	V
η	overpotential	V
η	dynamic (absolute) viscosity	$\text{kg m}^{-1} \text{s}^{-1}$
η_a	anodic overpotential	V
η_c	cathodic overpotential	V
η_{ac}	activation overpotential	V
η_{conc}	concentration overpotential	V
η_{iR_s}	resistance (Ohmic) overpotential	V
θ	opening angle of a rotating cone electrode	degree ($^\circ$)
θ	partial/fractional surface coverage	dimensionless
κ	specific conductivity of the solution	S cm^{-1}
κ	reciprocal Debye length	m^{-1}
λ	solvent reorganization energy	J mol^{-1}
λ_c	capillary length	m
μ_i	chemical potential of substance i	J mol^{-1}
μ^0	standard chemical potential	J mol^{-1}
$\bar{\mu}$	electrochemical potential	J mol^{-1}
Π	two-dimensional surface pressure	J m^{-2}
ρ	density	kg m^{-3}
ρ	reaction order	dimensionless
ρ	specific resistivity of the solution	$\Omega \text{ cm}$
σ	stored charge density	C m^{-2}
σ	surface tension	N m^{-1}
τ_c	time constant for the parallel combination of a capacitor and a resistor	s
τ_d	characteristic time constant for the diffusion process	s
τ_{pp}	total pulse time	s
ν	kinematic viscosity	$\text{m}^2 \text{s}^{-1}$
ϕ	angle between the metal and the insulator	rad
ϕ^α	the inner potential of phase α	V
ϕ^\ddagger	potential of the activated complex	V
ϕ_x	the potential at a distance x from the surface of the metal	V
ϕ_M	the electrode potential	V
ϕ_S	the potential in the bulk of the solution	V
$\Delta\phi$	the potential difference across the interface	V
$\Delta\phi_{rev}$	the value of $\Delta\phi$ at the reversible potential	V
χ	dimensionless rate constant	dimensionless
ω	angular velocity	rad s^{-1}

Abbreviations

AC	alternating current
ACD	anomalous codeposition
AES	Auger electron spectroscopy
AFC	alkaline fuel cell
AFM	atomic force microscope
AO	atomic oxygen
BET	Brunauer–Emmett–Teller
BEV	battery-electric vehicle
CE	counter electrode
CI	corrosion intensity
CMOS	complementary metal–oxide–semiconductor
CNT	carbon nanotube
CP	cathodic protection
CPE	constant phase element
CPR	corrosion penetration rate
CR	corrosion rate
CV	cyclic voltammetry
CVD	chemical vapor deposition
DC	direct current
DME	dropping mercury electrode
DMFC	direct methanol fuel cell
DPN	dip-pen nanolithography
DPP	differential-pulse polarography
EC	electrochemical capacitor
EcP	electrochemical printing
EDL	electrical double layer
EDLC	electrochemical double-layer capacitor
E-DPN	electrochemical dip-pen nanolithography
EDS	energy dispersive spectroscopy
EFAB	electrochemical fabrication
EIC	environmentally induced cracking
EIS	electrochemical impedance spectroscopy
EMF	electromotive force
EN	electrochemical noise
EPD	electrophoretic deposition
EQCM	electrochemical quartz crystal microbalance
ESC	environmental stress cracking
EV	electric vehicle
EW	equivalent weight
FC	fuel cell
FE	faradaic efficiency
FIB	focused ion beam
FPN	fountain pen nanofabrication
FRA	frequency response analyzer
FTIR	Fourier-transform infrared

HDME	hanging dropping mercury electrode
HE	hydrogen embrittlement
HER	hydrogen evolution reaction
HEV	hybrid electric vehicle
ICCP	impressed-current cathodic protection
ICE	internal-combustion engine
IHP	inner Helmholtz plane
LECD	localized electrochemical deposition
LIB	lithium-ion battery
LPR	linear polarization resistance
LSV	linear sweep voltammetry
MCED	meniscus-confined electrodeposition
MIC	microbiological corrosion
NHE	normal hydrogen electrode
NP	nanoparticle
NPP	normal-pulse polarography
OCP	open-circuit potential
OER	oxygen evolution reaction
OHP	outer Helmholtz plane
OPD	overpotential deposition
ORR	oxygen reduction reaction
PAFC	phosphoric acid fuel cell
PEM	polymer electrolyte membrane
PHEV	plug-in hybrid electric vehicle
QCM	quartz crystal microbalance
RConeE	rotating cone electrode
RCylE	rotating cylinder electrode
RDE	rotating disk electrode
RDS	rate-determining step
RE	reference electrode
RHE	reversible hydrogen electrode
RRDE	rotating ring disk electrode
SCC	stress corrosion cracking
SCE	saturated calomel electrode
SDME	static dropping mercury electrode
SECM	scanning electrochemical microscopy
SEI	solid/electrolyte interphase
SEM	scanning electron microscope
SGC	Stern–Geary coefficient
SHE	standard hydrogen electrode
SIMS	secondary ion mass spectrometry
SPE	solid polymer electrolyte
STM	scanning tunneling microscopy
SWP	square-wave polarography
UME	ultramicroelectrode
UPD	underpotential deposition
VCI	volatile corrosion inhibitor

WE	working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZRA	zero-resistance ammeter

Useful Units and Conversions

Å	Angstrom	$1 \text{ Å} = 10^{-10} \text{ m} = 10^{-8} \text{ cm} = 10^{-4} \text{ μm} = 10^{-1} \text{ nm}$
Ah	Ampere-hour	$1 \text{ Ah} = 3600 \text{ C}$
C	Coulomb	$1 \text{ C} = 1 \text{ A s}$
cal	calorie	$1 \text{ cal} = 4.1868 \text{ J}$
dm	decimeter	$10 \text{ dm} = 1 \text{ m}$
Eq	equivalent	1 Eq will neutralize 1 mol of H^+ or $(\text{OH})^-$ ions
erg	erg	$1 \text{ erg} = 10^{-7} \text{ J}$
eV	electron volt	$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$
F	Farad	$F \equiv \text{C V}^{-1} = \text{A}^2 \text{ s}^4 \text{ kg}^{-1} \text{ m}^{-2}$
Hz	Hertz	$1 \text{ Hz} \equiv \text{s}^{-1}$
J	Joule	$J \equiv \text{N m} = \text{kg m}^2 \text{ s}^{-2}$
kWh	kilowatt hour	$1 \text{ kWh} = 3600 \text{ kJ}$
L	liter	$1 \text{ L} = 1 \times 10^3 \text{ cm}^3 = 1 \text{ dm}^3$
M	molal	mol kg^{-1}
mil	mil	$1 \text{ mil} = 0.001 \text{ in.}$
mpy	mils per year	$1 \text{ mpy} = 25.4 \text{ μm y}^{-1}$
M	molar	mol L^{-1}
N	Newton	$N \equiv \text{kg m s}^{-2}$
rad	radian	$1 \text{ rad} = 360/2\pi = 57.2958^\circ$
S	Siemens	$1 \text{ S} \equiv 1 \text{ A V}^{-1} = \text{kg}^{-1} \text{ m}^{-2} \text{ s}^3 \text{ A}^2$
V	Volt	$V \equiv \text{W A}^{-1} = \text{J C}^{-1} = \text{kg m}^2 \text{ A}^{-1} \text{ s}^{-3}$
W	Watt	$W \equiv \text{J s}^{-1} = \text{kg m}^2 \text{ s}^{-3} \text{ A}^{-1}$
°F	degrees Fahrenheit	$^\circ\text{C} = 5/9 \cdot (^\circ\text{F} - 32)$
°K	degrees Kelvin	$^\circ\text{K} = ^\circ\text{C} + 273.15$
Ω	ohm	$1 \text{ Ω} \equiv 1 \text{ V A}^{-1} = \text{kg m}^2 \text{ s}^{-3} \text{ A}^{-2}$

Physical Constants¹

c	speed of light in vacuum	$2.99792 \times 10^8 \text{ m s}^{-1}$
e	elementary charge	$1.60218 \times 10^{-19} \text{ C}$
F	Faraday constant	$9.64853 \times 10^4 \text{ C mol}^{-1} = 23\,060 \text{ cal mol}^{-1} \text{ V}^{-1}$
g	standard acceleration of gravity	9.80665 m s^{-2}

¹ Taken from the CODATA Internationally Recommended 2014 Values of the Fundamental Physical Constants (<http://physics.nist.gov/cuu/Constants/>, last accessed July 12th, 2016).

h	Planck constant	$6.62607 \times 10^{-34} \text{ J s}$
k	Boltzmann constant	$1.38065 \times 10^{-23} \text{ J K}^{-1}$
K_w	equilibrium constant of water	$1.008 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$ at 25 °C
N_A	Avogadro's number	$6.02214 \times 10^{23} \text{ mol}^{-1}$
R	molar gas constant	$8.31447 \text{ J mol}^{-1} \text{ K}^{-1}$
v_{tr}	transverse velocity of sound	$3.34 \times 10^4 \text{ m s}^{-1}$ in AT-quartz
ϵ_0	permittivity of free space (electric constant)	$8.85419 \times 10^{-12} \text{ F m}^{-1}$
μ_{q}	shear modulus of quartz	$2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$
ρ_{q}	density of quartz	2.648 g cm^{-3}

Potentials of Reference Electrodes in Aqueous Solutions at 25 °C

Common name	Electrode	V versus SHE	Notes
Mercury/mercurous sulfate (MMS)	Hg/Hg ₂ SO ₄ /0.5 M K ₂ SO ₄	+0.680	Useful for avoiding chloride contamination of the test solution
Mercury/mercurous sulfate electrode (MSE)	Hg/Hg ₂ SO ₄ /saturated K ₂ SO ₄	+0.640	Useful for avoiding chloride contamination of the test solution
Calomel	Hg/Hg ₂ Cl ₂ /0.1 M KCl	+0.336	Better temperature stability than SCE
Copper/copper sulfate electrode (CSE)	Cu/saturated CuSO ₄	+0.316	Very robust, commonly used for cathodic protection
Normal calomel electrode (NCE)	Hg/Hg ₂ Cl ₂ /1 M KCl	+0.280	Better temperature stability than SCE
Saturated calomel electrode (SCE)	Hg/Hg ₂ Cl ₂ /saturated KCl	+0.241	The most common electrode in laboratory. Use of mercury introduces safety hazards. Potential decreases as the solubility of KCl increases at higher temperatures. Cannot be used above 50 °C
Saturated sodium calomel electrode (SSCE)	Hg/Hg ₂ Cl ₂ /saturated NaCl	+0.236	
Saturated silver/silver chloride	Ag/AgCl/saturated KCl	+0.197	Very easy to make, but light sensitive. Can be used up to 80–100 °C
Mercury/mercury oxide (MMO)	Hg/HgO/1 M NaOH	+0.140	Good for alkaline solutions
Standard hydrogen electrode (SHE)	H ₂ /H ⁺ , $a_{\text{H}^+} = 1 \text{ M}$, $f_{\text{H}_2(\text{g})} = 1 \text{ atm}$	0.000	Not to confuse with the normal hydrogen electrode (NHE) that implies $c_{\text{H}^+} = 1 \text{ M}$, $E^0 \cong 0.000 \text{ V}$

