UNDERSTANDING VOLTAMMETRY:

Problems and Solutions

伏安法教程题解

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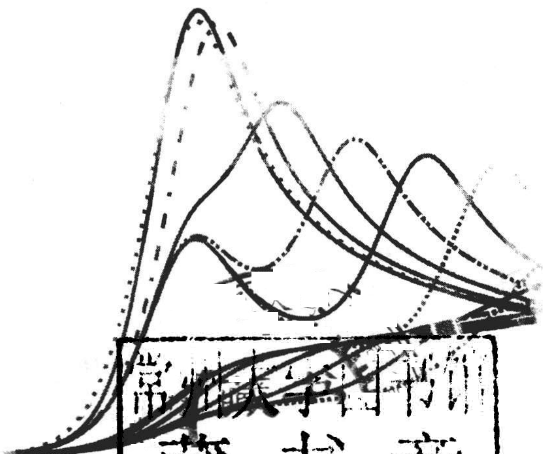

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Publisher's Foreword

Understanding Voltammetry: Problems and Solutions is a companion volume to the textbook *Understanding Voltammetry 2nd Edition*, by Richard G. Compton and Craig E. Banks, published in 2011. The structure of this volume follows that of the textbook.

Understanding Voltammetry considers how to go about designing, explaining and interpreting experiments centred around various forms of voltammetry, including cyclic, microelectrode and hydrodynamic, amongst others.

The book gives clear introductions to the theories of electron transfer and of diffusion in its early chapters. These are developed to interpret voltammetric experiments at macroelectrodes before considering microelectrode behaviour. A subsequent chapter introduces convection and describes hydrodynamic electrodes. Later chapters describe the voltammetric measurement of homogeneous kinetics, the study of adsorption on electrodes and the use of voltammetry for electroanalysis.

Glossary of Symbols and Abbreviations

Roman symbols

A	area	m^2
A	Debye-Hückel constant = $0.509\ mol^{-\frac{1}{2}}\ kg^{\frac{1}{2}}$	
a_i	activity of species i	
c_i	concentration of species i	$mol\ dm^{-3}$
$c_{i,0}$	surface concentration of species i	$mol\ dm^{-3}$
c^*	bulk concentration	$mol\ dm^{-3}$
D	diffusion coefficient	$(c)m^2\ s^{-1}$
E	cell potential	V
$E^\ominus$	reduction potential under standard conditions	V
$E_f^\ominus$	formal reduction potential	V
F	the Faraday constant = $96485.3\ C\ mol^{-1}$	
G	Gibbs energy	J
$\Delta G^\ominus$	change in Gibbs energy under standard conditions	$J\ mol^{-1}$
$\Delta G^\ddagger$	activation energy	$J\ mol^{-1}$
$\Delta H^\ominus$	change in enthalpy under standard conditions	$J\ mol^{-1}$
h	height or half-height of a cell	m
I	current passed	A
I_{pf}	forward peak current	A
I	ionic strength	$mol\ kg^{-1}$
J	flux	$mol\ m^{-2}\ s^{-1}$
K	equilibrium coefficient	

K	dimensionless rate constant	
K_a	acid dissociation constant	
K_{eq}	equilibrium coefficient (in follow-up kinetics)	
K_{sp}	solubility product	
k^0	heterogeneous rate constant	(c)m s^{-1}
k	rate constant	
m_i	molality of species i	mol kg^{-1}
n	number of electrons transferred	
p	pressure as a multiple of standard pressure	bar
pK_a	$\equiv -\log_{10} K_a$	
Q	reaction quotient	
Q	charge transferred	C
q_{rev}	reversible heat transferred	J mol^{-1}
q	charge	C
R	the gas constant = 8.31447 J K^{-1} mol^{-1}	
Re	the Reynolds number	
r	radius or radial coordinate	m
r_e	electrode radius	m
$\Delta S^\ominus$	change in entropy under standard conditions	J K^{-1} mol^{-1}
T	temperature	K
t	time	s
t_i	transport number of species i	
V_f	volume flow rate	m^3 s^{-1}
v	voltammetric scan rate	V s^{-1}
W	rotation speed	s^{-1}
w	electrode width	m
x	linear space coordinate	m
z_i	charge number of species i	

Greek symbols

α	Butler–Volmer transfer coefficient for reduction	
β	Butler–Volmer transfer coefficient for oxidation	
Γ	surface coverage	mol (c)m^{-2}
γ_i	activity coefficient of species i	m^3 mol^{-1}
δ	Nernst diffusion layer thickness	m
ϵ_0	the permittivity of free space = 8.854×10^{-12} F m^{-1}	
ϵ_s	relative permittivity or dielectric constant of a solvent	
Λ	the Matsuda–Ayabe parameter	
λ	Marcus reorganisation energy	J

μ_i	chemical potential of species i	$\mathrm{J\,mol^{-1}}$
ν_i	stoichiometric coefficient of species i	
ν	kinematic viscosity	$\mathrm{m^2\,s^{-1}}$
ρ	density	$\mathrm{kg\,m^{-3}}$
τ	Shoup–Szabo time coordinate $\equiv (4Dt/r_e^2)$	
ϕ	potential	V
ϕ_M	potential of a (metal) electrode	V
ϕ_s	potential of the solution phase	V
$\Delta\phi_{OD}$	ohmic drop	V
Θ	fractional surface coverage	
Θ	dimensionless potential $\equiv \phi \times (F/RT)$	
θ	dimensionless overpotential $\equiv (F/RT) \times (E - E_f^{\ominus})$	

Abbreviations

BDD	boron-doped diamond
BPPG	basal-plane pyrolytic graphite
EMF	electromotive force
EPPG	edge-plane pyrolytic graphite
erf(x)	the error function
erfc(x)	the complementary error function, $\equiv 1 - \mathrm{erf}(x)$
HOPG	highly ordered pyrolytic graphite
TBAP	tetra-n-butylammonium perchlorate
$[i]$	concentration of species i
$[i]_0$	surface concentration of species i
$\ominus$	standard state

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