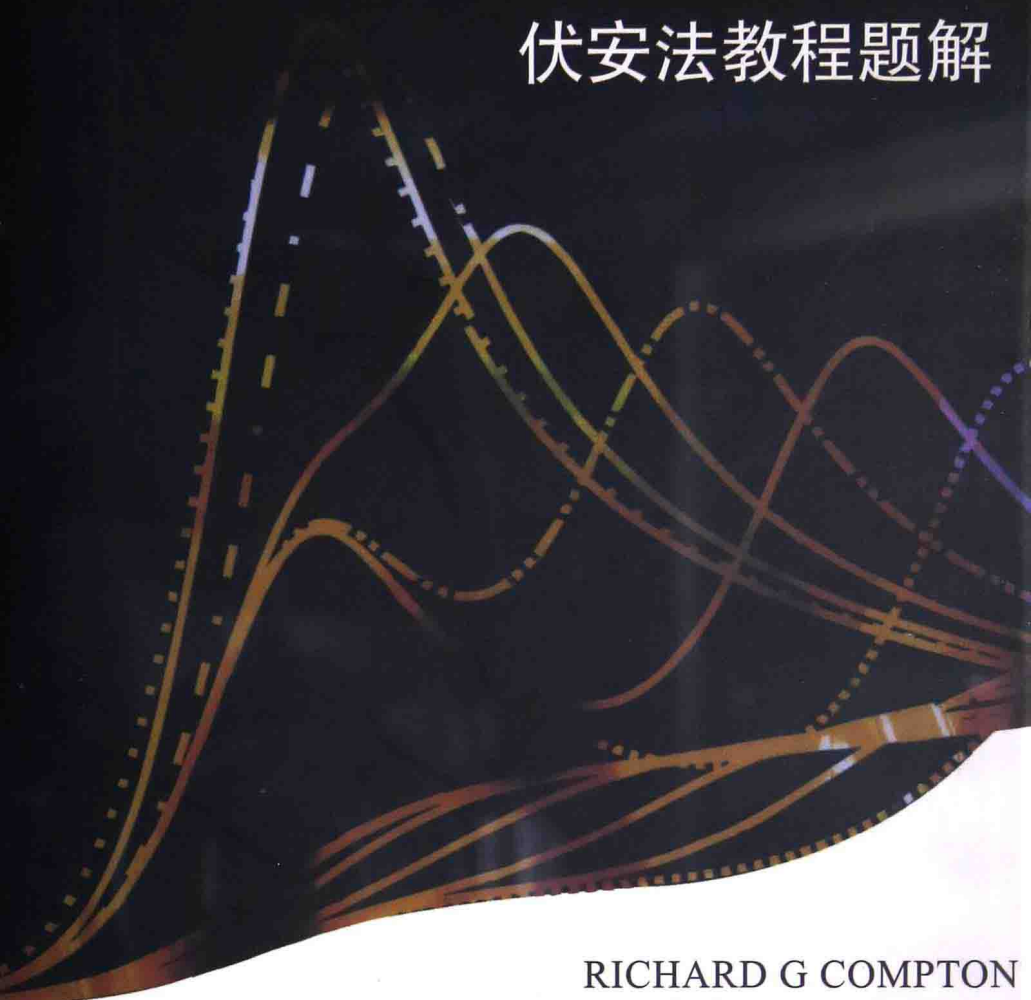


UNDERSTANDING VOLTAMMETRY

Problems and Solutions

伏安法教程题解



RICHARD G COMPTON
CHRISTOPHER BATCHELOR-MCAULEY
EDMUND J F DICKINSON

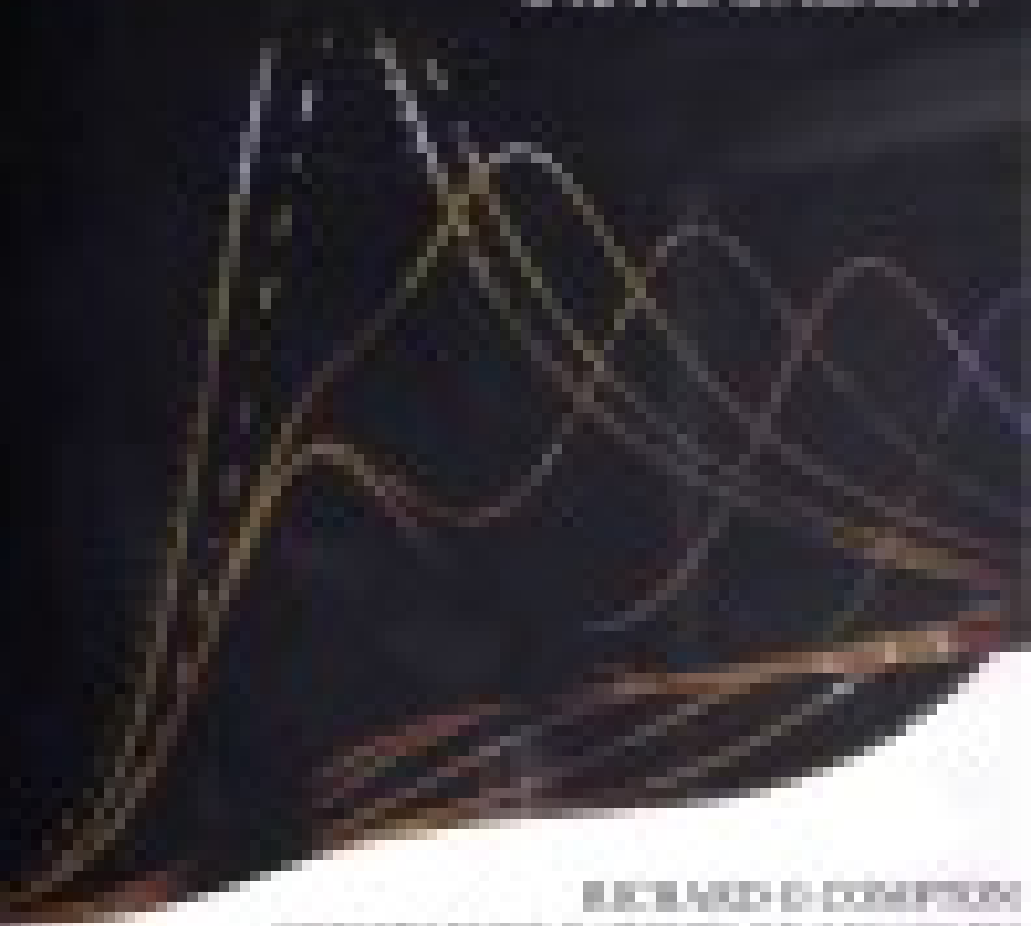
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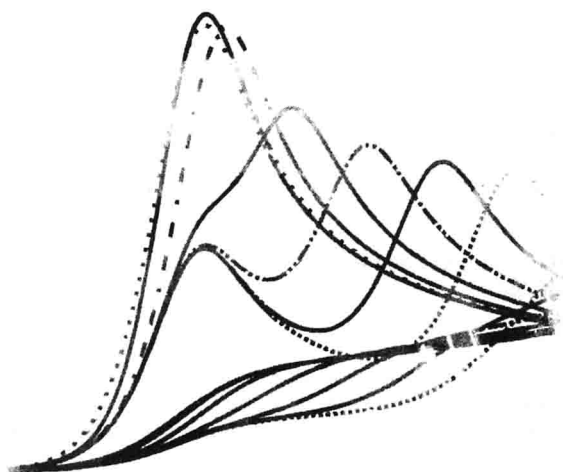


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UNDERSTANDING VOLTAMMETRY: **Problems and Solutions**



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Problems and Solutions

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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 = $0.509 \text{ mol}^{-\frac{1}{2}} \text{ kg}^{\frac{1}{2}}$	
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	$(\text{cm})^2 \text{ s}^{-1}$
E	cell potential	V
$E^\ominus$	reduction potential under standard conditions	V
$E_f^\ominus$	formal reduction potential	V
F	the Faraday constant = $96485.3 \text{ C mol}^{-1}$	
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	$\text{mol m}^{-2} \text{ s}^{-1}$
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	$(\text{c})\text{m s}^{-1}$
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 $= 8.31447 \text{ J K}^{-1} \text{ mol}^{-1}$	
Re	the Reynolds number	
r	radius or radial coordinate	m
r_e	electrode radius	m
$\Delta S^\ominus$	change in entropy under standard conditions	$\text{J K}^{-1} \text{ mol}^{-1}$
T	temperature	K
t	time	s
t_i	transport number of species i	
V_f	volume flow rate	$\text{m}^3 \text{ s}^{-1}$
ν	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	$\text{mol (c)}\text{m}^{-2}$
γ_i	activity coefficient of species i	$\text{m}^3 \text{ mol}^{-1}$
δ	Nernst diffusion layer thickness	m
ϵ_0	the permittivity of free space $= 8.854 \times 10^{-12} \text{ F m}^{-1}$	
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	J mol^{-1}
ν_i	stoichiometric coefficient of species i	
ν	kinematic viscosity	$\text{m}^2 \text{s}^{-1}$
ρ	density	kg m^{-3}
τ	Shoup–Szabo time coordinate $\equiv (4Dt/r_c^2)$	
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	
$\ominus$	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
$\text{erf}(x)$	the error function
$\text{erfc}(x)$	the complementary error function, $\equiv 1 - \text{erf}(x)$
HOPG	highly ordered pyrolytic graphite
TBAP	tetra- <i>n</i> -butylammonium perchlorate
$[i]$	concentration of species i
$[i]_0$	surface concentration of species i
$\ominus$	standard state

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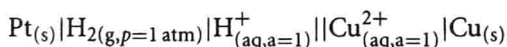
1

Equilibrium Electrochemistry and the Nernst Equation

1.1 Cell Thermodynamics

Problem

The measured electromotive force (EMF) for the cell



is +0.337 V. Write down the cell reaction and calculate the value of $\Delta G^\ominus$ for this reaction.

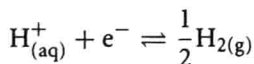
Solution

The potential determining equilibria are as follows:

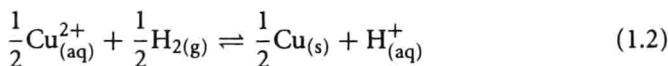
Right-hand electrode



Left-hand electrode



Note these are written as reductions involving one electron. We therefore subtract to obtain a cell reaction:



for which

$$\Delta G^\ominus = -FE^\ominus$$

All the species in Eq. 1.2 are present at unit activity, either as explicitly stated in the problem or implicitly in the case of copper since it is a pure solid and so must also be at unit activity. Note we assume that in the case of hydrogen at one atmosphere pressure that the gas will be sufficiently close to ideality that the effects of gas imperfections can be neglected.

It follows that

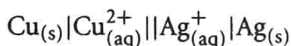
$$\begin{aligned}\Delta G^\ominus &= -F \times 0.337 \text{ V} \\ &= -32.5 \text{ kJ mol}^{-1}\end{aligned}$$

which is favourable. We conclude that hydrogen gas can thermodynamically reduce aqueous Cu(II) to metallic copper and, consequently, that the metal will not dissolve in acid solutions to form Cu^{2+} .

1.2 The Nernst Equation

Problem

For the following cell,



at 298 K:

- (i) State the cell reaction.
- (ii) Give the Nernst equation for the cell.
- (iii) Calculate the cell EMF when the ions are present at activities of (a) 1.0 and (b) 0.1.

The standard electrode potentials are:

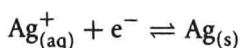
$$E_{\text{Ag}|\text{Ag}^+}^\ominus = +0.80 \text{ V}$$

$$E_{\text{Cu}|\text{Cu}^{2+}}^\ominus = +0.34 \text{ V}$$

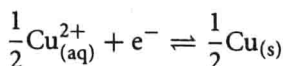
Solution

- (i) The potential determining equilibria are:

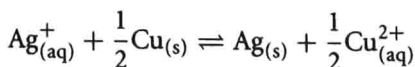
Right-hand electrode



Left-hand electrode



Subtracting gives the cell reaction



(ii) The Nernst equation for the cell is:

$$E = E^{\ominus} + \frac{RT}{F} \ln \left\{ \frac{a_{\text{Ag}^+}}{a_{\text{Cu}^{2+}}^{\frac{1}{2}}} \right\} \quad (1.3)$$

where

$$\begin{aligned} E^{\ominus} &= E_{\text{Ag}|\text{Ag}^+}^{\ominus} - E_{\text{Cu}|\text{Cu}^{2+}}^{\ominus} \\ &= 0.80 \text{ V} - 0.34 \text{ V} \\ &= 0.46 \text{ V} \end{aligned}$$

Note the absence of $\text{Cu}_{(\text{s})}$ and $\text{Ag}_{(\text{s})}$ from Eq. 1.3 since these are pure solids and hence have unit activity.

(iii) (a) Substituting

$$a_{\text{Ag}^+} = a_{\text{Cu}^{2+}} = 1$$

into Eq. 1.3 gives

$$E = 0.46 \text{ V}$$

(b) Similarly for

$$a_{\text{Ag}^+} = a_{\text{Cu}^{2+}} = 0.1$$

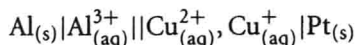
we find

$$E = 0.43 \text{ V}$$

1.3 The Nernst Equation

Problem

For the following hypothetical cell,



at 298 K:

- (i) State the cell reaction.
- (ii) Give the Nernst equation for the cell.
- (iii) Calculate the cell EMF when
 - (a) $a_{\text{Al}^{3+}} = a_{\text{Cu}^{2+}} = a_{\text{Cu}^{+}} = 1.0$
 - (b) $a_{\text{Al}^{3+}} = a_{\text{Cu}^{2+}} = a_{\text{Cu}^{+}} = 0.1$

The standard electrode potentials are:

$$E_{\text{Cu}^{+}|\text{Cu}^{2+}}^{\ominus} = +0.15 \text{ V}$$

$$E_{\text{Al}|\text{Al}^{3+}}^{\ominus} = -1.61 \text{ V}$$