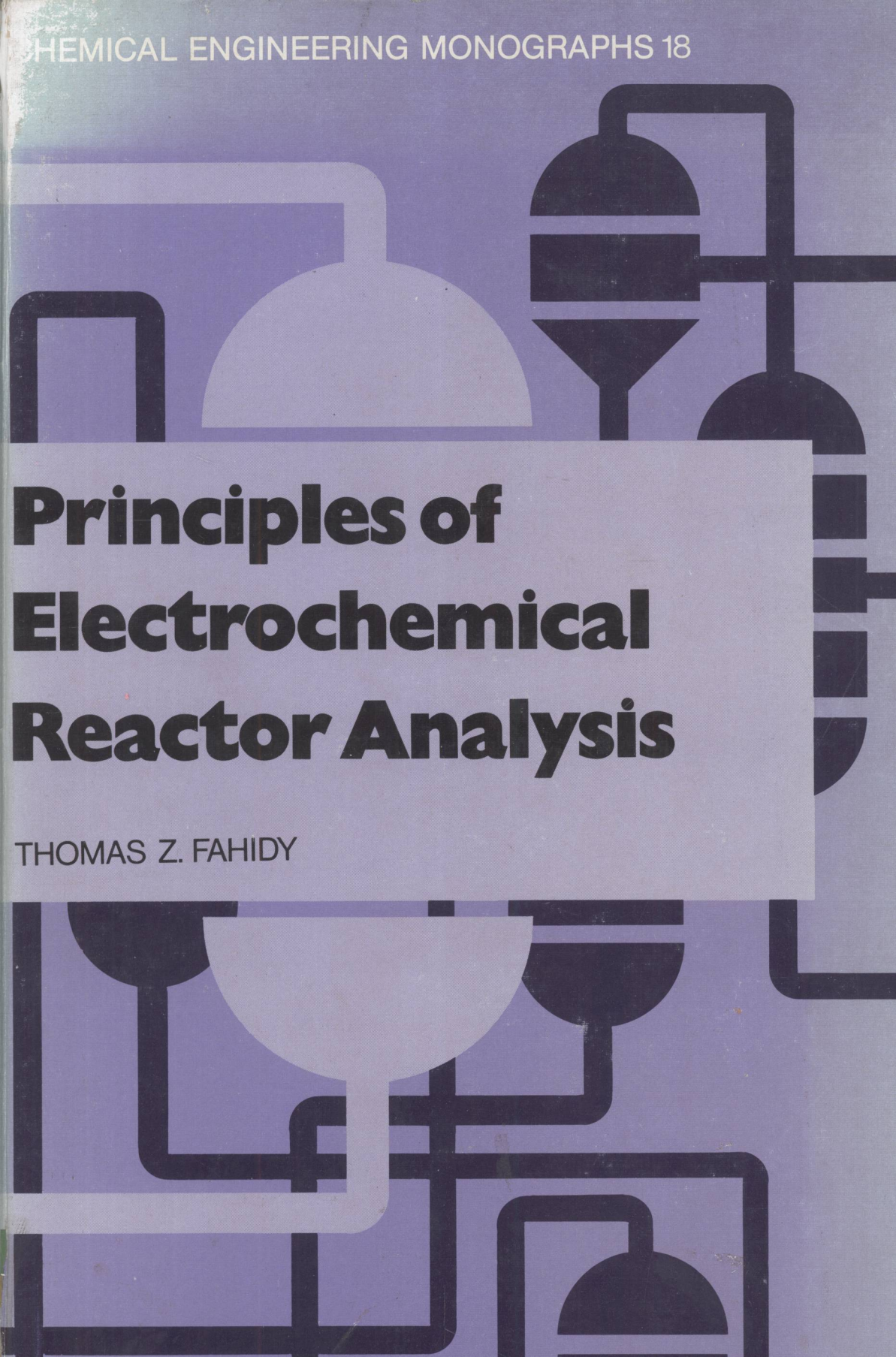


CHEMICAL ENGINEERING MONOGRAPHS 18

The background of the book cover features a stylized, high-contrast illustration of chemical reactor components. It includes several large, rounded vessels (reactors or storage tanks) connected by a network of thick, black lines representing pipes and conduits. The design is minimalist and industrial, using a limited color palette of black, white, and a muted purple/blue background. The text is overlaid on a white rectangular area in the center.

Principles of Electrochemical Reactor Analysis

THOMAS Z. FAHIDY

Principles of Electrochemical Reactor Analysis

THOMAS Z. FAHIDY

Department of Chemical Engineering, University of Waterloo (Canada)



ELSEVIER - Amsterdam — Oxford — New York —Tokyo 1985

ELSEVIER SCIENCE PUBLISHERS B.V.
Molenwerf 1
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
52, Vanderbilt Avenue
New York, NY 10017

ISBN 0-444-42451-2 (Vol.18)
ISBN 0-444-41295-6 (Series)

© Elsevier Science Publishers B.V., 1985

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science Publishers B.V./Science & Technology Division, P.O. Box 330, 1000 AH Amsterdam, The Netherlands.

Special regulations for readers in the USA — This publication has been registered with the Copyright Clearance Center Inc. (CCC), Salem, Massachusetts. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the USA. All other copyright questions, including photocopying outside of the USA, should be referred to the publisher.

Printed in The Netherlands

Principles of Electrochemical Reactor Analysis

CHEMICAL ENGINEERING MONOGRAPHS

Advisory Editor: Professor S.W. CHURCHILL, Department of Chemical Engineering,
University of Philadelphia, PA 19104, U.S.A.

- Vol. 1 Polymer Engineering (Williams)
- Vol. 2 Filtration Post-Treatment Processes (Wakeman)
- Vol. 3 Multicomponent Diffusion (Cussler)
- Vol. 4 Transport in Porous Catalysts (Jackson)
- Vol. 5 Calculation of Properties Using Corresponding State Methods
(Stěrbáček et al.)
- Vol. 6 Industrial Separators for Gas Cleaning (Štorch et al.)
- Vol. 7 Twin Screw Extrusion (Janssen)
- Vol. 8 Fault Detection and Diagnosis in Chemical and Petrochemical
Processes (Himmelblau)
- Vol. 9 Electrochemical Reactor Design (Pickett)
- Vol. 10 Large Chemical Plants (Froment, editor)
- Vol. 11 Design of Industrial Catalysts (Trimm)
- Vol. 12 Steady-state Flow-sheeting of Chemical Plants (Benedek, editor)
- Vol. 13 Chemical Reactor Design in Practice (Rose)
- Vol. 14 Electrostatic Precipitators (Böhm)
- Vol. 15 Toluene, the Xylenes and their Industrial Derivatives
(Hancock, editor)
- Vol. 16 Dense Gas Dispersion (Bitter and Griffiths, editors)
- Vol. 17 Gas Transport in Porous Media: The Dusty-Gas Model
(Mason and Malinauskas)
- Vol. 18 Principles of Electrochemical Reactor Analysis (Fahidy)
- Vol. 19 The Kinetics of Industrial Crystallization (Nývlt et al.)
- Vol. 20 Heat Pumps in Industry (Moser and Schnitzer)

To the Memory of NORBERT IBL
Who Was Scholar, Mentor and Friend

PREFACE

The analysis of electrochemical reactors by means of chemical engineering principles is a relatively new endeavour, tying together several scientific and engineering disciplines such as electrochemistry, physical chemistry, hydrodynamics, mass and heat transport phenomena, chemical reaction engineering, mathematical modelling and optimization. Very few university programs provide at the present time such a combination of backgrounds, at least at the undergraduate level where instruction rarely reaches beyond courses devoted essentially to subjects of classical electrochemistry. Practicing professionals who wish to get quickly acquainted with the field of electrochemical engineering can seldom afford the time and effort required for a systematic and detailed understanding of all these subjects, desirable as it may be, before they have to do electrochemical engineering. They need to get acquainted with basic principles and computation procedures in a relatively short time, without having to become immediately familiar with all details of the constitutive disciplines.

This book was written, therefore, with two goals in mind. The first goal was to create a book on electrochemical reactors which can be used as a text by undergraduate and junior graduate students in an electrochemical engineering course. The second goal was to address chemical engineers and electrochemists with a conventional background in their respective fields who wish to learn about electrochemical reactors essentially on a self-taught basis. The book could also serve, perhaps in a minor sense, as a reference-source of methods, procedures and equations for electrochemical engineers who already possess a good fundamental understanding of the subject matter. Major emphasis is placed on turning fundamental principles into tools for engineering computing; for this purpose, every chapter contains a number of illustrative examples and problems, and numerical techniques of importance are discussed at a depth normally not encountered in the few books available in electrochemical engineering.

The contents may be classified into two parts: basic concepts (Chapters 1-5) and advanced concepts (Chapters 6-11). In the first part, five principal subjects are discussed. Chapter 1 establishes the framework for fundamental calculations regarding electrochemical reactors from a strongly practical point of view; there is an almost immediate emphasis on mass transport-oriented thinking, which is so essential to the substance of the domain. It is followed

by reactor analysis via two basic reactor models: the plug flow model (PFM; Chapter 2) and the CSTER model (Chapter 3). Chapter 4 is a guide to the estimation of mass transport coefficients for electrode geometries of major engineering interest. Chapter 5 discusses the thermal behaviour of electrochemical reactors, and especially the estimation of steady state electrolyte temperatures. After having studied these five chapters, the reader should be able to carry out process analysis and design of simple electrochemical reactors.

The second portion of the text contains material beyond an elementary level of understanding and it consists of six chapters. Chapter 6 presents an overview of mathematical models more sophisticated than the PFM and CSTER model via the concept of dispersion. Chapter 7 explores certain aspects of convective diffusion theory with particular regard to axisymmetric electrode surfaces in order to provide a deeper understanding of mass transport phenomena and relationships presented in the first part. In Chapter 8 a refined approach to transport, which accounts for the influence of the electric field on the limiting current (the largest current attainable under mass transport control during the electrode reaction of a single ionic species) is presented; the topic serves also as an introduction to Chapter 9, where the spatial variations of electric potential and current in a reactor are examined in an introductory manner, but emphasizing the use of modern numerical techniques in solving distribution problems. Chapter 10 exposes the reader to a still scarcely explored area of electrochemical engineering of growing importance for process control: the dynamic behaviour of electrochemical reactors. Finally, Chapter 11 portrays the conceptual framework of optimizing reactor operation with a modicum of mathematical encumbrance. If used as a text, the first five chapters can be readily covered in an undergraduate course, while the remaining six chapters can serve as a base for a graduate course. The illustrative examples and separate problem sets employ consistently SI units; the serious reader is urged to work out these problems of various levels of difficulty (a common electronic slide rule and occasionally a programmable calculator will be needed for numerical work).

There are no specific references given within individual chapters for two major reasons. Firstly, this book is not intended to be a research report, or a guide-compendium of previous publications where the acknowledgement of individual contributions is de rigueur. Secondly, it is not necessary for the understanding of the material presented here to search for detailed information in individual research papers: in fact, such an activity would detract the reader from the pursuit of a reasonably rapid assimilation of principles and computation procedures. However, a selected list of recommended reference material is given in Appendix 1 for further perusal of the various aspects of

the science of electrochemical reactors which have been covered only to the necessary extent.

Finally, an expression of gratitude is due Nancy A. Stade for her prowess in deciphering and efficient typing, and to my family and colleagues for their patience. Living in the microchip age has been very useful for treating the subject matter with a strong mathematical propensity and arithmetic flavour.

T.Z. FAHIDY

CONTENTS

Preface	VII
CHAPTER 1 FUNDAMENTAL CONCEPTS AND CALCULATIONS.	1
1.1 A General View of Electrolytic Processes	1
1.2 Computational Aspects of the Current-Voltage Relationships in Electrolytic Reactors.	3
1.3 The Limiting Current Plateau	10
1.4 A More Sophisticated Approach: Summary of Convective Diffusion Theory	12
1.5 Dimensionless Groups	16
1.6 Convective Diffusion and the Mass Transport Coefficient.	17
1.7 Balances and Efficiency in Electrochemical Reactors.	20
1.8 Two Fundamental Modelling Concepts: Plug-Flow and Perfect Mixing	26
Problems for Chapter 1.	29
CHAPTER 2 THE PLUG FLOW MODEL (PFM) OF ELECTROCHEMICAL REACTORS.	32
2.1 Introduction and Simplified Analysis	32
2.2 Plug-Flow Model Analysis of Electrochemical Reactors Employing Parallel-Plate Electrodes.	35
2.3 PFM Analysis With Electrolyte Recycling.	41
2.4 The PFM and Real Electrochemical Reactors.	44
Problems for Chapter 2.	48
CHAPTER 3 THE CSTER MODEL OF ELECTROCHEMICAL REACTORS.	50
3.1 Introduction and Analysis of Simple CSTER Systems.	50
3.2 CSTER Cascades	52
3.3 CSTER Analysis of Batch Electrochemical Reactors	57
3.4 CSTER Analysis of Semi-Continuous Electrochemical Reactors	60
3.5 CSTER Analysis of Electrolyte Recycling.	63
3.6 CSTER With Simultaneous Electrochemical and Chemical Reactions	68
3.7 The CSTER and Real Electrochemical Reactors.	71
Problems for Chapter 3.	75
CHAPTER 4 THE ESTIMATION OF MASS TRANSPORT COEFFICIENTS.	78
4.1 General Concepts	78
4.2 The Estimation of Mass Transport Rates From Statistical Regression Relationships.	89
4.3 The Estimation of Mass Transport Coefficients At Commonly Occurring Electrodes	96
4.4 The Estimation of Mass Transport Coefficients Under Enhanced Convection Condition	101
Problems for Chapter 4.	107
CHAPTER 5 THE THERMAL BEHAVIOUR OF ELECTROCHEMICAL REACTORS.	110
5.1 General Aspects.	110
5.2 Thermal Behaviour Under CSTER Conditions	111
5.3 The Estimation of Heat Losses.	114
5.4 Thermal Behaviour Under PFR Conditions	119
5.5 Thermal Behaviour of Batch Electrochemical Reactors.	124
5.6 The Batch CSTER With Evaporation From the Electrolyte Surface.	128
Problems for Chapter 5.	135
CHAPTER 6 DISPERSION MODELS OF ELECTROCHEMICAL REACTORS.	137
6.1 General Concepts	137
6.2 Tracer Input Signal/Output Signal Configurations and Dispersion.	138
6.3 Axial Dispersion In Electrochemical Reactors	142
6.4 Axial Dispersion and Reactor Performance	145

6.5	Axial Dispersion Analysis Via Tanks-In-Series Model	148
6.6	Radial Dispersion In Electrochemical Reactors	150
6.7	The Effect of Dispersion On the Distribution of Electrolyte Concentration In An Electrolyzer.	156
6.8	The Problem of Current Distribution In Reactors With Dispersion .	158
6.9	Analysis of Two-Dimensional Dispersion.	160
	Problems for Chapter 6	162
CHAPTER 7 INTRODUCTION TO CONVECTIVE DIFFUSION THEORY AND MASS TRANSPORT AT AXISYMMETRIC ELECTRODE SURFACES (LIGHTHILL- ACRIVOS THEORY)		165
7.1	Theoretical Framework	165
7.2	Derivation of the Convective Diffusion Equation (1.16).	167
7.3	The Scope and Limitations of the Convective Diffusion Equation. .	169
7.4	Elements of the Theory of Convective Diffusion At Axisymmetric Surfaces.	170
7.5	The Analysis of Transport Mode Control Via Convective Diffusion Theory.	176
7.6	The Solution of the Convective Diffusion Equation In the Limiting Case of Zero Peclet Number	179
7.7	Elements of a Generalized Theory of Free Convection For Axi- symmetric Surfaces.	184
7.8	Concluding Remarks.	186
	Problems for Chapter 7	187
CHAPTER 8 MIGRATION EFFECTS ON ELECTROCHEMICAL MASS TRANSPORT		190
8.1	General Aspects	190
8.2	The Supporting Electrolyte Effect: Fundamentals of the (Stagnant) Nernst Layer Model	194
8.3	The Estimation of Limiting Currents	194
8.4	Inhibitive Effects of Migration On the Limiting Current	198
8.5	Interpolation of Tabular Data	200
8.6	Elementary Perturbation Theory: The Limiting Current On a Rotating Disk Electrode	202
	Problems for Chapter 8	206
CHAPTER 9 THE DISTRIBUTION OF ELECTRIC POTENTIAL AND CURRENT IN ELECTROCHEMICAL REACTORS.		209
9.1	General Aspects	209
9.2	Fundamental Notions of the Electric Potential Distribution; The Electroneutrality Condition	209
9.3	The Violation of the Electroneutrality Principle In the Electric Double Layer.	214
9.4	Potential Distribution In Reactors With Parallel Plate Electrodes .	215
9.5	Potential Distribution In Flow-Through Porous Electrodes.	221
9.6	Current Distribution In Electrochemical Reactors: The General Framework of Analysis	224
9.7	Primary Current Distribution On Plate Electrodes.	225
9.8	Secondary Current Distribution On Short Plate Electrodes Separated By A Large Distance	228
9.9	A General Approximate Method For Computing Current Distributions: Orthogonal Collocation.	229
9.10	Current Distribution Under Mass Transport Control	237
	Problems for Chapter 9	241
CHAPTER 10 INTRODUCTION TO THE PROCESS DYNAMICS OF ELECTROCHEMICAL REACTORS		244
10.1	Basic Notions of Process Dynamics	244
10.2	The Manipulation of Transfer Functions.	246
10.3	Transfer Function Representation of the Isothermal CSTER Model. .	252
10.4	Transfer Function Representation of the Isothermal PFER Model . .	255

10.5	Experimental Construction of Transfer Functions For Electro-chemical Reactors: Basic Methods	259
10.6	Experimental Construction Transfer Functions For Electrochemical Reactors: Guillemin's Method	263
10.7	An Extension of the Transfer Function Representation to Nonlinear Analysis: The Describing Function Approach	266
10.8	Prediction of Reactor Performance and Optimal Control Via Process Dynamics.	270
	Problems for Chapter 10.	274
	CHAPTER 11 INTRODUCTION TO THE OPTIMIZATION OF ELECTROCHEMICAL REACTORS	278
11.1	General Notions	278
11.2	Elementary Process Optimization: The Ibl Formula	278
11.3	Optimization of Electrorefining Processes: The Jaskula Formula	282
11.4	Optimization of A General Electrolytic Process: The Beck Formula	284
11.5	Optimization of Anode-Cathode Distance.	290
11.6	Optimization With Several Independent Variables	291
11.7	Graphical Optimization.	295
11.8	Optimization Via Computers.	295
	Problems for Chapter 11.	297
	APPENDICES	300
I-A	A List of Selected Literature In Applied Electrochemistry and Electrochemical Engineering	300
I-B	Further Readings In Subjects Covered In Chapters.	301
II	A Simple Root Finding Technique: Interval Halving.	303
III	Data Interpolation Via Lagrange's Method.	304
IV	A Rapid Approximate Method For Computing Definite Integrals	307
	ANSWERS TO SELECTED PROBLEMS	309
	INDEX.	312
	LIST OF PRINCIPAL SYMBOLS.	315

Chapter 1

FUNDAMENTAL CONCEPTS AND CALCULATIONS

1.1 A GENERAL VIEW OF ELECTROLYTIC PROCESSES

Electric current flow between an anode and cathode placed in an electrolyte is the combined result of electrode processes, charge transport and mass transport brought about by the imposition of an electric field across the electrodes. The relative strength of individual components in the total current flow depends essentially on the strength of the electric field if the nature and composition of the electrolyte is given. This is a simplistic view of an extremely complicated set of phenomena (amply treated in numerous textbooks of electrochemistry), but it will suffice for what we have in mind for an engineering analysis of electrochemical reactors.

In Figure 1.1, a typical current-voltage drop relationship is shown. At voltage drops below V_D (curve position OA) there is hardly any current flowing through the reactor (the small current flow is due to a transient capacitive and a so-called residual effect); this region is of no particular interest to practical electrolysis. The sharply rising curve past $V > V_D$ (portion AB) corresponds to the domain of electrolytic polarization where the current flow is determined to a large extent by the kinetics of electrode processes involved: the ohmic resistance of the electrolyte usually plays a much lesser role than the "kinetic resistance". The result of extrapolating portion AB to the abscissa, V_D is called the decomposition voltage of a given electrolyte in a given reactor. It is best interpreted for our purpose as the lower bound of practical potential drops between the electrodes. As the voltage drop is increased beyond point B, the rate of ionic transport via convection and diffusion become the major source of current flow: the portion BC of the (I,V) curve represents mixed control where kinetic, convective and diffusive components are all significant contributors to the overall transport process. The last two are increasingly important as V is increased and become fully predominant in the CD range. This range (plateau) is represented by the limiting current I_L , which is in principle the largest current that can flow between the electrodes, due to a particular set of electrode reactions. The rising portion DE represents the onset of new electrochemical processes, such as the electrolysis of water in an aqueous solution, following the cathodic deposition of a metal.

There are certain comments to be made at this point. Firstly, the CE curve shown in Figure 1.1 corresponds, strictly speaking, to systems where the

ionic reactions are truly consecutive. Many processes are known where ionic reactions occur simultaneously within a particular range of the imposed electric field causing considerable distortion in the AB and CD portions of the overall curve; in certain cases a limiting current plateau is not even distinguishable. Secondly, we could consider individual electrode potentials (measured by means of a suitable reference electrode) for the abscissa and obtain current versus electrode potential curves similar to Figure 1.1. Such polarization curves, although of great importance in the study of electrode kinetics, are less important for the electrochemical engineer who has to think more in terms of voltage drops between working anodes and cathodes than in terms of a potential drop between one working electrode and a reference electrode.

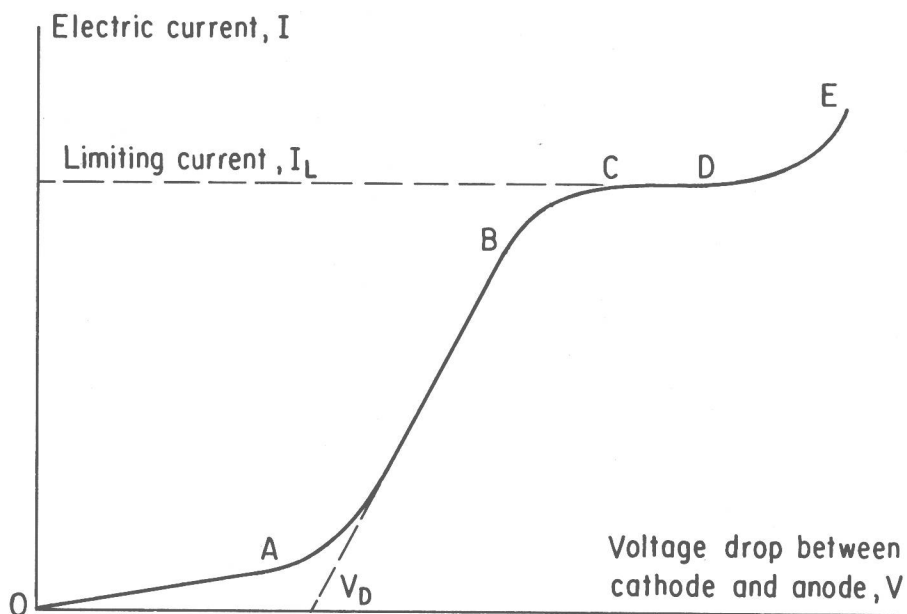


Figure 1.1. The variation of electric current in an electrochemical reactor with voltage drop across the anode and the cathode.

Very often the practitioner encounters only the AC or the AB portion of Figure 1.1 in industrial electrochemical processes.

Nevertheless, there are important situations where processes at one

particular electrode will sufficiently determine conditions for reactor design. Consider, for instance, the deposition of copper from an aqueous $\text{CuSO}_4/\text{H}_2\text{SO}_4$ or $\text{Cu}(\text{NO}_3)_2$ solution where the anode reaction results in oxygen gas evolution and the overall cathode reaction is the discharge of cupric ions to copper. The anode reaction will fall in the AB range of the anodic polarization curve, but the cathode reaction can occur in the CD range of the cathodic polarization curve if the voltage drop across the electrodes is properly set. Then, the overall ionic transport process will be governed by the limiting current at the cathode, therefore, cathodic conditions will be the significant factor in process analysis. Similarly, if the anode reaction is exactly the opposite of the cathode reaction (i.e., anodic oxidation of copper to cupric ions), both electrode processes can be run at limiting conditions, in principle, and conditions at one electrode would again determine overall reactor behaviour, because of the "mirror-image" of the two electrode processes.

1.2 COMPUTATIONAL ASPECTS OF THE CURRENT-VOLTAGE RELATIONSHIPS IN ELECTROLYTIC REACTORS

It follows from the preceding discussion that the computation of the (I,V) relationship depends on the specific portion of Figure 1.1 which corresponds to operating conditions: an overall voltage balance could be the starting point. Assume that we impose a specific voltage drop V across the electrodes. Then, as illustrated in Figure 1.2, the overall voltage balance may be written as

$$V = V_D + IR + \sum_j |\eta_j| \quad (1.1a)$$

where V_D is the decomposition voltage drop, IR is the ohmic voltage drop and $\sum_j \eta_j$ is the sum of the voltage drops due to activation polarization (i.e., kinetic effects) and concentration polarization, caused by concentration gradients between the electrode surfaces and the bulk electrolyte. The rigorous computation of $\sum_j |\eta_j|$ on a purely theoretical basis is often impossible in the instance of practical electrolytic processes and semi-empirical equations have to be used. The summation signs and absolute-value imply that the polarization voltage drops have to be considered for all constituent anodic and cathodic processes as additive quantities. The computation is rather involved, but it can be simplified to some extent in one case which occurs frequently in practice: the cathode is strongly polarized whereas the anodic polarization is low and concentration polarization for the anodic process is negligible. Then, (1.1) may be written as

$$V = V_D + IR + |\eta_{1,a}| + |\eta_{1,c}| + |\eta_{2,a}| \quad (1.1b)$$

where $\eta_{1,a}$ is the voltage drop due to activation polarization at the cathode, $\eta_{1,c}$ is the voltage drop due to concentration polarization at the cathode and $\eta_{2,a}$ the voltage drop due to activation polarization at the anode.

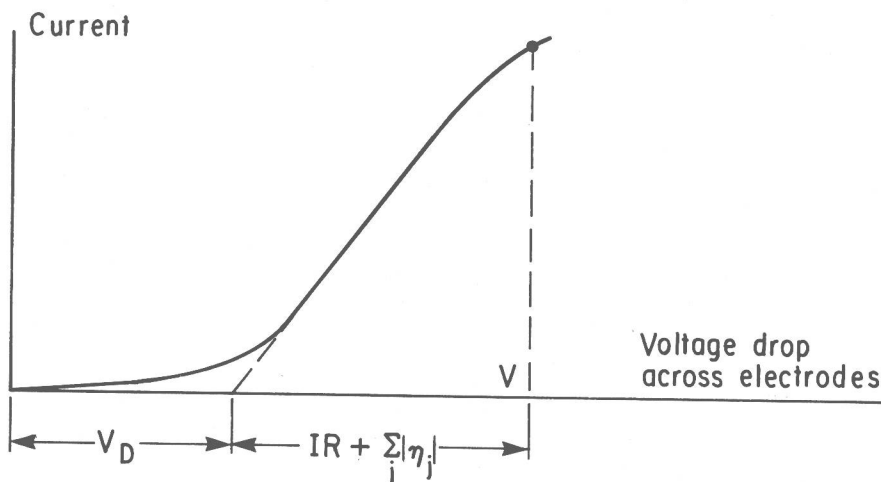


Figure 1.2. Illustration for Equation (1.1a).

The Decomposition Potential V_D

As shown in Section 1.1, the decomposition potential drop between two electrodes is an extrapolated quantity and although it has no theoretical significance, it is important for the estimation of the practical minimum voltage drop in an electrochemical process. Its numerical value depends on the electrode material, electrolyte composition and concentration, temperature and the experimental thoroughness in establishing the rising portion of the (I,V) curve. Care must be taken to avoid confusing V_D with the cell potential drop U computed from the free energy change of the overall electrochemical process:

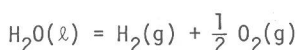
$$\Delta G = -zFU \quad (1.2a)$$

or its standard-state value, computed from the standard free energy change

$$\Delta G^\circ = -zFU^\circ \quad (1.2b)$$

where F , the Faraday number, is the product of the Avogadro number (6.023×10^{23} ion/mol) and the fundamental unit of electric charge (1.602×10^{-19} coulomb); its numerical value is 96.487 kC/mol or 26.8 A.h/mol. ΔG° is a measure of the minimum energy to be put into an electrolytic process at thermodynamically reversible conditions, hence U° is at best a fictitious "minimum" potential drop. Its value, computed from ΔG° obtained from standard free energies of formation of the reaction constituents, may be reasonably close to experimental V_D values in some instances.

Example 1.1: The standard free energy of the water decomposition reaction



is computed from the standard free energies of formation of $\text{H}_2\text{O}(\ell)$, $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ as

$$\Delta G^\circ = \frac{1}{2} \Delta G^\circ_{\text{O}_2(\text{g})} + \Delta G^\circ_{\text{H}_2(\text{g})} - \Delta G^\circ_{\text{H}_2\text{O}(\ell)}$$

at 25°C , $\Delta G^\circ = \frac{1}{2} 0 + 0 - 237.346$ kJ per one mol of H_2O or one mol of H_2 . Since two electrons are transferred per one mol of H_2O in the process,

$$U^\circ = \frac{-\Delta G^\circ}{zF} = \frac{237.346}{(2)(96.487)} = 1.23 \text{ V}$$

at 25°C . On the other hand, experimental decomposition potentials of water vary with the nature and concentration of the electrolyte, as shown in Table 1.1; they are larger than U° .

TABLE 1.1

Selected values of the decomposition potential of water at smooth platinum electrodes and 25°C

Electrolyte	Concentration, mol/L	V_D , volt
HCl	0.17	1.41
H_3PO_4	0.50	1.67
H_3PO_4	0.34	1.70
NaOH	1.00	1.69
KOH	1.00	1.69