Preface	•	•	•	•	•	•		•		•	v
Foreword	•	•	•	٠	•	•		٠		•	vii
Glossary of	Syr	nbols	•	•	•		•		•	•	ix
CHAPTER	1	Defin	ition c	of the	subje	et.		•			1
CHAPTER	2	Globa	l The	rmody	nami	cs.			•	•	5
CHAPTER	3	Local	Form	ulatio	on of '	Therr	nodyna	mics	•	•	8
·		П.	Phen	icit fo omen	orm o ologic	al rel	entrop ations brium	•	•	ion.	8 10 11
CHAPTER	4	Local	Bal	ance	Ther	mody	namics	s in	Elect	tro-	
		chem	ical Sy	ystem	s .	•	•	٠	•	٠	14
		I.	Intro	ductio	on					•	14
		II.	Elect	romag	gnetic	equa	tions—	-Pola	rizatio	on.	14
		III.	Pond	eromo	otive 1	force					16
							ion of 1		•		17
		v.			oscopi	e kir	netic e	nergy	bala	nce	
		***	equat		•	•	•	٠	٠	٠	19
			Conse					۰.	· ·	•	20
		V 11.	tial	ору, п	ree en	lergy	and cl	nemic	al pot	en-	00
	1	VTTT		ntron	whal	• • • • •	equatio	•	•	•	$\frac{22}{24}$
							tempe		no in	٠	24
		1 11,					m and			mi-	
			cal re		-						25
		Х.	Local	and	globa	l defi	nitions	s.			27
							n of e		ochem	ical	
			poten				•		•		30
a. *					valio	\mathbf{lity}	of loc	eal tl	nermo	dy-	
2			nami	cs.	•		•	٠	•	•	31
					xix						

CHAPTER 5	How Thermodynamic Relations Extend to sys-	
	tems for which the Permittivity depends on the Macroscopic Field	. 35
	I. Introduction . II. The free chemical energy density III. The free electrochemical energy density IV. The entropy density V. The internal (chemical) energy density and electrochemical energy density VI. The chemical potential VII. The electrochemical entropy density VIII. Numerical examples (A) The entropy density 1. Case of a weak field 2. Case of a strong field (B) The free energy densities (C) The energy densities	35 36 37 38 39 40 41 43 43 43 44 45 46 47
CHAPTER 6	Pressure in Polarized Systems	50
	I. Introduction	50
	II. Helmholtz's concept	50
	III. Calculation of the difference between	
	Kelvin's and Helmholtz's pressures .	57
	IV. Correlation effect	60
	V. Macroscopic field and field resultant .	60
CHAPTER 7	Mechanical Equilibrium. Distribution of Pres- sures in a Charged and Polarized System	63
	I. Introduction	63
	II. Kelvin pressure distribution. Mechanical	
	equilibrium	63
	III. Analytical method	64
	IV. Plane layer	65
	V. Geometrical method	65
	VI. Helmholtz pressure distribution	68
	VII. Thermodynamic approach of the pressure	
	distribution	69

	Contents				xxi
CHAPTER 8 Equi	librium Distribution of	Ions a	nd Dip	oles ir	ı
	an Electric Field .	•	• -	•	. 72
I.	Introduction .				. 72
II.	Dilute solutions .	•			. 72
III.	Comparison with the E	Boltzma	nn eq	uation	75
IV.	Gaseous mixtures .		• -		. 75
	Electrostriction .	•		•	. 76
VI.	Polarization effect and	l volun	ne effe	et .	. 79
	Standard functions	•	•	•	. 82
VIII.	Equilibrium distribution	ons of a	an unc	hargeo	1
	solvent	•	•	•	. 84
	ctric Constant and Mola			•	. 86
I.	Introduction .	·	•		. 86
II.	Introduction . Calculation of $\sum_{\gamma} C_{\gamma} \left(\frac{\partial}{\partial C} \right)$	$\left(\frac{\varepsilon}{D_{\nu}}\right) TE(\varepsilon)$	C)	•	. 86
111.	Calculation of $(\partial \varepsilon / \partial C_y)$	TEC			88
IV.	The derivatives in the o	case of	electro	lytes	. 89
V.	Calculation of $(\partial \varepsilon / \partial E)_{II}$	r,C	•	•	. 93
VI.	Molar volumes .	•	•	•	. 94
CILADEED 10 O.J.	- CMT	n			
	r of Magnitude of some l				
	xamples of Thermodyna	imicai	Quant	nies	. 99
I.	Introduction .	•	•		. 99
П.	Calculation of b_{γ} .	•	•	•	. 99
III.	Calculation of $p'_0 - p$ Calculation of $p_0 - p'$	•	•	•	. 100
IV.	Calculation of $p_0 - p'$	•	•	•	. 101
V.	Ionic distribution in th	ne field	•	•	. 101
	linia Decention of	(1	. 1	•	
UNAPIER II Equi	ibrium Properties of t		ectroci	iemica	
	Diffuse Plane Double I	layer	•	• •	103
I.	Introduction .		• *		. 103
	The Poisson equation		•		. 105
III.	The charge of the ideal	polariz	ed elec	ctrode	106
	Influence of the polari	zation	on the		-
	ential capacity of the			•	. 109
V.	Influence of the pola				1
	adsorption in the diffu	se dou	ble lay	er	. 111

VI. Discussion of the results	113
VII. Specific influence of the diffuse layer in	
electrochemical kinetics	114
VIII. Specific influence of the diffuse layer on	
the properties of the ideal polarized	
electrode	118
IX. Specific influence of the diffuse double	
layer in the presence of internal adsorption	121
X. Influence of the solvent on the diffuse	
specific adsorption	122
CHAPTER 12 Distribution of Potential, Field and Charge	
Density in the Electrochemical Diffuse Double	
	126
	140
I. Introduction	126
II. The distribution equation of the electrical	
potential	126
III. Activity coefficient at zero field	127
IV. Systems and boundary conditions	130
V. Discussion of the results	132
(A) Concentration effect	132
(B) Dielectric saturation effect	132
(C) Anion effect	133
(D) Cation effect	133
1. Effect of decrement $ \delta_+ $	133
Molar volume effect	134
(E) Curvature effect	134
(F) Activity coefficients effect	134
(G) Nomograms	135
1. Nomogram 1	135
2. Nomogram 2	136
CHAPTER 13 Association and Dissociation in the Electro	
chemical Diffuse Double Layer .	139
•	190
I. Introduction	139
II. Diffuse double layer with a partly dis-	100
sociated electrolyte	139
III. Calculation of the dissociation constant .	144
IV. Discussion	147

	Contents			:	xxiii
CHAPTER 14 Inter	facial Arientation_	_Extension	of the	Cibh's	
Theo		-Lixtonsion			151
		• •	•	•••	
	Introduction		•	• •	151
	Orientation varia				152
111.	Thermodynamics			ectro-	154
TV	capillary system Extension to open			• •	$\begin{array}{c} 154 \\ 157 \end{array}$
	Plane interphase			trically	107
	conducting phase			•	159
VI.	Partial equilibriu				100
	component may				
	1		•		160
VII.	Examples .		•		163
	Ideal polarized el		•		163
CHAPTER 15 Insol	uble Monolayer an	d Gibb's Su	rface M	[odel .	172
T	Introduction				172
	Gibbs' surface mo	del .	•	• •	172
	Various explicit fo		s of the	chemi-	
	cal potential in th				
		•	•		175
	0				
CHAPTER 16 Elect	ric Repulsion betw	een Two E	lectrock	iemical	
Diffu	se Layers. Applicat	tion to Thir	n Films		179
т	Introduction				179
	Survey of previou	 Is work	•		180
	Discontinuity of			plane	
	interface perpend				181
IV.	Total pressure ex	erted on a	n interf	ace by	
	a fluid.		•		182
	Surface of a solid				183
	Repulsion betwee				
	plates immersed i				184
VII.	Pressure in a liqu		neraliza	tion of	100
	Laplace's equation			• •	186
VIII.	Influence of the				100
τv	electric repulsion Comparison with				188
17.	equation .			CI DGGK	193
	Annual .	• •	•	• •	100

						potent		.nd		194
						ergy				195
						ission				200
		Second Street				trong e	lectro	vtes		202
	XII.		•			energy		•		
						herical				202
						120				204
CHAPTER 17	The	Tensor	of P	ressu	re in	Spheric	cal an	d P	lane	
		rocapil								210
	Ι.	Intro	luctio	m					•	210
	II.	Spher	ical la	ayer v	vitho	ut field	force			211
	III.	Plane	layer	r with	out f	ield for	ce		•	212
						n elect		ield 1	nor-	
		mal to		•		•	•	•		212
	V.	Plane	layer	with	an e	electrica	l field	nor	mal	
		to the								215
	VI.	The s	urface	e tens	ion a	s an ex	cess re	sult	ant.	
		The s	pherio	cal lay	/er					216
	VII.	Surve				ork				218
			~ -	-		ed by s	urface	e for	ces:	
						theory				219
	IX.					electro				220
CHAPTER 18	Nerns	st Law		•	×			•		227
	т	Intro	Inotic	m						227
					of d	issoluti	• 010	•	•	227
						issoluti		•	٠	230
		Conce				10001001	011	•	٠	233
						(or red	· ox) ce	lls		235
						•				
Conclusions	٠	•	•	•	٠	٠	•	·	•	239
Author Index	•	•	•	•		٠	•		•	245
Subject Index				•	٠	•				251

xxiv

.