

# Contents

<b>1 Getting started</b>	1
1.1 The scope and nature of this primer	1
1.2 Electrostatics, electricity, and electrode potentials	1
1.3 The origin of electrode potentials	8
1.4 Electron transfer at the electrode/solution interface	10
1.5 Thermodynamic description of equilibrium	12
1.6 Thermodynamic description of electrochemical equilibrium	14
1.7 Electrochemical experiments	16
1.8 The Nernst equation and some other electrode/solution interfaces	16
1.9 Concentrations or activities?	20
1.10 A general statement of the Nernst equation for an arbitrary potential determining equilibrium	20
1.11 Measurement of electrode potentials: the need for a reference electrode	22
1.12 The standard hydrogen electrode	25
1.13 Standard electrode potentials	27
1.14 The Nernst equation applied to a general cell	31
1.15 The relation of electrode potentials to the thermodynamics of the cell reaction	33
1.16 Standard electrode potentials and the direction of chemical reactions	37
1.17 Standard electrode potentials and disproportionation	42
1.18 Standard electrode potentials and pH	43
1.19 Latimer diagrams	44
1.20 Frost diagrams	45
1.21 Thermodynamics versus kinetics	49
1.22 The measurement of standard electrode potentials	50
<b>2 Allowing for non-ideality: activity coefficients</b>	53
2.1 Introduction	53
2.2 The entropy of mixing: ideal solutions	54
2.3 The interpretation of activity coefficients	55
2.4 Debye-Hückel theory	57
2.5 Limits of the Debye-Hückel theory	61
2.6 Applications of the Debye-Hückel limiting law	65

<b>3 Ions in motion</b>	71
3.1 Current density and voltage gradients	71
3.2 Molar conductivity	72
3.3 Measurement of conductivity and molar conductivity	73
3.4 Transport numbers	74
3.5 A simple model for single ion molar conductivities	76
3.6 Diffusion	80
3.7 Electrochemical potential gradients—linking diffusion and conductivity	81
<b>4 Going further</b>	83
4.1 Measurement of standard electrode potentials	83
4.2 Salt bridges	87
4.3 The calomel reference electrode	90
4.4 Measurement of the standard electrode potentials of reactive metals	91
4.5 Electrode 'poisoning' and the limitations of potentiometric measurements	92
<b>5 Further applications: chemical sensing and energy transformation</b>	97
5.1 Sensitivity and selectivity	97
5.2 Membrane potentials	98
5.3 Potassium-selective microelectrodes	100
5.4 Proton-selective glass electrodes	101
5.5 pH electrodes and the quantification of chemical equilibria	103
5.6 Carbon dioxide and ammonia gas sensing electrodes	105
5.7 Enzyme electrodes	106
5.8 Ion-selective field effect transistors (ISFETs)	107
5.9 Amperometric sensing	107
5.10 Analysis beyond molecules in solution; solid particles	111
5.11 Energy transformation: fuel cells and batteries	114
5.12 Electrosynthesis: using electricity to make chemicals	119
5.13 Electrochemistry—the Essential Science	120
<b>6 Worked examples and problems</b>	123
6.1 Worked examples	123
6.2 Problems	137
Index	143