

**Second Edition**



# **Non-Equilibrium Thermodynamics for Engineers**

**S Kjelstrup • D Bedeaux  
E Johannessen • J Gross**

 **World Scientific**

# Non-Equilibrium Thermodynamics for Engineers

**Second Edition**

**S Kjelstrup**

*Norwegian University of Science and Technology, Norway*

**D Bedeaux**

*Norwegian University of Science and Technology, Norway*

**E Johannessen**

*Norwegian University of Science and Technology, Norway*

**J Gross**

*University of Stuttgart, Germany*

 **World Scientific**

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI • TOKYO

*Published by*

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

*USA office:* 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

*UK office:* 57 Shelton Street, Covent Garden, London WC2H 9HE

**British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

**NON-EQUILIBRIUM THERMODYNAMICS FOR ENGINEERS**

**Second Edition**

Copyright © 2017 by World Scientific Publishing Co. Pte. Ltd.

*All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.*

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-3200-30-2

Desk Editor: Amanda Yun

Printed in Singapore by B & Jo Enterprise Pte Ltd

# Non-Equilibrium Thermodynamics for Engineers

**Second Edition**



*This book is dedicated to our children*



# Preface of the Second Edition

The popularity of the first edition has promoted a revised and enlarged new print. Original chapters have been revised, especially the chapters on entropy production minimization. Two chapters concerning phase transitions and membrane transport (Chapters 9 and 10) have been added to take advantage of recent developments in surface transport. The eight lecture videos mentioned in the Preface of the First Edition are now available on iTunesU and MIT Open Academy (in collaboration with TU Delft.)<sup>1</sup> IUPAC notation has been introduced for symbol dimensions.

The authors were inspired by the Opinion paper issued on October 2015 by the Physical, Chemical and Mathematical Sciences Committee of Science Europe, D/2015/13.324/6, *A common scale for our common future*. The paper recommends policy makers to (quote) “guide the establishment of *exergy destruction footprints* for commodities and services”. This, they argue, will enhance development of technologies with better energy efficiency.

In view of the impact such a development may have on climate issues, the teaching of non-equilibrium thermodynamics can become central, or even important. We hope that this book can help universities and schools worldwide to establish a curriculum in the field.

---

<sup>1</sup><http://theopenacademy.com/content/signer-kjelstrup>



As said in the Preface of our first edition, we continue to welcome comments and feedback from users to help improve this book.

Trondheim and Stuttgart, January 2016

Signe Kjelstrup  
signe.kjelstrup@chem.ntnu.no

Dick Bedeaux  
dick.bedeaux@chem.ntnu.no

Eivind Johannessen  
eivjohannessen@gmail.com

Joachim Gross  
gross@itt.uni-stuttgart.de

# Preface of the First Edition

Meeting the entropy challenge is probably more central than the issue of providing sufficient power to the world. The entropy production, not the energy used, can measure our wastes and the efficiency of work, or the limit of our activity. This book introduces non-equilibrium thermodynamics to engineers, and discusses how the theory can be useful for typical engineering problems.

The book has been written after many years of teaching the subject at the Norwegian University of Science and Technology, Trondheim, Norway, and the Technical University of Delft, Delft, The Netherlands. Early versions of the book have been used for short courses at the International Center of Thermodynamics, Istanbul, Chalmers Technical University, Gothenburg, Helsinki Technical University and Pennsylvania State University.

This book can be used in Bachelor or Master study programs after a basic course in thermodynamics, or for self study in the industry. The book requires knowledge of basic thermodynamics corresponding to that given by Smith, van Ness and Abbott in *Introduction to Chemical Engineering*, or in Moran and Shapiro's, *Fundamentals of Engineering Thermodynamics*.

To facilitate learning, exercises for the topics of the book and solutions to these, are available on the NTNU homepage.<sup>2</sup> Eight DVD lectures are also available there or from The Technical University of Delft.<sup>3</sup>

---

<sup>2</sup><http://www.chem.ntnu.no/nonequilibrium-thermodynamics/>

<sup>3</sup><http://collegerama.tudelft.nl/mediasite/Catalog/?cid=0cbe1b45-06c6-4d03-a692-92a6dad4711d>

Financial support from the Research Council of Norway is acknowledged. The authors are grateful to Statoil ASA for the cover picture from Mongstad.

The authors welcome comments and suggestions that can improve future editions.

Trondheim and Stuttgart, March 2010

Signe Kjelstrup  
signe.kjelstrup@chem.ntnu.no

Dick Bedeaux  
dick.bedeaux@chem.ntnu.no

Eivind Johannessen  
eijoh@statoil.com

Joachim Gross  
gross@itt.uni-stuttgart.de

# About the Authors



**Signe Kjelstrup** is Professor of Physical Chemistry since 1985 at the Norwegian University of Science and Technology (NTNU), Trondheim, Norway. Until 2015, she was also a part-time Chair on irreversible thermodynamics and sustainable processes at the Technical University of Delft, The Netherlands. Her works in irreversible thermodynamics concern electrochemical cells, membrane systems and entropy production minimization in process equipment. She holds an honorary doctorate from the University of North East China, and has been a guest professor at Kyoto University, Japan, University of Barcelona, Spain. Her book on irreversible thermodynamics, co-authored with K.S. Fjørland and T. Fjørland (Wiley, 1988 and 1994, Tapir 2001), has been translated into Japanese and Chinese.



**Dick Bedeaux** was Professor of Physical Chemistry at the University of Leiden, The Netherlands, from 1984 to 2002, and held (from 2002 to 2011) a part-time Chair at the Norwegian University of Science and Technology (NTNU), Trondheim, Norway. He is now emeritus at both places. Bedeaux, together with Albano and Mazur, extended the theory of irreversible thermodynamics to surfaces. He has worked on curved surfaces. Bedeaux is a fellow of the American Physical Society, and the recipient of the Onsager Medal from the Norwegian University of Science and Technology. Together with Jan Vlieger he wrote the book *Optical Properties of Surfaces* (Imperial College Press, 2002, and revised edition 2004).



**Eivind Johannessen** holds a Dr-Ing from the Norwegian University of Science and Technology (NTNU), Trondheim, Norway, and is presently a researcher at the Norwegian Energy Company, Statoil. His doctoral thesis on the state of systems with minimum entropy production was awarded Best doctor thesis defended at Norwegian University of Technology and Science in 2004.



**Joachim Gross** is Professor of Thermodynamics and Thermal Process Engineering at the University of Stuttgart, Germany. His research interest is in Molecular Thermodynamics and the development of Fluid Theories. After receiving his PhD from the University of Berlin, Germany, he worked in the Conceptual Process Design group of the BASF AG in Ludwigshafen for 4 years. In 2004, he became Associate

Professor at the Delft University of Technology, The Netherlands, in the Separation Technology group. In 2005, he was appointed Chair of Thermodynamics at the same university, before moving to Stuttgart in 2010.

# Contents

Dedication	v
Preface of the Second Edition	vii
Preface of the First Edition	ix
About the Authors	xi
1 Scope	1
2 Why non-equilibrium thermodynamics?	7
2.1 Simple flux equations . . . . .	8
2.2 Flux equations in non-equilibrium thermodynamics . .	10
2.3 The lost work of an industrial plant . . . . .	13
2.4 The second law efficiency. The exergy destruction footprint . . . . .	18
2.5 Consistent thermodynamic modeling . . . . .	21
3 The entropy production of one-dimensional transport processes	23
3.1 Balance equations . . . . .	25
3.2 Entropy production . . . . .	27
3.3 Examples . . . . .	31
3.4 The frame of reference for fluxes . . . . .	38
4 Flux equations and transport coefficients	41
4.1 Linear flux-force relations . . . . .	42
4.2 Transport of heat and mass . . . . .	45
4.3 Transport of heat and charge . . . . .	52
4.4 Transport of mass and charge . . . . .	58

4.4.1	The mobility model . . . . .	62
4.5	Concluding remarks . . . . .	63
<b>5</b>	<b>Non-isothermal multi-component diffusion</b>	<b>65</b>
5.1	Isothermal diffusion . . . . .	66
5.1.1	Prigogine's theorem applied . . . . .	67
5.1.2	Diffusion in the solvent frame of reference . . .	68
5.1.3	Maxwell-Stefan equations . . . . .	70
5.1.4	Changing a frame of reference . . . . .	73
5.2	Non-isothermal diffusion . . . . .	77
5.3	Concluding remarks . . . . .	80
<b>6</b>	<b>Systems with shear flow</b>	<b>81</b>
6.1	Balance equations . . . . .	82
6.1.1	Component balances . . . . .	82
6.1.2	Momentum balance . . . . .	82
6.1.3	Internal energy balance . . . . .	83
6.2	Entropy production . . . . .	83
6.3	Stationary pipe flow . . . . .	91
6.4	The plug flow reactor . . . . .	93
6.5	Transport coefficients: viscosity and thermal conductivity . . . . .	94
6.6	Concluding remarks . . . . .	97
<b>7</b>	<b>Chemical reactions</b>	<b>99</b>
7.1	The Gibbs energy change of a chemical reaction . . . .	101
7.2	The reaction path . . . . .	105
7.2.1	The chemical potential . . . . .	106
7.2.2	The entropy production . . . . .	108
7.3	A rate equation with a thermodynamic basis . . . . .	108
7.4	The law of mass action . . . . .	110
7.5	The entropy production on the mesoscopic scale . . . .	112
7.6	Concluding remarks . . . . .	114
<b>8</b>	<b>The lost work in the aluminum electrolysis</b>	<b>115</b>
8.1	The aluminum electrolysis cell . . . . .	116
8.2	The thermodynamic efficiency . . . . .	118
8.3	A simplified cell model . . . . .	120
8.4	Lost work due to charge transfer . . . . .	122
8.4.1	The bulk electrolyte . . . . .	122

---

8.4.2	The diffusion layer at the cathode . . . . .	122
8.4.3	The electrode surfaces . . . . .	123
8.4.4	The bulk part of the anode and cathode . . . . .	123
8.5	Lost work by excess carbon consumption . . . . .	124
8.6	Lost work due to heat transport through the walls . . . . .	125
8.6.1	Conduction across the walls . . . . .	125
8.6.2	Surface radiation and convection . . . . .	127
8.7	The exergy destruction footprint . . . . .	127
8.8	Concluding remarks . . . . .	129
<b>9</b>	<b>Coupled transport through surfaces</b>	<b>131</b>
9.1	The Gibbs surface in local equilibrium . . . . .	132
9.2	Balance equations . . . . .	134
9.3	The excess entropy production . . . . .	138
9.4	Stationary state evaporation and condensation . . . . .	144
9.5	Equilibrium at the electrode surface. Nernst equation . . . . .	147
9.6	Stationary states at electrode surfaces. The overpotential . . . . .	149
9.7	Concluding remarks . . . . .	151
<b>10</b>	<b>Transport through membranes</b>	<b>153</b>
10.1	Introduction . . . . .	153
10.2	Osmosis . . . . .	154
10.3	Thermal osmosis . . . . .	156
10.3.1	Water and power production . . . . .	157
10.4	Electro-osmosis at constant temperature . . . . .	158
10.4.1	Contributions from the electrodes . . . . .	159
10.4.2	Contributions from the membrane . . . . .	159
10.5	Transport of ions and water across ion-exchange membranes . . . . .	161
10.5.1	The isothermal, isobaric system . . . . .	162
10.5.2	The isothermal, non-isobaric system . . . . .	164
10.5.3	The non-isothermal, isobaric system . . . . .	165
10.6	The salt power plant . . . . .	168
10.7	Concluding remarks . . . . .	170



<b>11 The state of minimum entropy production</b>	<b>171</b>
11.1 Isothermal expansion of an ideal gas . . . . .	173
11.1.1 Expansion work . . . . .	174
11.1.2 The entropy production . . . . .	176
11.1.3 The optimization idea . . . . .	177
11.2 Optimal control theory . . . . .	179
11.3 Heat exchange . . . . .	183
11.3.1 The entropy production . . . . .	185
11.3.2 Optimal control theory and heat exchange . . .	187
11.4 The plug flow reactor . . . . .	191
11.4.1 The entropy production . . . . .	192
11.4.2 Optimal control theory and plug flow reactors . . . . .	196
11.4.3 A highway in state space . . . . .	197
11.4.4 Reactor design . . . . .	201
11.5 Distillation columns . . . . .	203
11.5.1 The entropy production . . . . .	205
11.5.2 The state of minimum entropy production . . .	207
11.5.3 Column design . . . . .	212
11.6 Concluding remarks . . . . .	214
<b>Appendix A</b>	<b>217</b>
A.1 Balance equations for mass, charge, momentum and energy . . . . .	217
A.1.1 Mass balance . . . . .	218
A.1.2 Momentum balance . . . . .	220
A.1.3 Total energy balance . . . . .	222
A.1.4 Kinetic energy balance . . . . .	223
A.1.5 Potential energy balance . . . . .	223
A.1.6 Balance of the electric field energy . . . . .	224
A.1.7 Internal energy balance . . . . .	224
A.1.8 Entropy balance . . . . .	225
A.2 Partial molar thermodynamic properties . . . . .	228
A.3 The chemical potential and its reference states . . . .	230
A.3.1 The equation of state as a basis . . . . .	231
A.3.2 The excess Gibbs energy as a basis . . . . .	232
A.3.3 Henry's law as a basis . . . . .	233
A.4 Chemical driving forces and equilibrium constants . . .	234
A.4.1 The ideal gas reference state . . . . .	235