

HANSEN SOLUBILITY PARAMETERS

A User's Handbook

Second Edition

HANSEN SOLUBILITY PARAMETERS

A User's Handbook

Second Edition

Charles M. Hansen



CRC Press

Taylor & Francis Group

Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an informa business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2007 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works
Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-10: 0-8493-7248-8 (Hardcover)
International Standard Book Number-13: 978-0-8493-7248-3 (Hardcover)

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

No part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (<http://www.copyright.com>) or contact the Copyright Clearance Center, Inc. (CCC) 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data

Hansen solubility parameters : a user's handbook. -- 2nd ed. / edited by Charles Hansen.
p. cm.

Rev. ed. of: Hansen solubility parameters / Charles M. Hansen. c2000.

Includes bibliographical references and index.

ISBN 0-8493-7248-8 (alk. paper)

1. Solution (Chemistry) 2. Polymers--Solubility. 3. Thin films. I. Hansen, Charles M. II. Hansen, Charles M. Hansen solubility parameters.

QD543.H258 2007

547'.70454--dc22

2006051083

Visit the Taylor & Francis Web site at
<http://www.taylorandfrancis.com>

and the CRC Press Web site at
<http://www.crcpress.com>

Contributors

Dr. John Durkee

Consultant in Critical and Metal Cleaning
Hunt, Texas
U.S.A.

Dr. techn. Charles M. Hansen

Consultant
Hoersholm, Denmark

Prof. Georgios M. Kontogeorgis

Technical University of Denmark
Department of Chemical Engineering
Lyngby, Denmark

Prof. Costas Panayiotou

Department of Chemical Engineering
University of Thessaloniki
Thessaloniki, Greece

Tim S. Poulsen

Sr. Research Scientist
Molecular Pathology
Glostrup, Denmark

Dr. rer. nat. Hanno Priebe

Sr. Research Scientist
Chemical Development – Process Research
GE Healthcare
Amersham Health AS
Oslo, Norway

Per Redelius

Research Manager
Nynas Bitumen
Product Technology
Nynashamn, Sweden

Prof. Laurie L. Williams

Department of Physics & Engineering
Fort Lewis College
Durango, Colorado
U.S.A.

Preface to the First Edition

My work with solvents started in Denmark in 1962 when I was a graduate student. The major results of this work were the realization that polymer film formation by solvent evaporation took place in two distinct phases and the development of what has come to be called Hansen solubility (or cohesion) parameters, abbreviated in the following by HSP. The first phase of film formation by solvent evaporation is controlled by surface phenomena such as solvent vapor pressure, wind velocity, heat transfer, etc., and the second phase is controlled by concentration-dependent diffusion of solvent molecules from within the film to the air surface. It is not controlled by the binding of solvent molecules to polymer molecules by hydrogen bonding as was previously thought. My solubility parameter work was actually started to define affinities between solvent and polymer to help predict the degree of this binding which was thought to control solvent retention. This was clearly a futile endeavor as there was absolutely no correlation. The solvents with smaller and more linear molecular structure diffused out of the films more quickly than those with larger and more branched molecular structure. HSP were developed in the process, however.

HSP have been used widely since 1967 to accomplish correlations and to make systematic comparisons which one would not have thought possible earlier. The effects of hydrogen bonding, for example, are accounted for quantitatively. Many of these correlations are discussed later, including polymer solubility, swelling, and permeation; surface wetting and dewetting; solubility of inorganic salts; and biological applications including wood, cholesterol, etc. The experimental limits on this seemingly universal ability to predict molecular affinities are apparently governed by the limits represented by energies of the liquid test solvents themselves. There had/has to be a more satisfactory explanation of this universality than just “semiempirical” correlations.

I decided to try to collect my experience for the purpose of a reference book, both for myself and for others. At the same time, a search of the major theories of polymer solution thermodynamics was undertaken to explore how the approaches compared. A key element in this was to explain why the correlations all seemed to fit with an apparently “universal” 4 (or 0.25 depending on which reference is used). This is described in more detail in Chapter 2 (Equation 2.5 and Equation 2.6). My present view is that the “4” is the result of the validity of the geometric mean rule to describe not only dispersion interactions but also permanent dipole–permanent dipole and hydrogen bonding (electron interchange) interactions in mixtures of unlike molecules. The Hildebrand approach uses this and was the basis of my earliest approach. The Prigogine corresponding states theory yields the “4” in the appropriate manner when the geometric mean rule is adopted (Chapter 2, Equation 2.11). Any other kind of averaging gives the wrong result. Considering these facts and the massive amount of data that has been correlated using the “4” in the following, it appears proven beyond a reasonable doubt that the geometric mean assumption is valid not only for dispersion-type interactions (or perhaps more correctly in the present context those interactions typical of aliphatic hydrocarbons) but also for permanent dipole–permanent dipole and hydrogen bonding as well.

For those who wish to try to understand the Prigogine theory, I recommend starting with an article by Donald Patterson.¹ This article explains the corresponding states/free volume theory of Prigogine and coworkers in a much simpler form than in the original source. Patterson² has also reviewed in understandable language the progression of developments in polymer solution thermodynamics from the Flory–Huggins theory, through that of Prigogine and coworkers, to the so-called “New Flory Theory.”³ Patterson also has been so kind as to aid me in the representations of the earlier theories as they are presented here (especially Chapter 2). All of the previous theories and their extensions also can be found in a more recent book.⁴ For this reason, these more classical

theories are not treated extensively as such in this book. The striking aspect about all of this previous work is that no one has dared to enter into the topic of hydrogen bonding. The present quantitative treatment of permanent dipole–permanent dipole interactions and hydrogen bonding is central to the results reported in every chapter in this book. An attempt to relate this back to the previous theories is given briefly here and more extensively in Chapter 2. This attempt has been directed through Patterson,¹ which may be called the Prigogine–Patterson approach, rather than through the Flory theory, as the relations with the former are more obvious.

I strongly recommend that studies be undertaken to confirm the usefulness of the “structural parameters” in the Prigogine theory (or the Flory theory). It is recognized that the effects of solvent molecular size, segment size, and polymer molecular size (and shapes) are not fully accounted for at the present time. There is hope that this can be done with structural parameters.

The material presented here corresponds to my knowledge and experience at the time of writing, with all due respect to confidentiality agreements, etc.

I am greatly indebted to many colleagues and supporters who have understood that at times one can be so preoccupied and lost in deep thought that the present just seems not to exist.

Charles M. Hansen

October 19, 1998

REFERENCES

1. Patterson, D., Role of Free Volume Changes in Polymer Solution Thermodynamics, *J. Polym. Sci. Part C*, 16, 3379–3389, 1968.
2. Patterson, D., Free Volume and Polymer Solubility. A Qualitative View, *Macromolecules*, 2(6), 672–677, 1969.
3. Flory, P. J., Thermodynamics of Polymer Solutions, *Discussions of the Faraday Society*, 49, 7–29, 1970.
4. Lipatov, Y. S. and Nesterov, A. E., *Polymer Thermodynamics Library, Vol. 1, Thermodynamics of Polymer Blends*, Technomic Publishing Co., Inc., Lancaster, PA, 1997.

Preface to the Second Edition

When the question about a second edition of this handbook was posed, I was not in doubt that several additional authors were necessary to meet the demands it would require. The writings of the five contributors that were chosen speak for themselves. There is theoretical impact in Chapter 3 (Costas Panayiotou) and in Chapter 4 (Georgios M. Kontogeorgis). Chapter 3 introduces statistical thermodynamics to confirm the division of cohesive energy into three parts enabling separate calculation of each. Chapter 4 describes how the Hansen solubility parameters (HSP) fit into other theories of polymer solutions. The practical applications and understanding provided in Chapter 9 (Per Redelius) related to asphalt, bitumen, and crude oil should accelerate new thinking in this area and emphasize that simple explanations of seemingly complex phenomena are usually the right ones. The thermodynamic treatment of carbon dioxide given in Chapter 10 (Laurie L. Williams) is a model for similar work with other gases and emphatically confirms the usefulness of Hansen solubility parameters for predicting the solubility behavior of gases in liquids and therefore also in polymers.

Chapter 11 (John Durkee) goes through the process of demonstrating how “designer” solvents can be used in cleaning operations to replace, or partly replace, ozone-depleting solvents, in spite of the problem of their HSP not being sufficiently close to the HSP of the soils that are to be removed.

I have added two chapters because of apparent need. Chapter 14 discusses environmental stress cracking (ESC). ESC is a major cause of unexpected and sometimes catastrophic failure of plastics. The recent improved understanding provided by HSP seemed appropriate for inclusion in this context. Chapter 16 discusses absorption and diffusion in polymers. Many of the HSP correlations presented in this handbook cannot stand on HSP alone but must include consideration of absorption and diffusion of chemicals in polymers. These effects are often disguised by use of a molecular volume, as molecular size/volume correlates reasonably well with diffusion coefficients, especially at low concentrations. Polymer surface layers are often significantly different from the bulk polymer. Surface mobility of polymer chain segments plays an important role in surface dewetting, ESC, and resistance and/or delays to the absorption of chemicals. This chapter tries to unify the effects of a verifiable surface resistance and verifiable concentration-dependent diffusion coefficients. Solutions to the diffusion equation simultaneously considering these two effects explain the “anomalies” of absorption and also correctly model desorption phenomena, including the drying of a lacquer film from start to finish.

Each of the chapters in the first edition has been reviewed and added to where this was felt appropriate without increasing the number of pages unduly. There is still a lack of significant activity in the biological area, in controlled release applications, and in other areas discussed in Chapter 18, such as nanotechnology. The relative affinity of molecules or segments of molecules for each other can be predicted and in many cases controlled in self-assembly with the understanding provided by HSP.

Chapter 15 treating biological materials has been expanded more than the others included in the first edition. This was done with the help of Tim Svenstrup Poulsen. Perhaps the most surprising of the additions in Chapter 15 is a HSP correlation for the (noncovalent) solvent interactions with DNA. The δ_D ; δ_P ; δ_H values of 19.0; 20.0; 11.0 for DNA, all in $\text{MPa}^{1/2}$, clearly show that hydrogen bonding interactions (H) contribute much less to the noncovalent interactions that determine the structure of the DNA than the dispersion (D) and dipolar interactions (P). Only about 14% of the cohesion energy involved in what is commonly called “hydrogen bonding” derives from hydrogen bonding.

Table Appendix A.1 is greatly expanded both in number and in information. The latter is due to the generous help of Hanno Priebe, the extent of which is clearly evident for those familiar with the first edition. There are close to 1200 entries in this table vs. the approximately 860 in the first edition. However, please be advised that most of these are calculated and not experimental values as indicated in the comments to the table. Table Appendix A.2 is not greatly expanded. There have been too many restrictions on what may be published to allow any major expansion of this table. The majority of my work as a consultant has usually involved agreements that prohibit or severely limit publication of results paid for by private sources. I have also included Appendix A.3 with the original solubility data on which the division of the energy was based. I have regularly found this more specific data of considerable interest.

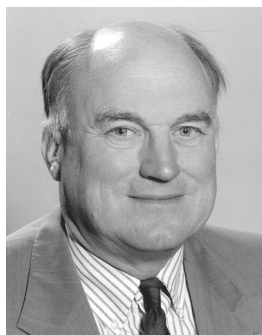
Once more resources and timing have not been conducive to do a complete literature search to provide additional explanations of phenomena that should have had Hansen solubility parameters included in their interpretation. In view of the large expansion in the number of pages over the first edition it is hoped that the principles, both theoretical and practical, are well illuminated. For those who still lack information in a given situation I can suggest a search using the key words "Hansen solubility parameters" followed by additional key words as required. This is true both for Internet searches as well as for searches in the more traditional literature.

It has been satisfying to see how much can be interpreted with very simple observations and calculations. If it cannot be done simply, then rethink.

I want to once more thank those who have contributed to this second edition. Let us hope others will take up the effort and relate their findings for the benefit of all.

Charles M. Hansen

The Author



Charles M. Hansen consults on the topics covered by this book. He works from his home in Hoersholm, 22 kilometers north of Copenhagen, Denmark. He received a BChE from the University of Louisville and an MS degree from the University of Wisconsin. After being awarded the Dr. techn. degree from the Technical University of Denmark in 1967, he held leading positions with PPG Industries in Pittsburgh, and as director of the Scandinavian Paint and Printing Ink Research Institute in Hoersholm, Denmark. Dr. Hansen dealt with polymers at FORCE Technology, Broendby, Denmark, for the 17 years prior to the start of the current state of semi-retirement.

Dr. Hansen is perhaps best known for his extension of the Hildebrand solubility parameter to what are now called Hansen solubility parameters. These have been found mutually confirming with the I. Prigogine corresponding states theory of polymer solutions and can be used to directly calculate the Flory–Huggins interaction coefficient. The statistical thermodynamics approach developed by Costas Panayiotou and coworkers, which is reported in Chapter 3 of this second edition, also confirms the viability of the division of the cohesion energy into separate parts, and allows their independent calculation.

Dr. Hansen has published widely in the fields of polymer solubility, diffusion and permeation in polymers and films, surface science, and coatings science. He is currently vice president of the Danish Society for Polymer Technology, having recently completed a 5-year period as president. He frequently reviews papers for leading journals, and is on the editorial board of *Progress in Organic Coatings*, as well as being a member of the Danish Academy of Technical Sciences (ATV).

Key to Symbols

Note: The symbols used in Chapters 3 and 16 are so numerous and different that they have been placed in these chapters, respectively.

A_{12}	Energy difference defined by Chapter 2, Equation 2.12
D	Diffusion coefficient in Chapter 13
D	Dispersion cohesion (solubility) parameter — in tables and computer printouts
DM	Dipole moment — debyes
E_D	Dispersion cohesion energy
E_P	Polar cohesion energy
E_H	Hydrogen bonding cohesion energy
ΔE_v	Energy of vaporization (=) cohesion energy
G	Number of “good” solvents in a correlation, used in tables of correlations
G	Gibbs Energy in Chapter 4
ΔG^M	Molar free energy of mixing
$\Delta G^M_{\text{noncomb}}$	Noncombinatorial molar free energy of mixing
H	Hydrogen bonding cohesion (solubility) parameter — in tables and computer printouts
ΔH_v	Molar heat of vaporization
ΔH^M	Molar heat of mixing
K_H	Henry’s law constant in Equation 10.5
L	Ostwald coefficient in Equation 10.6
P	Permeation coefficient in Chapter 13
P	Polar cohesion (solubility) parameter — in tables and computer printouts
P	Pressure in Chapter 10
Q	Solvent quality number
P^*	Total pressure, atm. (Chapter 13, Figures 13.4 and 13.5)
R	Gas constant (1.987 cal/mol K)
Ra	Distance in Hansen space, see Chapter 1, Equation 1.9 or Chapter 2, Equation 2.5
RA	Distance in Hansen space, see Chapter 2, Equation 2.7
R_M	Maximum distance in Hansen space allowing solubility (or other “good” interaction)
Ro	Radius of interaction sphere in Hansen space
RED	Relative energy difference (Chapter 1, Equation 1.10)
S	Solubility coefficient in Chapter 13
ΔS^M	Molar entropy of mixing
T	Absolute temperature
T	“Total” number of solvents used in a correlation as given in tables
T_b	(Normal) boiling point, degrees K
T_c	Critical temperature, degrees K
T_r	Reduced temperature, Chapter 1, Equation 1.12
V	Molar volume, cm ³ /gram molecular weight

V	Total volume in Chapter 4
V_f	Free volume (Equation 4.2)
V^*	Hard core or close packed volume in Equation 4.2
V_w	van der Waals volume
V_M	Volume of mixture
a	Constant in van der Waals equation of state (Chapter 4)
a_i	Activity coefficient of the “i”th component in Appendix 10.A.1
b_i	Coefficients in Equations 10.17 and 10.19
b	Constant in van der Waals equation of state (Chapter 4)
c	Dispersion cohesion energy density from Chapter 1, Figure 1.2 or Figure 1.3
c	Concentration in Chapter 8, Equation 8.4
c_i	Coefficients (state constants) in Equations 10.17 and 10.19
f	Fractional solubility parameters, defined by Chapter 5, Equations 5.1 to 5.3
f_i	Fugacity of the “i”th component in Appendix 10.A.1
f_i^0	Fugacity at standard state in Appendix 10.A.1
i	Component “i” in a mixture
k	Constant in Equation 6.1
k	Constant in Equations 10.21–10.23
n	Coefficient in Equation 10.13
n	Coefficient in Equations 10.21, 10.22, and 10.23
n_D	Index of refraction in Equation 10.25
p	Partial pressure (of carbon dioxide) in Chapter 10
p_i	Partial pressure of the “i”th component in Appendix 10.A.1
p_i^s	Saturation pressure of the “i”th component in Appendix 10.A.1
r	Number of segments in a given molecule, Chapter 2
r	Ratio of polymer volume to solvent volume (Chapter 4)
t_s	Sedimentation time, see Chapter 7, Equation 7.1
x	Mole fraction in liquid phase (Chapter 13, Figures 13.4 and 13.5, and Chapter 10)
y	Mole fraction in vapor phase (Chapter 13, Figures 13.4 and 13.5, and Chapter 10)
H	Ratio of cohesive energy densities; Chapter 2, Equation 2.6
Ω	Bunsen coefficient (Equation 10.6)
Ω_i^∞	Infinite dilution activity coefficient
Σ	Summation
Δ_T	Lydersen critical temperature group contribution
α	Thermal expansion coefficient
α	Constant in Equation 4.15
β	Constant in Chapter 2, Equation 2.1
β	Compressibility in Chapter 10
δ_D	Dispersion cohesion (solubility) parameter
δ_H	Hydrogen bonding cohesion (solubility) parameter
δ_P	Polar cohesion (solubility) parameter
δ_t	Total (Hildebrand) cohesion (solubility) parameter
δ	Prigogine normalized interaction parameter, Chapter 2, Equation 2.8
ϵ	Cohesive energy for a polymer segment or solvent in Chapter 2
ϵ	Dielectric constant in Equation 10.25
γ	Surface free energy of a liquid in air or its own vapor
γ	Activity coefficient in Chapter 4

η	Viscosity of solvent, Chapter 7, Equation 7.1
η_s	Viscosity of solution
η_o	Viscosity of solvent
$[\eta]$	Intrinsic viscosity, see Chapter 8, Equation 8.4
$[\eta]_N$	Normalized intrinsic viscosity
ϕ_i	Volume fraction of component “i”
μ	Dipole moment
ν	Interaction parameter, see Chapter 2, Equation 2.11
Θ	Contact angle between liquid and surface
Θ_a	Advancing contact angle
Θ_r	Receding contact angle
ρ	Prigogine parameter for differences in size in polymer segments and solvent, Chapter 2, Equation 2.10
ρ	Density in Chapter 7, Equation 7.1
ρ	Density in Chapter 10
ρ_p	Particle density in Chapter 7, Equation 7.1
ρ_s	Solvent density in Chapter 7, Equation 7.1
σ	Prigogine segmental distance parameter, Chapter 2, Equation 2.10
χ	Polymer–liquid interaction parameter (Flory–Huggins), Chapter 2
χ_{12}	Interaction parameter — “New Flory Theory”
χ_c	Critical polymer–liquid interaction parameter, Chapter 2
χ_{lit}	Representative χ value from general literature
χ_s	Entropy component of χ
1	(Subscript) indicates a solvent
2	(Subscript) indicates a polymer (or second material in contact with a solvent)
D	(Subscript) dispersion component
P	(Subscript) polar component
H	(Subscript) hydrogen bonding component
d	(Subscript) dispersion component
p	(Subscript) polar component
h	(Subscript) hydrogen bonding component

Table of Contents

Chapter 1	Solubility Parameters — An Introduction	1
	Abstract	1
	Introduction	1
	Hildebrand Parameters and Basic Polymer Solution Thermodynamics	2
	Hansen Solubility Parameters	4
	Methods and Problems in the Determination of Partial Solubility Parameters	6
	Calculation of the Dispersion Solubility Parameter δ_D	13
	Calculation of the Polar Solubility Parameter δ_p	16
	Calculation of the Hydrogen Bonding Solubility Parameter δ_H	17
	Supplementary Calculations and Procedures	17
	Temperature Dependence	18
	Some Special Effects Temperature Changes	19
	Effects of Solvent Molecular Size	19
	Computer Programs.....	20
	Hansen Solubility Parameters for Water	21
	Conclusion.....	22
	References	24
Chapter 2	Theory — The Prigogine Corresponding States Theory, χ_{12} Interaction Parameter, and Hansen Solubility Parameters	27
	Abstract	27
	Introduction	27
	Hansen Solubility Parameters (HSP).....	28
	Resemblance between Predictions of Hansen Solubility Parameters and Corresponding States Theories.....	30
	The χ_{12} Parameter and Hansen Solubility Parameters.....	32
	Comparison of Calculated and Experimental χ_{12} Parameters	34
	Polybutadiene	35
	Polyisobutylene.....	36
	Polystyrene	38
	Polyvinylacetate.....	39
	Polyacrylonitrile	39
	General Discussion	39
	Postscript	40
	Conclusion.....	41
	References	42
Chapter 3	Statistical Thermodynamic Calculations of the Hydrogen Bonding, Dipolar, and Dispersion Solubility Parameters.....	45
	Key words	45
	Abstract	45
	Introduction	45

Theory	46
The Equation-of-State Framework	46
The Contribution from Dipolar Forces	50
Applications	52
Discussion and Conclusions	59
Acknowledgments	62
List of Symbols Special to this Chapter.....	63
References	64
Appendix 3.I: The Acid Dimerization.....	65
Appendix 3.II: An Alternative Form of the Polar Term.....	66
Appendix 3.III: A Group-Contribution Method for the Prediction of δ and δ_D	66
Chapter 4 The Hansen Solubility Parameters (HSP) in Thermodynamic Models for Polymer Solutions	75
Abstract	75
Group Contribution Methods for Estimating Properties of Polymers.....	76
The Group-Contribution Principle and Some Applications (Density, Solubility Parameters)	76
GC Free-Volume-Based Models for Polymers (Entropic-FV, Unifac-FV).....	77
The Free-Volume Concept	77
The UNIFAC-FV Model	77
The Entropic Model	78
The Flory–Huggins Model and the Regular Solution Theory	80
Rules of Thumb and Solvent Selection Using the Flory–Huggins Model and Solubility Parameters	81
Activity Coefficients Models Using the HSP.....	82
Flory–Huggins Models Using Hildebrand and Hansen Solubility Parameters (HSP)	82
The FH/Hansen Model vs. the GC Methods.....	84
Applications.....	85
Solvent Selection for Paints (Activity Coefficients at Infinite Dilution)	85
Mixed Solvent–Polymer Phase Equilibria	88
Conclusions and Future Challenges	90
List of Abbreviations.....	91
Symbols in this Chapter.....	92
Appendix 4.I: An Expression of the Flory–Huggins Model for Multicomponent Mixtures	92
References	93
Chapter 5 Methods of Characterization — Polymers	95
Abstract	95
Introduction	95
Calculation of Polymer HSP	97
Solubility — Examples.....	98
Swelling — Examples	106
Melting Point Determinations — Effect of Temperature.....	106
Environmental Stress Cracking.....	107
Intrinsic Viscosity Measurements	107
Other Measurement Techniques	109
Conclusion.....	109
References	110

Chapter 6 Methods of Characterization — Surfaces.....	113
Abstract	113
Introduction	113
Hansen Solubility Parameter Correlations with Surface Tension (Surface Free Energy).....	113
Method to Evaluate the Cohesion Energy Parameters for Surfaces.....	114
A Critical View of the Critical Surface Tensions.....	116
A Critical View of the Wetting Tension	117
Additional Hansen Solubility Parameter Surface Characterizations and Comparisons	118
Self-Stratifying Coatings.....	120
Maximizing Physical Adhesion	122
Conclusion.....	122
References	122
 Chapter 7 Methods of Characterization for Pigments, Fillers, and Fibers	125
Abstract	125
Introduction	125
Methods to Characterize Pigment, Filler, and Fiber Surfaces	126
Discussion — Pigments, Fillers, and Fibers	127
Hansen Solubility Parameter Correlation of Zeta Potential for Blanc Fixe.....	131
Carbon Fiber Surface Characterization	131
Controlled Adsorption (Self-Assembly).....	132
Conclusion.....	134
References	134
 Chapter 8 Applications — Coatings and Other Filled Polymer Systems.....	137
Abstract	137
Introduction	137
Solvents	137
Techniques for Data Treatment.....	142
Solvents and Surface Phenomena in Coatings (Self-Assembly)	144
Polymer Compatibility.....	145
Hansen Solubility Parameter Principles Applied to Understanding Other Filled Polymer Systems	147
Conclusion.....	147
References	148
 Chapter 9 Hansen Solubility Parameters of Asphalt, Bitumen, and Crude Oils	151
Abstract	151
Symbols Special to Chapter 9	151
Introduction	151
Models of Bitumen	152
Asphaltenes	154
Molecular Weight	154
Polarity.....	155
Solubility Parameters of Bitumen.....	155
Testing of Bitumen Solubility.....	156
Hildebrand Solubility Parameters.....	156
Hansen Solubility Parameters (HSP).....	158

The Solubility Sphere	159
Computer Program for Calculation and Plotting of the Hansen 3D Pseudosphere	161
Components of Bitumen	164
Bitumen and Polymers.....	166
Crude Oil.....	169
Turbidimetric Titrations	170
BISOM Test	170
Conclusion.....	173
References	174

Chapter 10 Determination of Hansen Solubility Parameter Values for Carbon Dioxide177

Abstract	177
Introduction	177
Methodology	178
One-Component Hildebrand Parameter as a Function of Temperature and Pressure.....	187
Three-Component (Hansen) Solubility Parameters — Pure CO ₂	189
Temperature and Pressure Effects on HSPs: δ_d	190
Temperature and Pressure Effects on HSPs: δ_p	191
Temperature and Pressure Effects on HSPs: δ_h	191
Conclusion.....	196
Acknowledgments	196
Chapter 10 Addendum	196
Symbols Special to this Chapter.....	197
References	197
Appendix 10.A.1: Ideal Solubility of Gases in Liquids and Published CO ₂ Solubility Data	199
Ideal Solubility of Gases in Liquids.....	199
References	201

Chapter 11 Use of Hansen Solubility Parameters to Identify Cleaning Applications for “Designer” Solvents203

Abstract	203
Introduction	203
A Variety of Solvents.....	204
Pathology of Soils.....	204
HSP of Multiple-Component Soils.....	204
Method for Calculating HSP of Composites (Soils or Solvents).....	205
More Realistic View about Evaluating HSP of Composite Soils.....	206
Method for Choice of Suitable Solvents	206
Reference Soils for Comparison.....	208
Identification of Designer Solvents	208
An Open Question — Answered.....	208
Limiting R _A Value for Expected Good Cleaning Performance	210
Application of HSP Methodology to Cleaning Operations	212
Analysis of Capability of Designer Solvents	213
Conclusions	215
Notes	227

Chapter 12 Applications — Chemical Resistance	231
Abstract	231
Introduction	231
Chemical Resistance — Acceptable-or-Not Data	232
Effects of Solvent Molecular Size	232
Chemical Resistance — Examples	233
Tank Coatings	233
PET Film Coating	234
Acceptable or Not — Plastics	234
Tensile Strength	237
Special Effects with Water	238
Conclusion	239
References	240
Chapter 13 Applications — Barrier Polymers	243
Abstract	243
Introduction	243
Concentration-Dependent Diffusion	244
Solubility Parameter Correlations Based on Permeation Phenomena	245
Solubility Parameter Correlations of Breakthrough Times	245
Solubility Parameter Correlation of Permeation Rates	248
Solubility Parameter Correlation of Polymer Swelling	250
Solubility Parameter Correlation of Permeation Coefficients for Gases	251
Laminates	253
General Considerations	255
Conclusion	256
References	257
Chapter 14 Applications — Environmental Stress Cracking in Polymers	259
Abstract	259
Introduction	259
ESC Interpreted Using HSP	260
ESC with Nonabsorbing Stress Cracking Initiators	263
Discussion	264
Conclusion	267
References	267
Chapter 15 Hansen Solubility Parameters — Biological Materials	269
Abstract	269
Introduction	270
Hydrophobic Bonding and Hydrophilic Bonding (Self-Association).....	271
DNA	273
Cholesterol	275
Lard	277

Human Skin.....	277
Proteins — Blood Serum and Zein	279
Chlorophyll and Lignin.....	279
Wood Chemicals and Polymers	279
Urea	283
Water	289
Surface Mobility	290
Chiral Rotation, Hydrogen Bonding, and Nanoengineering.....	290
Conclusion.....	291
References	291
Chapter 16 Absorption and Diffusion in Polymers	293
Abstract	293
List of Symbols Used in This Chapter.....	293
Introduction	294
Steady State Permeation	296
The Diffusion Equation.....	296
Constant Diffusion Coefficients	296
Concentration Dependent Diffusion Coefficients	297
Surface Resistance	298
Mathematical Background.....	298
Surface Resistance in Absorption Experiments.....	300
Surface Resistance in Permeation Experiments	301
Surface Resistance — A Discussion.....	302
Side Effects	304
Measuring Diffusion Coefficients with Surface Resistance and Concentration Dependence.....	304
Film Formation by Solvent Evaporation	305
Anomalous Diffusion (Case II, Super Case II).....	306
General Comments.....	308
Conclusion.....	308
References	309
Chapter 17 Applications — Safety and Environment	311
Abstract	311
Introduction	311
Substitution.....	311
Alternative Systems	312
Solvent Formulation and Personal Protection for Least Risk.....	313
The Danish Mal System — The Fan.....	313
Selection of Chemical Protective Clothing	315
Uptake of Contents by a Plastic Container	315
Skin Penetration	316
Transport Phenomena.....	316
Conclusion.....	317
References	318

Chapter 18 The Future	321
Abstract	321
Introduction	321
Hansen Solubility Parameter Data and Data Quality.....	324
Group Contribution Methods.....	328
Polymers as Points — Solvents as Spheres	328
Characterizing Surfaces	330
Materials and Processes Suggested for Further Attention	332
Surface Active Agents	332
Surface Mobility (Self-Assembly)	333
Water	334
Gases.....	336
Organic Salts	337
Inorganic Salts	337
Organometallic Compounds.....	338
Aromas and Fragrances.....	338
Absorption of Chemicals in Plastics.....	339
Chemical Resistance.....	339
Controlled Release.....	339
Nanotechnology	340
Theoretical Problems Awaiting Future Resolution.....	341
Polymer Solubility.....	341
Surface Phenomena	342
Conclusion.....	342
References	342
Appendix A: Comments to Table A.1	345
References	346
Table A.1	347
Appendix A: Comments to Table A.2	485
References	490
List of Trade Names and Suppliers.....	491
Table A.2	493
Appendix A: Comments to Table A.3	507
Table A.3	508