

## Unified Separation Science

By J. Calvin Giddings, Wiley, New York, 320 pp., 1991.

What does an outstanding analytical and physical chemist have to say to chemical engineers about separations? The author states that this book was written for a graduate-level course in analytical separations. Thus, the coverage is very strong on chromatography, field flow fractionation, and electrophoresis, but lacks in details of methods used for large-scale industrial separations. This book won't directly help the chemical engineer design a better distillation column. It, however, will help the engineer:

1. Understand the analytical chemists he or she works with.
2. Understand the strengths and weaknesses of chromatography.
3. Appreciate the molecular basis of separations.
4. See new connections among separation techniques.
5. Gain new insights.

Indirectly, the result may eventually be better understanding and design of separation systems.

The author writes in an abstract style that is appropriate for a unifying approach, but which is inappropriate for neophytes. Some previous knowledge of separations, particularly chromatography, is necessary to fully benefit from this book. The chemical engineer reading this book must also accept that the author's viewpoint differs from those in engineering books. Giddings relies more on physical insight and approximate derivations than is the norm in current chemical engineering books. This difference is also the book's major strength. He shows connections and explains separations in a way that does not occur in chemical engineering books.

After the required introductory chapter, the author discusses the thermodynamic basis for separation. The author's use of chemical potential as the driving force for separation is a useful unifying concept. Chapter 3 on "Separative Transport" focuses on diffusion, while

chapter 4 discusses "Flow Transport and Viscous Phenomena." These chapters are probably more familiar reading for engineers than chemists. One interesting detail is Giddings' suggestion that 270 be used in the Karmen-Kozeny equation instead of 180 or 150. This represents the bias of a chromatographer who uses columns of carefully packed small particles. Chapter 5 discusses zone spreading and introduces the Gaussian function or the related error function as the central distribution function in analytical chemistry. A random walk analysis is used to explain why Gaussian functions occur, and in section 5.4 is used to explain how flow fluctuations (eddy dispersion) cause the commonly used Fickian axial dispersion form. This explanation is a prime example of how the author's different viewpoint can give engineers new insight. Chapter 6 continues the discussion of zones. All chemical engineers who occasionally rely on analytical chemists for the analysis of complex mixtures should read sections 6.7 and 6.8 to understand the problem of overlapping peaks in chromatography.

A natural dividing point in the book occurs in chapter 7 where separation methods are first classified and compared. The chemical potential profile and the flow relative to this profile are used to classify separations. This scheme shows some surprising comparisons of separations. For example, reverse osmosis, ultrafiltration, and zone melting are all classified alike.

The remaining four chapters focus on specific analytical separation methods. Chapter 8 is on electrophoresis and centrifugal sedimentation, while chapter 9 is an overview of field flow fractionation (FFF) and chromatography. Since the author invented FFF, the coverage of FFF is understandably a bit heavy. Chapters 10 to 12 discuss chromatography in considerably more detail. This amount of attention is justified by the central importance of chromatography in analytical chemistry. A large part of these three chapters closely follows Giddings' 1965 classic, *Dynamics of Chromatography*. The physical insights into

zone spreading and optimization are useful for anyone interested in chromatography. The author's interest in analytical separations is evident in chapter 12 where he optimizes for resolution or analysis time, but not for throughput.

The book appears to be well-crafted and there are few typographical errors. One nagging problem is the author's somewhat excessive citing of his own publications. For example, Appendix II, which lists many of his publications, seems unnecessary. However, this is a very good book that could be accurately titled "Unified Analytical Separation Science."

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## Porous Media: Fluid Transport and Pore Structure

By F. A. L. Dullien, Academic Press, 574 pp., 1992

The second edition of Dullien's book is a significant improvement over the earlier edition. The research in porous media transport proliferated in the decade that followed the original publication. The second edition includes many of those advancements in addition to improved presentation of the original material. The strength of the book lies in exposing the relation between pore structure and fluid transport; those sections have been further reinforced with new research findings. The weakness still lies in the treatment of some of the fluid mechanical and mathematical aspects of flow. The update misses on some of the significant and relevant research of the last decade outside the interest area of the author. This edition is an excellent research monograph, but not a comprehensive text or general reference.

Chapter 1 describes pore structure. The exposition was excellent in the original edition. It has been improved further by

addition of the discussions on reconstructed three-dimensional pore structure, use of stochastic theory, fractal pore morphology, and geostatistics. The new section on field-scale characterization is written at an introductory level, but adds to the completeness of the chapter. Putting this chapter ahead of the chapter on capillarity phenomena (chapter 2) makes this edition more readable than the first.

Chapter 2 reveals the relationship between pore structure and capillary hydrostatics. The discussions of the percolation models developed in the 80s and deficiencies of common interpretations of mercury porosimetry are some of the significant additions to this strong chapter.

Chapter 3 illustrates the relation between pore structure and single-phase flow. Inclusion of hydraulic conductivity concept, new empirical models, and mechanistic network models of permeability are some of the notable improvements.

Chapter 4 is a brief discussion of some of the applications. It is a weak chapter and has not been significantly updated for any recent work.

Chapter 5 shows the relationship between pore structure and two-phase flow, another strong chapter in the book. It has been vastly improved by including discussions on two-phase flow with coupling, effect of wettability and viscosity on waterflood history, dynamic capillary pressure, pore-level flow mechanisms, and the network models developed in the 80s.

The last chapter deals with miscible displacement and dispersion in tube and porous media. Significant additions have been the discussions on non-Fickian dispersion and dispersion in wetting and nonwetting phases. The section on instability is weak and not updated with the new developments. I liked the enlargement of the figures, but noticed a few typographical errors in some equations and chapter numbers.

This review of the field of transport in porous media is not exhaustive, as the author states, owing to limitation of space, time and author's own interest. This monograph missed the developments in the following topics in the last decade: Rate-controlled porosimetry and its modeling (chapter 2), calculations using lattice gas techniques for single- and two-phase flow (chapters 3 and 5), space renormalization techniques for flow in

heterogeneous media (chapters 3 and 5), and modeling of instability in miscible and immiscible flow (chapter 6). I consider these developments to be significant and wish they were included in this monograph.

In summary, this edition is a significantly expanded and updated version of the original book. It is limited in scope, but still the best monograph on relating pore structure to transport in porous media. It is clearly written and should be quite useful to anyone doing research in porous media.

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### **The Chemistry and Technology of Petroleum, Second Edition, Revised and Expanded**

*By James G. Speight, Marcel Dekker, New York, 1991*

This book sets out to describe petroleum chemistry and technology from deposition of geological sediments to petrochemicals for an audience of engineers and chemists. Chemical engineers who have an interest in refining should read the sections on petroleum and bitumen formation and chemistry, particularly the excellent sections on the composition of heavy fractions such as the asphaltenes. It, however, is not recommended as a reference on refinery processes.

The initial chapters on the genesis and occurrence of crude oil and bitumen, the history of its use over the past 6,000 years, and the brief summary of petroleum drilling and production provide an informative review. The best sections of the book are in the middle portion, covering the physical and organic chemistry of the raw products and separated fractions. Chapters 7 and 9 cover the composition of crude oils and bitumens, including elemental analysis and the major compound classes and solubility fractions. In the best chapter of the book (chapter 11), results from a wide range of experimental studies are combined with the constraints imposed by the origin and geochemistry of crude oil to develop a molecular description of the asphaltenes.

Coverage of the measurement of physical and thermodynamic properties and

chemical composition is much weaker (chapters 8 and 10). Correlations are listed in chapter 8 for some properties, such as specific heat and thermal conductivity, but the origin and accuracy of the equations are not discussed at all. The use of the corresponding states approach to PVT calculations is recommended, but methods for estimating pseudo-critical properties are not discussed or provided. The reader is not referred to more comprehensive sources of data and methodology for thermodynamic and physical property calculations.

Chapter 10, titled "Identification," gives a good description of gas chromatography and the theory of other analytical chromatography methods, but no example results are provided for any petroleum fractions. The coverage of mass spectrometry is inadequate; no mention is made of methods for analyzing ring classes in distillates or field-ionization mass spectrometry (FIMS). Estimation of aromatic carbon content is presented mainly via correlations using refractive index, which are only of historical interest; the existence of  $^{13}\text{C}$ -NMR and its routine application for direct measurement of aromatic carbon content are not mentioned. The methods discussed in this chapter, therefore, fail to give chemical engineers insight into the range of facilities and analytical methods used at a typical refining research laboratory.

The final portion of the book on refining opens with a good general discussion of the chemistry of how refinery processing modifies the carbon framework and removes hetero-atoms (chapter 12). Chapters 13 to 18 describe various refinery processes from crude distillation to product finishing. These chapters suffer from serious faults that would mislead an uninformed reader; many of the processes discussed are out of date (for example, thermal cracking for gasoline production), current process technology is often lacking, and quantitative information on process conversion, yield, selectivity, and utility requirements is not given. For example, chapter 17 on "Product Improvement" describes nine reforming processes, each in 1 to 2 paragraphs with reference to a block process diagram. The catalysts for reforming are discussed separately, toward the end of the chapter, with an emphasis on platinum on  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ; no mention is made of the platinum bimetallic catalysts (such as Pt/Ir and Pt/Re), which have gradu-