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Book Reviews

Two Views of Non-equilibrium Thermodynamics

Over the past few months two closely related but strongly contrasting books on non-equilibrium thermodynamics have been received for review, both from Wiley and from The Netherlands, where so much good work in this area has been done. The earlier of the two, by Ross Taylor and R. Krishna, puts the greater emphasis on applications and is focused on mass transfer, where the most useful applications of this somewhat esoteric subject have been found. The second, by G. C. D. Kuiken, is much more fundamental in its approach, and includes rheology as well as the more familiar mass transfer. Each is a worthwhile contribution and of particular interest to the readers of Chemical Engineering Science.

Multicomponent Mass Transfer. By ROSS TAYLOR and R. KRISHNA, Wiley Series in Chemical Engineering, 1993, 579 pages, ISBN#0-471-57417-1

This is an important book in bringing together a wealth of information about a poorly understood field in a style understandable to those familiar with diffusional processes at the senior-graduate level of American universities. The book is divided into three parts entitled *Molecular Diffusion, Interphase Transfer and Design*, and it comes with a 3.5 in. diskette for IBM compatible machines to aid in solving the examples in Chaps 1–13. However, this diskette must be used in conjunction with the commercial package *Mathcad*, which is of course not supplied. A separate software package, *Chemsep*, is needed for some of the exercises in Chap. 14, and the reader is referred to Prof. Taylor, who teaches at Clarkson University, Potsdam, New York, for further information on it. Also included is an extensive and well-organized nomenclature list, compatible with standard references to a surprising degree considering the wide range of topics covered.

Part I contains six chapters, entitled Preliminary Concepts, The Maxwell-Stefan Relations, Fick's Law, Estimation of Diffusion Coefficients, Solution of Multicomponent Diffusion Problems: the Linearized Theory and Solution of Multicomponent Diffusion Problems: the Effective Diffusivity Method. Chapter 1 presents the conventions, measures of concentration and mass fluxes, and the differential conservation equations to be used throughout the text as well as general references for more specialized treatments. Chapters 2–6 present the primary results of diffusion theory and provide a quantitative basis for describing diffusional processes. They compare the respective merits of the Maxwell–Stefan equations with generalizations of Fick's law and the Onsager formulations in Chaps 3 and 4, and they provide means for converting from one set of flux expressions to another. They also compare multicomponent and binary diffusion and provide a surprising amount of data for the latter. Chapter 4 is a useful critical survey of estimation methods for multicomponent diffusivities of gases and liquids. Finally, in Chaps 5 and 6 they contrast two widely used approximate methods for describing diffusion processes and show that linearization of the Maxwell–Stefan equations is generally much more reliable than the pseudo-binary effective diffusivity method

This section is very useful and well done. It updates the prior literature and collects a great deal of useful information previously unavailable in such compact and well-organized form. It is the real heart of this text.

The second section of this book deals with the modification of the familiar binary mass transfer models to provide estimates of mass transfer rates in complex flow systems. Chapter 7 provides basic definitions of mass-transfer coefficients, and Chap. 8, almost half of this section, is devoted to the classic stagnant-film model. Chapters 9 and 10 deal with elementary penetration and laminar sublayer models which are not the most realistic available, and these discussions are of somewhat limited utility. Chapter 11 provides a thorough and authoritative introduction to combined heat and mass transfer and is well done.

The third section is devoted largely to distillation, and it is an ambitious effort quite different in emphasis than the rest of the text. It contains four chapters devoted, respectively, to mass-transfer models already treated in section two, efficiency models, a non-equilibrium stage model and condensation of mixed vapors. Each chapter contains extensive examples, and the last two include design studies and comparisons with experiment.

The book concludes with appendices on matrix algebra, equation solving and estimation of the thermodynamic matrix $\Gamma = [\partial \ln a/\partial \ln x]_{T,p}$

This is a major contribution notable for a wealth of detail, numerous carefully worked examples and a great deal of actual data. It should prove the definitive reference for some years to come and a valuable reference for anyone seriously interested in multicomponent diffusion.

Thermodynamics of Irreversible Processes. By GERARD D. C. KUIKEN, Wiley Tutorial Series in Theoretical Chemistry, 1994, 426 pages, $54.95, ISBN#0-471-94844-6

This is a serious major work in a series designed for those who are engaged in practical research, in teaching and those who wish to learn about the role of theory in chemistry today. It is less accessible than the Taylor and Krishna text reviewed above and does not concern itself with applications at the unit operations level. However, it goes much deeper into underlying theory and provides a basis for describing a wider range of phenomena: the author defines the thermodynamics of irreversible processes (TIP) as describing within the framework of a continuum point of view all systems obeying linear constitutive equations of state. It thus unifies formulations of continuum theory used in many branches of physics and chemistry such as mechanics, fluid dynamics, magnetohydrodynamics, mass transport and thermodynamics. Moreover, the results often apply to quasi-linear systems.

After a short introduction to continuum theory and its place in the description of natural phenomean the author recapitulates the primary results of classical continuum theromdynamics in Chap. 2: the zeroth through third laws. This chapter, which also includes an elegant discussion of modeling theory and orders of magnitude, is accessible to undergraduate students, and it is unusually lucid and easy to follow.

The basic axioms of TIP, the concept of conservation relations and the pehnomenological equations, are introduced and thoroughly discussed in chap. 3, which concludes with examples of anisotropic heat conduction and the Kedem-Katchalsky equations for macroscopic description of membrane transport. In Chap. 4, the conservation equations for mass, momentum, angular momentum, energy and entropy for multicomponent systems are formulated.

The Onsager, or Onsager–Casimir relations as the author prefers to call them, are intoduced in Chap. 5. To this reviewer, who started examination of Dr. Kuiken's monograph with only a very limited grasp of the origin of these famous relations, this chapter is the most interesting of the book. The author's development does not take Boltzmann's entropy identification for granted but derives the probability distribution from the Fokker–Planck equation for aged systems. In this way he shows that microscopic reversibility only yields the Onsager reciprocal relations if one starts with the Boltzmann distribution. This is the most lucid and authoritative treatment I have seen.

The second half of the book deals with application of the general theory of the TIP, to multicomponent diffusion in Chap. 6 and to rheology in Chap. 7. Chapter 6 overlaps to a considerable degree with the Taylor and Krishna book reviewed above, and, on balance, it is the less useable and less complete from such practical standpoints as estimating diffusion coefficients or converting from one set of flux equations to another. This reviewer had particular problems with the nomenclature which make it difficult to differentiate between velocities and molar volumes: both lower and upper case v's are used for both, and the various subscripts, superscripts and overlines are not easy to remember. Chapter seven is the longest chapter in the book and includes extensive general discussions of relaxation phenomena as well specific examples on linear viscoelasticity. These discussions are clearly for the specialists, and they are not readily accessible to others.

Chapter 6 is on balance not very helpful since the primary results are already known and presented more conveniently elsewhere. I suspect that Chap. 7 would provide some useful insights to the theoretical rheologist but no specific new means for describing the behavior of non-Newtonian fluids. However, Chap. 7 is unique in bringing together in an organized way material which to date has been scattered in the periodical literature. This monograph is a scholarly tour de force and helpful to those wishing more insight into the origins and applicability of well-known equations. It does not seem to present any new and practically significant results. These characteristics are in keeping with the viewpoints of both the author and the editors of the tutorial series, but they are somehwat disappointing to the practical researcher, identified by the author as a significant part of his audience. This negative aspect is perhaps inevitable as TIP has always been a bit disappointing from a purely practical standpoint. On the other hand, it should prove quite satisfying to the theoretician interested in the basic nature of TIP.

The typography and figures are of high quality, and the secondary features are quite impressive. There are two extensive appendices, the first deriving Maxwell's electromagnetic field equations and the second summarizing vector and tensor notation. The nomenclature list is very helpful, and there are both author and subject indexes.

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This is followed by a qualitative discussion of when to use chemical solvents, on the thermal effects found in absorption and desorption, and on the differences between simulations for design and for operating purposes. Packed columns have their own chapter with brief discussions of the different types of packing, of liquid maldistribution, liquid hold-up, pressure drop relations and relations for the different mass transfer parameters. This part is very empirical, but the authors have made choices out of the many available correlations. It may be a useful quick reference. This chapter contains a discussion on the shooting method for solving countercurrent multicomponent problems. This is a method which, unfortunately, seldom converges because it is so sensitive to initial estimates. The chapter on plate columns is similar, with discussions on flooding, weeping and operating regimes, mixing in the liquid and gas phase and a small collection of empirical equations for all mass transfer parameters. It also contains a fairly extensive derivation of the Kremser equation and a discussion of the matrix method for solving equilibrium stage problems. Unfortunately, I found the discussion of the most important problem rather superficial. That is on how to include multicomponent mass transfer and chemical reactions in computer calculations. The book ends with a short (again mainly empirical) chapter on bubble columns.

I found this book unbalanced. The first part is a good starting point for an advanced course on multicomponent mass transfer, but the rest is introductory and very much in the conventional fragmented style of treating separation processes. One strong point is the large number of worked examples. Teachers may find the the book a treasury for assignments.

Multicomponent Mass Transfer

by Ross Taylor and R. Krishna, John Wiley and Sons, 1993, ISBN 0-471-57417-1, price £58.00, xxxiv + 579 pp.

This book also consists of three, roughly equal, parts. The first covers the theory of multicomponent, molecular diffusion. The second deals with the description of multicomponent mass transfer in the thin layers or 'films' next to phase boundaries. The third part deals with multicomponent non-equilibrium design methods for distillation, absorption and condensation equipment.

Part I of the book covers 'Molecular Diffusion'. The weakest chapter of the book is the first: 'Preliminary Concepts'. It contains a dour and dry summary of the different forms of the balance equations for multicomponent mass transport. Run through it quickly; the book really begins with 'The Maxwell–Stefan Relations'. This starts with a qualitative, but instructive derivation of the multicomponent diffusion relations from an ideal gas mixture, then extends these by analogy to liquid mixtures. It ends with extensions of the Maxwell–Stefan (MS) equations to include driving forces such as centrifugal and electrical gradients. 'Fick's Law' introduces an alternative description of multicomponent mass transfer. It also describes a few aspects of the behaviour of diffusivities in non-ideal solutions. This subject is pursued further in 'Estimation of Diffusion Coefficients'. This shows how MS-diffusivities behave much more simply than Fick diffusivities, especially in non-ideal and in multicomponent mixtures. It briefly describes how diffusivities can be estimated in dilute solutions. These values are then used with interpolation to estimate MS-diffusivities in concentrated mixtures, as from these the Fick diffusivities. We now know the transport equations and have values of the diffusivities. So we progress to 'The Linearized Theory', which deals with various methods for solving the multicomponent Fick equations. Here we also see some 'strange' effects that may be expected in multicomponent diffusion problems. One of these is 'reverse diffusion', where a component diffuses against its concentration gradient. Surprisingly, the elegant explanation that the MS-equations provide for these phenomena is hardly discussed. The last section of this part, 'Effective Diffusivity Models', shows that these methods are not good. These methods, which have been popular, consider the mixture to behave as a pseudo binary. They often give acceptable results, but unfortunately it is difficult to see when and where they will fail.

Part II discusses 'Interphase Mass Transfer'. In most parts of engineering equipment, convection dominates transport. However, in thin layers near phase boundaries, much of the flow normal to the boundary dies out. There, diffusion becomes the dominant transport mechanism. This part of the book analyses multicomponent mass transfer in such boundary layers or 'films'. Chapter 7 defines Fick mass transfer coefficients in multicomponent systems, showing how their behaviour parallels that of the Fick diffusivities. It then discusses the problem that diffusion equations only describe relative motion within a mixture, and that an extra 'bootstrap' relation is required to determine the problem. Such relations can be obtained from the special behaviour of one component (for example if the component cannot traverse the phase boundary because it is insoluble). They can also be obtained from mass or energy balances, or from the stoichiometry of chemical reactions. 'Film Theory' is one of the longest chapters of the book. It begins with the binary form of the theory including flux corrections. This is worked out for several different cases which are important in distillation, absorption, condensation and in chemical reactors. The multicomponent equations are 'just' matrix generalisations of the binary forms. Different schemes for solving these equations are discussed, including linearisation and effective diffusivity approximations. Then the effects of thermodynamic non-idealities are taken into account. The chapter finishes on making estimations of multicomponent mass transfer coefficients from dilute binary data. (We usually do not have any better data available.) This chapter parallels the developments on molecular diffusion in Part I. 'Unsteady State Mass Transfer Models' summarises the various binary surface renewal models and show which extensions have been made so far to multicomponent systems. The chapter ends with multicomponent versions of the penetration model for spheres and cylinders; these are rough models for mass transfer to bubbles and drops and to jets. 'Mass Transfer in Turbulent Flow', contains a description of turbulence models of boundary layers. It shows how molecular and turbulent diffusivities are combined in binary models and extended to multicomponent mixtures with analogous matrix equations. The chapter also contains a discussion of the estimation of mass transfer coefficients fluid/solid boundaries. 'Simultaneous Mass and Energy Transfer' covers a partial form of the transport equations for energy, which includes conduction and convection. The diffusion equation for non-isothermal diffusion is presented, but otherwise not used in the text. For different mass transfer models, the influence of heat and mass transfer on each other, are then worked out. These effects are primarily convective contributions of mass transfer to heat transfer and thermal effects on phase equilibria.

Part III, 'Design', takes up almost 40 percent of the book. It deals with the non-equilibrium or 'rate based' multicomponent models of the classical chemical engineering operations of distillation, absorption and condensation. This part of the book brings the reader to the state of the art in this subject. Chapter 12 deals with multicomponent distillation in tray and packed columns. It starts with binary models, discussing conventional concepts such as overall mass transfer coefficients and numbers of mass transfer stages, which lead to efficiency models. This part ends with a model of a tray which describes both the bubble and the spray regimes, with their transition. (I find the mathematics a little detailed, compared with the rough way that two phase flow is modelled. Also, the model parameters cannot be easily predicted.) The extension of the model equations to multicomponent systems is then worked out. This involves a lot of matrix algebra. The chapter ends with a parallel development of design equations for packed columns. 'Efficiency Models' deals with the common method of designing distillation columns using equilibrium stages, corrected with an 'efficiency'. In binary mixtures such a Murphree efficiency is well behaved. It often has a value of around 0.7 for both components and varies little over the length of the column. No such simple behaviour is observed in multicomponent distillation. The chapter contains many examples, showing how efficiencies vary wildly, even in distillation of ideal mixtures. They can be anywhere between plus and minus infinity! The 'efficiency' in multicomponent systems is shown to be a confusing concept, which is probably best avoided altogether. 'A Non-equilibrium Stage Model' develops a complete multicomponent model of a distillation column. This includes heat and mass transfer resistances in both phases, but only simple models of two phase flow in the column. Solving this model on a computer is discussed and the results of many design simulations are presented. These include distillation of simple ideal mixtures, extractive distillation with strong nonidealities, vacuum distillation with pronounced pressure variations and an absorber with large heat effects. A comparison with experimental studies show that the non-equilibrium multicomponent model is superior to the combination of the equilibrium model with efficiencies, although the differences are usually not dramatic. The last chapter deals with 'Condensation of Vapor Mixtures'. In multicomponent condensers heat and mass transfer interact strongly. Here the difference between 'simple' conventional models and the more fundamental multicomponent nonequilibrium models can be substantial. Occasionally the conventional models even predict a wrong direction of the transport of certain components in the condenser.

The book contains a large number of worked examples throughout the text. Most are given as Mathcad files on a separate disk, so you can play with them. (The column simulations are not on the disk).

The book has been written by two men with long experience both in multicomponent mass transfer and in computation. This shows. Even so, the book does have a few weaknesses:

1. It is not as general as the title suggests. The book is primarily on mass transfer in distillation and condensation. It does set up the multicomponent mass transfer relations clearly and generally, but the general form of the equations is only used in a few examples.

2. The book treats multicomponent mass transfer with a mix of two methods: the Maxwell–Stefan and the multicomponent Fick descriptions. The MS-equations usually give the clearest description of what is going on. The Fick equations are more convenient numerically, but difficult to understand. I would have preferred to have more of the explanations using the MS equations.

3. I find the authors defensive in their position against conventional descriptions of mass transfer. The ideas in the equations of multicomponent diffusion are simple and straightforward (which does not mean that subject is easy!). They form a much better base, than the mess of (pseudo) binary models with empirical modifications, efficiencies, numbers of mass transfer units and HETPs that we engineers are still using.

4. In the comparison between the different models, only a little is said about the effects of transport parameters in the models. These parameters (such as mass transfer coefficients and interfacial areas) are very unpredictable, and the values used will certainly have an influence on the outcome of calculations.

Having said this, I must say that I found this a very good book. Anyone seriously involved in research or development of multicomponent separation processes should read it. Even designers (who may be using the techniques of the book in their programs without knowing), can learn a lot. They can probably best start in the last part of the book to see what the results of the 'new' way of modelling are.

A final word of warning. The authors say that they think the content of the book can be covered in a single semester of a graduate course. I think this is optimistic (although it does depend on the length of your semester...). Mastering multicomponent mass transfer, may take a few years. For a young chemical engineer it is worth the trouble.

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Experiments in Heat Transfer and Thermodynamics

edited by R.A. Granger, Cambridge University Press, 1994, ISBN 0-521-44925-1 Hardback, £35.00, ISBN 0-521-45115-9 Paperback, £14.95.

The preface states that ''we learn by doing'' and suggests that engineering students will gain a better understanding of the principles of thermodynamics and heat transfer by performing well-designed experiments. The editor has collected together 32 experiments from well-known figures in the heat transfer literature and produced a very readable volume which should be useful to anyone interested in teaching heat transfer at the graduate or undergraduate level.

The chapters are organized into sections on heat transfer (conduction (six experiments), convection (ten), boiling (four), diffusion (two), radiation (one), heat exchange (two) and thermodynamics (seven)). The book is aimed at heat transfer so the thermodynamics section covers topics related to heat transfer (water superheat, vapour pressure, latent heat and multiphase flow volume fractions) rather than heat engines or other areas of engineering thermodynamics. The book is intended as a resource to supplement taught courses and this is reflected in the appendices, which include comprehensive lists of other experiments and demonstrations in heat transfer and thermodynamics as well as films illustrating heat transfer phenomena.

Each chapter describes an experiment and follows a general format. The principle, objective and theoretical background are followed by descriptions of the experimental apparatus and procedure. The experimental section is supplemented by questions for the student, samples of results and references for further reading. The description of experimental apparatus and procedure is generally very good but the references are likely to be required reading for some of the more complicated experiments. Each chapter finishes with a brief pen portrait of the contributor.

The experiments cover a range of difficulty and complexity. Several are ideally suited for lecture demonstrations while others require space, apparatus or conditions in a suitably equipped laboratory. Few of the experiments involve expensive pieces of equipment and most feature water or air as the transfer medium. The most evident trend in the book is that the experiments from Japanese contributors tend to involve more complex apparatus and analysis. There is a notable lack of reference to safety in a book of this nature; there is more discussion of burnout of heaters rather than potential sources of injury to personnel. One experiment involves evaporation of drops of benzene or tetrachloromethane, which is unlikely to comply with the reviewer's departmental safety guidelines. The mixture of US, Japanese and European authors is also evident from the mixing of SI and US units. The editor refers to other texts for a description of error analysis.

This book does not provide a template for a heat transfer teaching laboratory. It does, however, represent a readable and thought-provoking resource for anyone involved in teaching heat transfer to students in chemical or mechanical engineering.

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Thermodynamics of Irreversible Processes: Applications to Diffusion and Rheology

by G.D.C. Kuiken, Wiley, 1994, ISBN 0-471-94844-6, xxxii + 425pp, £29.95.

This book is a thorough and clear exposition of the underlying principles of the linear thermodynamics of irreversible processes (TIP). The monograph admirably satisfies the goals of the Wiley tutorial series in theoretical chemistry and although it is primarily aimed at undergraduate students it should also serve as an excellent reference textbook for research as well as teaching.

Introductory concepts are provided by the author in Chapters 1 and 2. The first chapter clearly defines the scope to which macroscopic (continuum) theory is restricted and those topics which are of primary concern in the monograph. The concept of local equilibrium is discussed at length and the author rationalizes how truly equilibrium intensive measures can be considered to be useful definitions for non-equilibrium systems. In Chapter 2 the fundamental concepts and laws of classical equilibrium thermodynamics are introduced and an interesting method of heat engine representation is provided via vector diagrams. I am also pleased to see the inclusion of Caratheodory's statement with the Clausius and Kelvin–Planck statements of the second law.

Chapters 3, 4, and 5 are, in sum, an important prelude to the major emphasis of the book which is to appear later in Chapters 6 and 7. In Chapter 3 the axioms of TIP are carefully enumerated and described, with preliminary comments on entropy dissipation and the phenomenological equations, the Onsager–Casimir reciprocal relations, and axioms which specify invariance of the TIP equations to various transformations. A clear mathematical development of the symmetry principles for both isotropic and anisotropic materials is also provided.

In Chapter 4 the author extends the topics of classical equilibrium and non-equilibrium thermodynamics to multicomponent fluids which do not possess internal ''hidden'' variables. The material balance, diffusion equations, and elec-

Multicomponent Mass Transfer

by Ross Taylor and R. Krishna, Wiley, New York, 1993, 579 pp.

This is an important book on multicomponent mass transfer, written by two leading investigators in the field. It is meant for readers already acquainted with the theory of mass transfer and the fundamentals of transport phenomena at the undergraduate level. The book is notable for its wealth of examples, including real data and useful comparisons of alternate models and methods for multicomponent problems. It is attractively printed and illustrated, with numerous graphs and schematic drawings.

Part I, entitled Molecular Diffusion, contains the following chapters:

1. Preliminary Concepts
2. The Maxwell-Stefan Relations
3. Fick's Law
4. Estimation of Diffusion Coefficients
5. Solution of Multicomponent Diffusion Problems: The Linearized Theory
6. Solution of Multicomponent Diffusion Problems: Effective Diffusivity Methods

Chapters 2–6 are very useful and well done. Nonideal mixtures and electrolytes are treated in the latter part of Chapter 2. The relative merits of the Maxwell-Stefan and generalized Fick diffusion coefficients are well treated in Chapters 3 and 4. Chapter 4 is a useful survey of diffusivity estimation methods for gases and liquids. Chapters 5 and 6 compare two popular approaches for solving multicomponent diffusion problems and should be required reading for workers in this field. The pitfalls of effective diffusivity approaches are thoroughly demonstrated in Chapter 6.

Part II, entitled Interphase Transfer, contains the following chapters:

7. Mass-Transfer Coefficients
8. Film Theory
9. Unsteady-State Mass-Transfer Models
10. Mass Transfer in Turbulent Flow
11. Simultaneous Mass and Energy Transfer

These chapters review selected mass-transfer models for binary systems and develop analogous methods for multicomponent systems. Chapter 7 deals with definitions, starting from a binary mass-transfer coefficient and generalizing the definition to multicomponent systems. Chapter 8 is a thorough treatment of the authors' multicomponent film model, with many examples. Chapters 9 and 10 are less complete; the surface-renewal model and laminar sublayer model given there are historically important, but more realistic models are available. Chapter 11 is extensive and well done, including detailed numerical examples on distillation and stripping in binary and ternary systems.

Part III, entitled Design, contains the following chapters:

12. Multicomponent Distillation: Mass-Transfer Models
13. Multicomponent Distillation: Efficiency Models
14. Multicomponent Distillation: A Nonequilibrium Stage Model
15. Condensation of Vapor Mixtures

Chapters 12 and 14 treat selected nonequilibrium models, and Chapter 13 treats equilibrium-stage models modified by stage efficiencies. Each chapter has extensive examples, and the last two include design studies and comparisons with experiments.

Appendices are provided on matrix algebra, equation-solving and estimation of the thermodynamic derivative matrix $\Gamma = [\partial \ln a/\partial \ln x]_{T,P}$.

A computer diskette is provided with the book; the examples in Chapters 1–13 are solvable using this diskette and the commercial package Mathcad which the user must obtain. A separate software package, *Chemsep*, is needed for some of the exercises in Chapter 14; information on it is available from Ross Taylor. With these computational aids and the extensive examples provided, this book is a very useful resource for chemical engineers in academia and industry.

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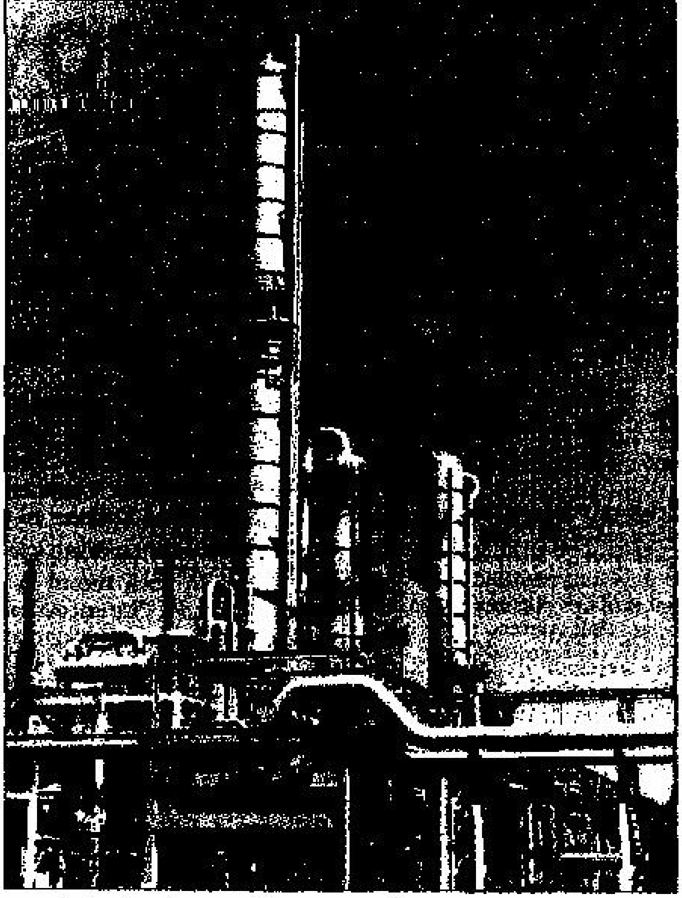

This huge distillation plant at Pascagoula produces 506,000 t/y of high-purity benzene (photo: Krupp Koppers)

Books

Multicomponent mass transfer

R Taylor and R Krishna, John Wiley & Sons 1993, 579pp, £66.00, ISBN 0 471 57417 1

Reviewed by Michael Biddulph, University of Nottingham

In processes which have been studied and applied for centuries, for example distillation, traditions of calculation and approach become very firmly established. The approach of most designers is still to produce an equilibrium-stage simulation to provide an estimate of the number of ideal stages required, followed by a correction involving the use of an estimated overall column efficiency, or maybe a Murphree Tray efficiency.

The first of these calculations, the ideal stage simulation, has been the subject of intense development for thirty years or so, resulting in the availability of many sophisticated computer packages. The second part of the calculation, the conversion of the ideal stage solution to actual trays required, is still difficult, in spite of much study. However, designers still feel comfortable with this approach, accepting the limitations and inaccuracies.

This book brings together the results of the efforts of the authors to change the approach to the design of process equipment for multicomponent mixtures. It has been known for more than fifty years that mixtures containing three or more components, known as multicomponent systems, can behave differently from binary systems. However, it is really only in the last twenty years that the theory has developed, supported by experimental observations in tray columns and packed columns.

Consideration is given to the question of whether the addition of an extra species to a binary mixture influences the process of mass transfer. This is accepted to be the case. The authors then consider the nature of the influences in detail.

The book is divided into three main parts. Part I introduces the basis of mass, momentum and energy transfer in multicomponent systems, and aspects of diffusion. Part II considers mass-transfer models and mass-transfer coefficients. Both molecular and eddy diffusion mechanisms are covered, together with the effects of simultaneous mass and energy transfer. Part III deals with the applications to process design. Distillation tray columns are covered in detail including the significance of point efficiencies in multicomponent systems. Absorption columns and condensers for multicomponent mixtures are also included. Appendices explain the mathematical techniques in detail. Many problems are used as illustrations.

The textbook is intended for use in high-level academic courses, and by design engineers and researchers interested in the complications introduced by multicomponent mixtures. It is intended as a sequel to basic texts on mass transfer.

The great value of this book is that it brings together all the work that has been directed towards a different, and more satisfactory, approach to the simulation of modern distillation columns. It is widely accepted that currently-used equilibrium-stage models have severe deficiencies. These can be overcome but this book, in my view, points the way to a better approach. It will be many years before the familiar methods are replaced but for non-ideal mixtures and mixtures containing trace components this approach is demonstrated as being better. Considerable computer power is required for the matrix formulations, but this becomes less and less of a problem as time goes by.

This is an excellent addition to the literature on mass transfer, and one I recommend highly.

Books received

Industrial energy management

V Kaiser, Editions Technip 1993, 118pp, FF220 (appx £27.20), ISBN 2 7108 0645 2

This book presents the latest

BOOK REVIEWS

Catalysis of Organic Reactions

J. R. Kosak and T. A. Johnson (Editors)
Marcel Dekker Inc., New York, 1993
608 pp, $185.00
ISBN 0–8247–9140–1

This work arises in a series of reference and text books relating to the Chemical Industries. It is a collection of the technical papers and short poster synopses given at the 14th Conference on Catalyses of Organic Reactions. The majority of contributions are from the USA with a smaller number from Europe although no one contribution arises from the United Kingdom. Several of the contributors are from major industrial companies as well as from academia.

The variety of catalysed *organic* reactions covered is wide and includes hydrogenation, amination, oxidation, etc. New catalyst materials are mentioned including copper exchanged zeolites and copper aluminium borates, titanium based mixed metal oxides and zeolites. Some papers give detail which might enable further scale-up of a proposed process but these are few and far between. As one might imagine, a book based upon papers from industrial and academic chemists is full of detail and the reader will have to search through the work to find that particular paper which is of interest and of use. Indeed, this is not an easy read but is more a reference book covering some up-to-date developments in catalysis chemistry. The papers vary in quality and length.

Some papers review the field rather than give specific details of a new synthesis route. The review paper in 'New technology for olefin production' is a particularly worthwhile contribution. In contrast, a paper on 'The catalytic oxidation of hydrocarbons', whilst wide ranging in nature, needed some important examples to be cited.

The catalysts and their preparation are described in some instances. Zeolites are detailed for the synthesis of pharmaceutical intermediates. Titanium mixed metal oxides are prepared and used in a variety of reactions. The recently discovered titanium silicate molecular sieves are described. The pore openings in these structures are at least 8 Å, they have moderate acidity and their catalytic behaviour is consistent with large-pore zeolites.

Interestingly, the development of polymer supported catalysts can lead to advantages in the areas of processing and the environment. A new family of copper aluminium borate catalysts can be used for dehydrogenation and dehydrocyclization reactions. In this last case catalytic activity is well controlled by sol/gel synthesis techniques.

In this work it follows that only some topics will appeal to this reader's personal interests. A most interesting paper on 'Catalysis of organic reaction by inorganic solids' caught the reader's eye. The author of this paper addresses a modern theme, i.e. the challenge for chemistry to find catalysts which help to avoid environmental pollution resulting from some catalytic processes. Clays and their derivatives might be just those catalysts to achieve the above goal. This last paper reviews the role of clays as catalysts and highlights some important effects. Thus montmorillonite modified by zinc chloride becomes an effective catalyst for Friedel-Crafts reactions which can be used in place of a conventional material such as aluminium chloride, but in smaller quantities. Could this be one of the first environmentally friendly catalysts?

This work is nicely presented with clear print and diagrams and the index is usual. However, at $185 the book is likely to end up as a useful reference book in a library rather than in one's personal collection.

M. A. Hughes

Multicomponent Mass Transfer

Ross Taylor and R. Krishna
John Wiley & Sons Ltd, 1993
616 pp, £58.00
ISBN 0–471–57417–1

This is a splendid book: timely, scholarly, well-written and important. If you ever have to deal with mass transfer problems, then it is probably worth your while to familiarise yourself with the concepts and techniques which the authors lay before you (and which they have themselves done much to develop). The ideas may look unfamiliar, the maths unappetising, for not everyone has acquired a taste for eigenvalues, but the effort will prove worthwhile for two profound reasons. First, multicomponent mixtures have characteristics fundamentally different from those of two component mixtures, such as fluxes that go *up* concentration gradients. So if your education in these matters is restricted to the usual undergraduate account of binary diffusion, you will learn about new, interesting and important phenomena. Secondly, that usual undergraduate account is peculiarly deficient in that it yields no tool with which to assess its limitations. For example, is the diffusion of acetone vapour in air a binary problem, acetone/air, or is it a multicomponent problem acetone/nitrogen/oxygen ... ? The theory of binary diffusion gives you no help in answering the question whilst the multicomponent theory immediately explains the circumstances in which the binary approximation is good while also explaining what to do when it fails.

Our authors lead us as follows. After careful definitions of concentrations, fluxes, reference velocities and balances, we meet the Maxwell-Stefan relations, the fundamental laws of multicomponent and binary diffusion.

These relations are deduced from gas kinetic theory by momentum transfer arguments. (The reader should beware of any book which approaches diffusion through mean free path arguments from kinetic theory: they lead to expressions for diffusion coefficients that are strongly composition-dependent, in defiance of experiment. Or, they provide attempts to correct the error with elaborate implausibilities about persistence of velocities.) We are restricted to cases where system pressure is uniform over the diffusion path so that, for instance, many cases of diffusion in porous solids are excluded. Fick's law, its generalisation to multicomponent mixtures and its defects are introduced (the browser will find a helpful discussion on pages 93–4). A chapter is devoted to the estimation of diffusion coefficients, the material on liquid mixtures requiring familiarity with activity coefficient models of liquid nonideality. Chapter 5 is the keystone of the book: the linearized theory of multicomponent diffusion is explained. Chapter 6 is devoted to robustly disparaging the alternative 'effective diffusivity' approach.

Before the concluding section on design is reached, with its chapters on multicomponent distillation (using three different approaches) and condensation of vapour mixtures, it is necessary to extend the diffusion theory to cover convective mass transfer. Chapter 7 on mass transfer coefficients starts usefully by distinguishing between coefficients corresponding to finite rates of mass transfer and the limiting low-flux coefficients. Even for binary systems, not all chemical engineering departments make this distinction clear to their students. Then, in turn, we meet the film model, unsteady-state models (e.g. surface renewal), mass transfer in turbulent flow and simultaneous mass and energy transfer. And then, as advertised, design.

The book comes complete with a floppy disk holding Mathcad files for the many worked examples in chapters 1–13. Your reviewer lost by having no access to Mathcad, but perhaps gained by being familiar with the simple approximate solution methods discussed in the short, jolly, informal volume *Mass Transfer*, J. A. Wesselingh and R. Krishna, (Ellis Horwood, 1990). He certainly gained in understanding and enthusiasm by reading most of the 579 pages of Taylor and Krishna. It brought together much that he did know in an organised and clarifying way (which of his far-sighted teachers exposed him to Toor-Stewart-Prober in the late 60s?) and taught him a good deal more that he did not know.

Who must read this book? Separation process people and most reaction engineers. Who should read this book? Most chemical engineers who retain an intellectual interest in the discipline, plus university teachers, even if they don't. I suggest that many university departments ought to greet the publication of this book by reviewing their teaching of diffusion and mass transfer. Even if they cannot agree on how much of this material to teach late in their courses, they must surely start thinking furiously on how best to modify their introductory teaching of diffusion and mass transfer to eliminate any need for un-teaching unsatisfactory materials later on.

And, dear reader, if you are still not convinced that this book is worth the effort to study, consider this remark from the 'postface':

'One of the most exciting possibilities afforded by a proper appreciation of the theory of multicomponent mass transfer is that we are able to effect separations that would otherwise not be possible using "simple-minded" binary-like approaches.'

W. R. Paterson

On the Bookshelf

Multicomponent Mass Transfer

Ross Taylor and R. Krishna

In *Multicomponent Mass Transfer*, authors Ross Taylor and R. Krishna provide a reference for chemical engineers working with multicomponent mixtures—systems containing three or more species. The authors' point of departure is that multicomponent systems exhibit transport characteristics completely different from those of a simple binary system, a conventional model for multicomponent systems.

The book is divided into three major sections. Part One deals with the basic equations of diffusion in multicomponent systems, such as the Maxwell-Stefan relations, Fick's law for binary mixtures and multicomponent systems, and procedures for estimating diffusion coefficients in multicomponent mixtures.

In Part Two, the authors show ways to estimate rates of mass and energy transport in multicomponent systems. Part Three covers various applications of multicomponent mass transfer models to process design. The book's fifteen chapters include several dozen detailed, worked-out numerical examples based on actual physicochemical data with direct relevance to equipment design. (A typical example is to compare different methods of estimating effective diffusivities in a system composed of H_2, N_2, and CCl_2F_2.) Several appendices review necessary mathematical background in matrix algebra, solving differential equations, and solving systems of nonlinear algebraic equations.

The authors note that most multicomponent mass transfer calculations are computationally demanding and are best done using software. A diskette accompanying *Multicomponent Mass Transfer* contains complete Mathcad implementations of 64 examples worked-out in detail in the text, and these same Mathcad files (both DOS Mathcad 2.5 format and Windows Mathcad 3.1 format are provided) can be easily modified to solve many of the exercises. A library of FORTRAN 77 routines for performing multicomponent mass transfer calculations is also available.

Multicomponent Mass Transfer *is a volume in the Wiley Series in Chemical Engineering. John Wiley & Sons, Inc., New York, 1993. 579 pp. ISBN 0-471-57417-1. Hardcover. $69.95. To order, phone: 1-800-225-5945.*

Visualizing Data

William S. Cleveland

"Visualization is critical to data analysis," begins William S. Cleveland of AT&T Bell Laboratories in this visually appealing and accessible discussion of tools—some well known and others on the cutting edge of exploratory data analysis—for visualizing statistical data. The tools include graphical methods such as coplots, 3-D rendering, multiway dot plots, brushing, and 45° banking, as well as methods for fitting mathematical functions to data, including loess and bisquare.

The book is organized around applications of the visualization tools to an eclectic selection of data sets: from scientific studies: barley yields in Minnesota, heights of singers in the New York Choral Society, scattering of sunlight in the atmosphere, concentrations of pollutants in automobile exhaust, food chai lengths in ecosystems, bin packing data, atmospheri carbon dioxide concentrations, galaxy velocities, animal physiology data, and livestock populations in European countries, just to name a few. This organization shows the role each tool plays in data analysis and the class of problems it solves. A key element in the book is its ability to demonstrate the power of visualization. For many of the data sets, the tools show that effects were missed in the original analyse or incorrect assumptions were made about the behavior of the data. Throughout, the applications convey the excitement of discovery that visualization brings to data analysis.

Cleveland's workhorse software tool in performin the original visualizations of the data that inspired the many illustrations in the book was "S," the software system developed by Richard Becker, John Chambers, and Allan Wilks of AT&T Bell Laboratories. Users of MathSoft's S-PLUS product will recognize some of the data analysis methods and enjoy the book's exploratory data analysis flavor. Cleveland's visualization tricks are available in the Trellis Graphics add-on to S-PLUS. Anyone with a basic knowledge of statistics who needs to visualize data will appreciate Cleveland's insights in this carefully produced book.

Visualizing Data *is available through Hobart Press, Summit, New Jersey, 1993. 360 pp. ISBN 0-9634884-0-6. Hardcover. $40.00. To order, phone: 1-800-258-2235.*

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