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the inter-pretation and use of rate data: the rate concept

revised printing

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THE INTERPRETATION AND USE OF RATE DATA: THE RATE CONCEPT

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THE INTERPRETATION AND USE OF RATE DATA:

The Rate Concept

Close to the western summit there is the dried and frozen carcass of a leopard. No one has explained what the leopard was seeking at that altitude.

Ernest Hemingway
The Snows of Kilimanjaro

To

The white goddess* who eschews both theory and experiment.

and

To those who must master:

Algorithms for solving
n-th order, finite
difference equations;
K-values, Bode diagrams and too many
unit operations;
mixed mean velocity, eddy viscosity,
asymptotic expansions, mean delta *T*,
enzymatic reactions and *BOD*;
natural convection, aromatic rings,
transport phenomena, more practical things,
equilibrium stages, thermodynamics,
rheology, non-Newtonian mechanics;
entropy, dimensional analysis,
Damkoehler numbers, Ziegler catalysis,
underflows, distillation,
shock waves and detonation;
air pollution, other troubles,
Gibbs equations, funny bubbles,
Ideal gases, retrograde condensation;
stirred tanks, plug flow and isomerization;
zeolites, ion exchange, stoichiometry,
optimization and
orthogonality.

*"The White Goddess," Robert Graves, Knopf, N.Y., 1948.

"Begin at the beginning," the King said gravely, "and go on til you come to the end; then stop."
Alice through the Looking Glass

PREFACE

This Preface is intended to provide an orientation for teachers and practicing engineers. Students are welcome to read it but are advised to proceed directly to the Introduction or even to Chap. 2.

In the beginning was the Word.
John, I, 1

The unified treatment of process calculations in terms of the rate concept was originated by Robert Roy White and this book was started as a joint project with him when we were both on the faculty of the University of Michigan. We were, however, diverted and separated by other challenges and responsibilities. When I resumed the project, he chose not to continue. I hope that he will recognize some of his brain children and yet be pleasantly surprised by their growth.

I admit that mathematical science is a good thing. But excessive devotion to it is a bad thing.
Aldous Huxley, Interview, J. W. N. Sullivan

My first mentor in mathematics, Professor Clyde E. Love, asserted that an introductory book on mathematics could not be written successfully for both students and mathematicians. A book accessible to students would be vulnerable to criticism on grounds of insufficient rigor, and a book acceptable to mathematicians would suffocate the student in split hairs. I have tried to write this book for students.

Events are writ by History's pen.
Praed

This material has been taught as a one semester course to sophomores and juniors in chemical engineering over a period of 15 years. It has also been taught to juniors in general engineering and in various modifications to seniors and graduate students in chemistry, pharmacology and public health; to graduate students in aeronautical, chemical, mechanical and metallurgical engineering; and to practicing engineers in the chemical process industries. It has evolved to its present form through these experiences.

"Or in the night, imagining some fear,
How easy is a bush supposed a bear!"
Shakespeare, A Midsummer-Night's Dream, Act V, Sc. 1

The emphasis on chemical conversions runs the risk of frightening away non-chemical engineers. However, this fear is unfounded. Students from other branches of engineering and from other disciplines have had no difficulty in this respect and have found the material appropriate to their interests.

Convictions are more dangerous foes of truth than lies.
Nietzsche

Chemistry students do have difficulty unlearning some of the habits and false concepts they have acquired. For example, most chemistry books focus attention on batch reactions in closed systems. Hence, they develop the equations for the conversion of chemical species only in Lagrangian form. Such expressions are difficult to apply directly to flow systems in which the density changes or diffusion occurs. Chemistry students are inclined to try to apply or adapt the familiar Lagrangian expressions rather than rederiving the balances in Eulerian form from scratch as is done herein. Worse, many chemistry books fail to note that the rate of reaction in a closed system is measured by $-(dN_A/dt)/V$ and that $-dC_A/dt$ is valid only for constant volume. Understandably, students who have blindly accepted this oversimplification are confused and resist the notion that their previous textbook may be wrong on such a basic level.

Can the Ethiopian change his skin, or the leopard his spots?
Jeremiah, XIII, 23

Graduate students similarly resist the notion that the correlations they have previously learned to use may be uncertain and arbitrary. For example, they find it hard to accept that the roughness ratio used in conjunction with the friction factor and Reynolds number is merely an empirical constant without physical meaning which forces the relationship for commercial pipe to conform to that for artificial, uniform roughness at large Reynolds number.

Entities are not to be multiplied without necessity.
Occam's Razor

It is logical and tempting to derive the most general possible equations and then reduce them to the various special applications. This path is followed somewhat in "Transport Phenomena"[1] and is carried to the extreme in a recent paper by Fulford and Pei.[2] Such treatments are quite useful if you have already mastered the subject, but students do not learn as quickly or as well by this route. They are forced to accept the general equations and the simplifications largely on faith since they have insufficient experience to provide a critical counterbalance. Unfortunately, this procedure also avoids comparisons with experimental data and evaluations of uncertainty since data of sufficient precision and breadth to test or justify the general equations are seldom available.

To climb steep hills requires a slow pace at first.
Shakespeare, Henry VIII, Act 1, Sc. 1

Students appear to learn more rapidly and effectively when they are introduced to problems of limited scope which are derived directly from physical concepts. Such derivations do not necessarily have to encompass all conditions. Limitations in the derivation and restrictions on the results can be merely mentioned and the details deferred to a later stage when more complex situations are considered. Thus, students can be taught Newton's laws of motion and merely informed that these are a special case of more general laws valid only for velocities much less than the speed of light.

He that increaseth knowledge increaseth sorrow.
Ecclesiastes, I, 18

Educational experiments have shown that factual information can be taught satisfactorily, at least as measured by the ability to repeat back the information, by the methods of programmed learning. For example, this method is successful in teaching how to keypunch. It is, however, inappropriate in a subject in which the degree of uncertainty is high and in which the student should be involved as a skeptic and critic. This latter attitude is the essence of engineering and should be encouraged in engineering education.

> Many ingenious and pleasing re-arrangements of a problem are possible. Some of these offer considerable economies in equipment, or other advantages. When they are used, however, the direct correspondence between the analogue and the real system is lost. For this reason a more pedestrian approach is usually better.
>
> *Anon., American Scientist*

Various orders of presentation have been tested with the material in this book. The chosen order proceeds from the description of rates to their measurement, then to the correlation of rate data. Finally, the descriptions and correlations are utilized for process calculations. Exactly the reverse order can be used: the design problem is first posed; this generates a demand for rate data which leads backward through correlations to experimental measurements. However, experience has shown that the chosen order is most successful with undergraduates. Furthermore, the prior focus on measurement emphasizes that the process calculations are affected by experimental uncertainties. A brief treatment in the reverse order is presented in Chap. 2 as an illustration of the content and purpose of the book.

> We are trying to make a conscious effort to stop talking about the famous compounds "A" and "B" and use examples involving real chemical systems.
>
> *R. Byron Bird, Chem. Eng. Educ., vol. 2, no. 1, p. 4, Winter 1968*

This book is perhaps unique in the extent of its use and reliance on measured values. An effort has been made to deal only with real, raw data in all the examples and problems. I have manufactured apocryphal data for a few problems because none of the desired type appeared to be available. I hope to eliminate these few exceptions in later editions. If necessary, my students and I will carry out experiments to produce the needed data.

> Round numbers are always false.
>
> *Samuel Johnson*

> There is a divinity in odd numbers.
>
> *Shakespeare, The Merry Wives of Windsor, Act IV, Sc. 1*

In the course of preparing one of the examples, it came as a shock to discover that a rather classical set of data had been manufactured or at least smoothed. This example was retained because it provides a pointed lesson that one should be suspicious of near-perfect data.

. . . , imaginary gardens with real toads in them.
Marianne Moore, Poetry

Regrettably, most of the methods recently proposed in the literature for the analysis and correlation of data use such manufactured values in all illustrative calculations. Ironically, several of them use the particular set of false values mentioned in the previous paragraph.

Science is a first-rate piece of furniture for a man's upper chamber, if he has common sense on the ground floor.
O. W. Holmes, The Poet of the Breakfast Table

This book is not opposed to the use of theory, although this may appear to be so at first glance. It merely attempts to put theory in its proper place in engineering, as a guide to correlation and occasionally as a source of a priori predictions. Theory may also, as an anonymous reviewer of this book asserts, provide a framework for understanding and intuition. Books and courses on "engineering science" have this objective and are largely concerned with the construction and manipulation of models. Such books rarely evaluate the model or the consequences of uncertainty in the model. The manipulation and the solution of the equations which comprise a theoretical model are often confused with theory itself. Such manipulations and solutions are the legitimate concern of applied mathematics and engineering science. They are not a primary concern of this book.

The attitude of the engineer to mathematics must be quite different from that of the pure mathematician. The engineer is concerned with truth not with mere consistency.
Biot

Philosophers and mathematicians may properly be concerned with whether a theory is true or false in some universal sense. We will instead ask how successful and reliable and convenient a particular theory is for correlation and prediction. How well does it conform to the experimental data? Is its usefulness limited to a particular range? Is there a simpler expression that also represents the data within their experimental uncertainty?

A little learning is a dangerous thing;
Drink deep, or taste not the Pierian spring.
Alexander Pope

The principles involved in the description of rates, in the derivation of rates from experimental measurements, in the correlation of rate data and in process calculations are so simple it is tempting to believe that they need only be elucidated in general terms without repeated examples involving messy details. Indeed, the principles of the rate process concept can be outlined successfully in an hour or two of lecturing. However, experience indicates that the difficulty is not with the principles but in recognizing a problem as it appears in real life, in expressing the problem in canonical form and in dealing with peripheral matters such as the stoichiometry of the reaction or the conversion from mole fraction to moles per mole of feed.

> In this theatre of man's life, it is reserved only for Gods and angels to be lookers-on.
>
> *Pythagoras*

Students and even professors seem to acquire proficiency in these matters only by practice. The problems are, therefore, an integral part of the book. They illustrate and expand upon many matters that are only asserted or mentioned in the text itself. A representative set of problems should, therefore, be assigned for each chapter. Sufficient problems are provided so that repeated use of the same ones is not necessary, although a few problems are unique in illustrating a particular point.

> It is one of the maxims of the civil law, that definitions are hazardous.
>
> *Samuel Johnson*

The most critical portion of the book is Part II in which rates of change (accumulation and net input by flow) are defined in the form of derivatives or finite differences and equated to the fundamental process rates such as rates of transfer and chemical reaction. The resulting equations are not definitions of the process rate but merely special cases of the equations of conservation. The teacher should emphasize this distinction.

> You cannot teach a man anything; you can only help him to find it within himself.
>
> *Galileo*

Despite the repeated distinctions and warnings in Chaps. 1, 2, 3 and 4, some students seem to arrive at the end of the book with the firm notion that process rates are defined in terms of derivatives. Dixon[3] suggests that this misconception can be avoided if the equations of conservation are written in more general form so that both the flow and accumulation terms appear as derivatives. His solution is a good one for advanced treatments but defeats the simplicity which is sought in this book.

> The beginnings and endings of all human undertakings are untidy.
> *John Galsworthy, Over the River*

The principle difficulty in preparing this volume has been to decide where to stop. The decision to restrict the presentation with only a few exceptions to one-dimensional problems and separable, ordinary, differential equations is somewhat uncomfortable because of the possible inference that the rate concept is applicable only to such simple processes. Indeed, the concepts and procedures are even more helpful in interpreting and treating complex processes. Such advanced applications will be covered in subsequent volumes which will be organized by types of processes, such as heat transfer, rather than by procedures.

> One of the great maladies of our time is the way sophistication seems to be valued above common sense.
> *Norman Cousins*

The book runs the risk of being considered too elementary in some aspects: (1) the more complex equations which characterize the transport phenomena approach are largely avoided because they are not needed within the scope of this volume; (2) only elementary techniques of statistical analysis are introduced since more high-powered methods are not really appropriate for data of the type and quality encountered herein; (3) the use of the computer is not specifically required; (4) the mathematical requirements are so slight that even a knowledge of differential equations is not absolutely necessary.

> The essence of engineering, as a crusty veteran once told his engineering rookies, is to be only as complicated as you have to be. What he left unsaid, though not undemonstrated, is that you must also be as able to get as complicated as the problem demands.
> *D. E. Gushee, Ind. Eng. Chem., vol.* 57, *no. 10, p. 5, October 1965*

The awful truth is that the majority of the problems in unit process design can be solved by elementary means. Advanced methods are needed in only a small class of problems. Of course, as Aris[4] points out, the modern engineer must master advanced theories and techniques because he will sooner or later face a problem for which they are required.

No rule is so general, which admits not some exception.
Richard Burton, Anatomy of Melancholy

Chapter 9 constitutes an exception to the general restriction to one-dimensionality in this book. Models in the form of partial differential equations are considered. However, attention is confined to the determination of the minimum set of dimensionless variables and parameters for use in correlation rather than to solution of the models. This procedure requires facility in partial differentiation and a familiarity with partial differential equations but not a knowledge of methods for their solution. Subsequent chapters are not strongly dependent on Chap. 9 and it can, therefore, be omitted if desired.

Delay is ever fatal to those who are prepared.
Lucan

The use of computers with this material deserves a further comment. The computational procedures described in the book do not have sufficient complexity and do not generally involve sufficient detail to justify the use of a computer. The computer can, however, be used in most of these steps and should be used when the individual processes are synthesized into a plant design. Well-prepared students will solve some of the elementary problems on the computer even without encouragement.

"What is the use of a book," thought Alice, "without pictures or conversations."
Alice's Adventures in Wonderland

Most sophomore and junior students are not familiar with the behavior, performance or even the names of the equipment used for the processes treated herein. Hence, the decision to omit detailed drawings and photographs of process equipment has been a difficult one. The teacher can enhance the course by supplying such descriptions in response to inevitable inquiries.

Politics is perhaps the only profession for which no preparation is thought necessary.
Robert Louis Stevenson

There is no comfortable solution to the problem of preparation and prerequisites for a subject as comprehensive as that of this book. To require complete preparation in all topics which are touched upon would essentially narrow the clientele to seniors and graduate students in chemical engineering. To incorporate sufficient preparation for sophomores in all fields of science and engineering would expand the book ridiculously and would risk boring many of the readers with familiar material. To restrict the coverage to topics for which all possible readers are prepared would be self-defeating.

> The ultimate goal of the educational system is to shift to the individual the burden of pursuing his own education.
>
> *John W. Gardner, Self-Renewal*

Hence, the risk has been taken to presume that the occasional missing preparation in thermodynamics, stoichiometry, chemistry, fluid mechanics or the like can be supplied by the teacher or by self-study. In many cases, the consequence of lack of nominal preparation is not as serious as it appears at first glance. For example, one can learn the technique of dimensional analysis in Chap. 9 without advance familiarity with the mathematical models. This stretching of a student's preparation and capability and the requirement of some independent study are indeed worthy objectives in themselves.

> To lead an untrained people to war is to throw them away.
>
> *Confucius*

As suggested by the above comments, the absolute prerequisites for the course are rather minimal: elementary chemistry, elementary physics, thermodynamics and mathematics through calculus. Courses in stoichiometry, fluid mechanics and the use of the computer are very helpful but not essential.

> Of making many books there is no end; and much study is a weariness of the flesh.
>
> *Ecclesiastes, XII, 12*

The direct continuation of the course is in the advanced material to be presented in subsequent volumes and in plant design. A course in transport phenomena may either precede or follow. The point of view is sufficiently different so that the duplication which occurs is tolerable in either order. Courses in unit operations, reactor design and continuous separations should follow rather than precede. However, it may be advantageous to redesign some conventional courses in these subjects to avoid duplication and to take full advantage of the new capability of the student.

> Be sure of it; give me the ocular proof.
>
> *Shakespeare, Othello, Act III, Sc. 3*

A unit operations laboratory is an excellent supplement and perhaps the best link with this book. Although logic might say that such a laboratory should follow, experience has shown that simultaneous scheduling stimulates the student and provides healthy reinforcement.

> To everything there is a season, and a time to every purpose under the heaven.
>
> *Ecclesiastes, III, 1*

For chemical engineers, these constraints suggest that a course based on this book be given in the junior year. For other engineers and scientists, the timing is less critical.

> I heartily beg that what I have done may be read with forbearance; and that my labors. . . may be examined, not so much with the view to censure, as to remedy their defects.
>
> *Newton, Principia, Preface to 1st ed., May 8, 1686*

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