



FIGURE 5. Sensor Output

ChE book reviews

DIFFUSION IN LIQUIDS

by H. V. Tyrrell, and K. R. Harris.

Butterworths (1984). 448 pages, \$75.00.

Reviewed by E. N. Lightfoot
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This book, originally conceived as a revision of Tyrrell's "Diffusion and Heat Flow in Liquids," is intended to give the non-specialist a balanced summary of the literature on both theoretical and practical aspects of diffusion in liquids, of sufficient depth to provide effective access. Both translational and rotational diffusion under the influence of arbitrary driving forces, in binary as well as multi-component systems, are discussed. It was deemed that heat flow could no longer be included in a book of reasonable length without undue sacrifice of depth.

The first four chapters are used to establish the foundations of transport theory, starting with the classical phenomenological description. The phenomenological introduction is followed by a summary of non-equilibrium statistical mechanics which permits, at least in principle, the calculation of transport properties from molecular parameters. The primary purpose of these chapters is to pro-

vide a unified treatment adequate for understanding modern methods of interpreting experimental data.

Chapter 5 provides rather detailed descriptions of the most widely useful techniques for gathering data, and Chapters 6 to 8 are devoted to interpreting experimental results in terms of kinetic theory and physical models.

Translational diffusion coefficients have been measured for well over a century, and many classic techniques have been highly refined and are still widely used. Among those described by the authors are optical techniques based on Gouy and Rayleigh interference phenomena (much improved in the last decades by the availability of lasers), diaphragm cells, use of Taylor dispersion (which has become important because of its speed), and light scattering.

Photon correlation techniques have made light scattering methods particularly important for macromolecules such as proteins, but effective use of these methods requires understanding of the underlying physics, as does the use of nuclear magnetic resonance for description of rotational diffusion. Largely because of this need Chapter 5 is rather long and detailed.

Chapter 6 is devoted to the interpretation or

ACKNOWLEDGEMENT

We would like to thank Robert J. Murcek for his ideas and time in implementing the CALS.

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k	kinds of atoms or elements
n(i)	number of moles of the ith species
n°(i)	initial number of moles of the ith species
N	species
p	number of phases
r	independent reaction equilibria
r*	maximum number of independent reaction equilibria
RHL	H/Cl atom ratio
RNL	N/Cl atom ratio
s	stoichiometric constraints
t	special or additional constraints
u	special or additional variables
x(i)	mole fraction of the ith species
Greek letters	
ϵ_i	extent of reaction for the ith reaction

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correlation of experimental data, via kinetic theory and, more extensively, such approximations as hydrodynamic and free volume theories. A separate section is provided for electrolytes. The utility of these theories is discussed for binary and ternary nonelectrolytes in Chapter 7 and for binary electrolytes and fused salts in Chapter 8.

This is a densely written book of high technical quality, and it is difficult to write a definitive review without extensive study, a procedure not feasible for this reviewer. However, I think it fair to say that this is a useful and reliable treatise, but that it will not attract large numbers of chemical engineers as readers. Much of the material presented is available elsewhere in equivalent form, and little attention has been paid to the problems of those wishing to use the subject matter in typical engineering applications. However, this book should prove valuable to those engaged in serious experimental or theoretical investigations and who wish to be sure that the basis of their work is sound. A few examples are given below to back up these comments.

The phenomenological discussion of Chapters 2 and 3 is representative of both the strengths and weaknesses of this book. The discussion of the Onsager reciprocal relation clears up a number of widely held misconceptions in a clear definitive manner, but little is done to provide the reader with convenient sets of diffusion equations, or of means to test and interrelate the wide variety of apparently different expressions found in the diffusion literature. The authors confine them-

selves largely to the flux expressions used by a relatively narrow group of physical chemists cited in the acknowledgement. These have not for the most part found widespread acceptance by chemical engineers, and it is not a simple matter to relate them to those which are more common. The means for making these inter-relations is provided in Chapter 3, but this reviewer did not find the treatment a convenient one to use. However, the definitions of mutual, self- and intra-diffusion coefficients in Chapter 1 are quite clear, and very useful as there has been much confusion about these terms.

Chapter 5 is, in this reviewer's opinion, highly useful, and a real strength of the book. The discussion of experimental techniques is detailed and practical, and also generally sound in terms of underlying theory. I do have a minor criticism in the discussion of Taylor dispersion in that the extensive literature on departures from Taylor's asymptotic theory is not referenced. Such departures can be important and may result from end effects or a variety of flow disturbances. This objection is, however, more than balanced by the strength of the discussion of errors in the use of light scattering. The authors have done much here to clear up longstanding controversies as to the significance of measurements made in concentrated solutions.

I found the organization of Chapters 6 through 8 awkward, but it may be that I did not take enough time to accommodate to it. It is clear that the authors have a prejudice which results in more attention to even doubtful theory than to useful empiricism. Thus they ignore many useful empirical and semi-empirical correlations totally. However, they do present a substantial amount of data and discuss it critically in the light of available theory, and these discussions should prove highly useful to many readers. They do seem more concerned with the experimental proof of the Onsager reciprocal relation than with the practical description of multicomponent diffusion problems, but in this they are constrained by the limited amount of practically useful information available.

On balance I expect to find this monograph a most welcome addition to my library, and a challenge to those like myself, with more applied tastes than the authors, to meet the above objections. I think this is the most authoritative source available in the area of diffusion, which is accessible to an engineering audience. □