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Book Review [1]

The Law of Mass Action. By Koudriavtsev, A.B. (D.Mendeleev University of Chemical Technology of Russia, Moscow, Russia, akoudri@online.ru); Jameson, R.F. (The University of Dundee, Scotland, UK. rjdundee@aol.com); Linert, W. (Technical University Vienna, Austria, wlinert@mail.zserv.tuwien.ac.at). Springer-Verlag: Heidelberg, New York. 2002. Hardcover. 328 pp. €74.95. ISBN 3-540-41078-3

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During the weekend I quickly browsed through this book [2] with great interest and recommend all chemists, whether experimental chemists or theoretical chemists, to read it. It is also suitable for chemistry students as a supplement to their physical chemistry textbook. One reason I recommend this book is that, to my knowledge, very few active chemists have made such a serious, insightful and fair treatment of the concept of entropy, which has long been my favorite topic of study. Many authors of thermodynamics and statistical mechanics books have ignored the Gibbs Paradox [3], whereas in this book a section with three full pages (section 1.4, pages 21-23) is devoted to it. As a chemist I spent a large part of my time working on this paradox and related problems. In my opinion, if someone has never spent days or even years, certainly at least hours, considering the Gibbs Paradox, he or she is not really a serious chemist or a scientist because he or she demonstrates no curiosity! This book also adequately treats

$$H = k \ln W$$

as a statistical function and considers the identity of H and the thermodynamic entropy S only as an empirical postulate (page 10).

A new edition of this book should be produced in future. I have some minor suggestions for that purpose. In the preface (page viii), the authors said that the laws of mass action would breakdown if the number of particles (chemical species) is small and mentioned that 10^7 molecules of water would result in the number of ion pair per vesicle being either one or zero if pH=7. It is correct that the statistical significance applies to a large number of particles but it is also applicable to even a single particle considered over a long time frame (e.g. over a period of 10^7 years, there will be all together a whole year when such a water molecule is in the state of an ion-pair!) Many chemical processes such as an irreversible decomposition reaction (and many irreversible decay processes in atomic physics) do not involve interactions (e.g. ^{14}C decay). Chemists call them first-order processes. This book considers, of course, the multi-molecular processes and chemical equilibrium, and normally reversible processes (e.g., the ion-pair can form a water molecule). Kinetically speaking, a single molecule process can also be characterized by statistical or probability parameters. In the new edition, editorial or typographic errors should be corrected: for example, on page 303, the paragraph following equation (10.2) should be corrected: "The problem of finding..." at the beginning should be deleted and "... equal o zero" at the end should be changed to "... equal to zero"; on the following page 304, "*d*t" should be added or inserted into equations (10.7)–(10.9). Maybe a web-site can be set up for the corrections and discussions related to this book and the topic of the mass action law.

The following paragraph was copied from the publisher's web-site [2]: The theoretical basis of this book is developed *ab ovo*. This requires dealing with several problems arising in physical chemistry including the concept of entropy as a thermodynamic coordinate and its relation to probability. Thus Maxwell Boltzmann and Gibbs statistical thermodynamics and quantum statistics are made considerable use of. A statistical mechanical derivation of the law of mass action for gases and solids is presented, and the problems arising in the application of the law of mass action to the liquid state are addressed. Molecular interactions and how to take them into account when deriving the law of mass action is discussed in some detail sketching a way alternative to the use of activities. Finally, attention is drawn to the statistical mechanical background to Linear Free Energy Relationships (LFER's) and of Isokinetic Relationships (IKR's) and their connections with molecular interactions.

Acknowledgements: The reviewer is very grateful to Professor Linert [4] and the publisher for sending me this book immediately after its publication, and to Professor Jameson for English corrections.

References and Notes

1. *Editor's Note*: The brief summary and the contents of the books are reported as provided by the author or the publishers. Authors and publishers are encouraged to send review copies of their recent books of potential interest to Dr. Shu-Kun Lin, MDPI, Saengergasse 25, CH-4054 Basel, Switzerland. Tel. +41 79 322 3379, Fax +41 61 302 8918, E-mail: lin@mdpi.org. Some books will be offered to the scholarly community for the purpose of preparing full-length reviews.
2. The URL for the book is http://www.springer.de/cgi-bin/search_book.pl?isbn=3-540-41078-3.
3. Gibbs paradox of Entropy of Mixing website: http://www.mdpi.org/entropy/entropyweb/gibbs-paradox.htm
4. The website for Linert is http://www.ias.tuwien.ac.at/research/fgwl.