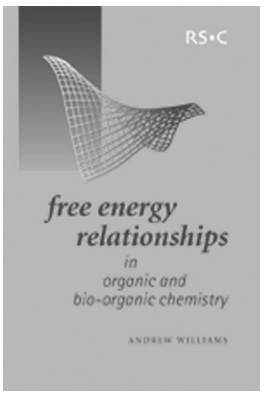
*Uta Wille**



Free Energy Relationships in Organic and Bio-Organic Chemisty

by Andrew Williams
RSC, Cambridge
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Free energy relationships are the simplest and easiest of techniques to use for studying reaction mechanisms, but the results are often not easy to interpret. Because the most recent undergraduate texts devoted to free energy relationships were published some thirty years ago and applications of free energy relationships to the study of organic and bio-organic reaction mechanisms have undergone substantial transformations since then, this book aims to demonstrate these methods, with a special emphasis on the concepts of *effective charge* and *similarity*, to senior undergraduates and postdoctoral workers engaged in such investigations.

After a general introduction into the physico-chemical origin of free energy relationships in chapter 1, chapter 2 is dedicated to the derivation of the various existing equations, starting with the most familiar, e.g. the Hammett, Taft, and Brønsted equations, followed by those modelling the nucleophilic substitution reaction at an sp^3 carbon (Swain–Scott and Richie equations) and solvent influences on the reactions mechanism (Grunwald–Winstein and Hansch equations). The concept of effective charge, which simplifies the interpretation of the slopes of linear free energy relationships from polar substituent effects (this is relevant, as the linear free energy equations do not directly give charge characteristics of a reaction), is introduced in chapter 3. Chapter 4 is devoted to the description of the transmission of polar substituent effects to a reaction centre, e.g. via σ-inductive, field, or resonance effects, and introduces the various equations, which take these effects into account. Chapter 5 presents formalisms that consider the influence of substituent variation on the slope of the free energy relationship by either cross- or self-interactions. Some anomalies, special cases, and non-linear behaviour are described in chapter 6, whereas chapter 7 presents applications of the various free energy correlations to organic and bio-organic reaction systems. Derivations for selected equations, which were, due to their length not included in the respective chapters, are given in the Appendix, which also contains extensive tables, listing structure and linear free energy parameters. Each chapter contains, besides references, a list of recommended further literature and problems, for which the answers are also given in the Appendix.

This book has positive but also negative aspects. A clear plus is chapter 7 containing the potential applications of free energy correlations for the diagnosis of a mechanism, demonstration of intermediates, parallel reactions, and concerted mechanisms, and which also shows how physico-chemical constants can be calculated and kinetically equivalent mechanisms resolved from linear free energy relationships. Very useful for the potential applicant of this technique is also the compilation of the structure and linear free energy parameters, although the author recommends checking the data against the quoted literature prior to use.

On the other hand, the remaining chapters dealing with the introduction or derivation, respectively, of the various equations might only be understandable to those who are already working in this field. Unfortunately, the extensive use of simplifications and introduction of parameters, often without further or only very poor explanation (the reader is instead referred to the quoted literature) and the prosaic style makes the book very difficult to read, so that potential new users of this technique could be discouraged. In addition to this, the book is not without mistakes: many figures show a logarithm of a rate constant with a unit.

To conclude, this book provides a broad overview about the existing linear free energy equations. With its many literature references, it could prove to be a very useful compilation for students already familiar with this area. However, it cannot be regarded as a textbook providing an inspiring entry into the interesting and important field of free energy relationships as a tool in mechanistic studies, and for those in search of something like that this book cannot be recommended.

**Uta Wille graduated from her PhD in physical chemistry in 1993 and completed a Habilitation in 1999, both at the Universität Kiel. After a postdoctoral stay with Bernd Giese in Basel in 1997/98, she was appointed as a Privatdozent at the Universität Kiel (1999), and in 2003 as a Lecturer at the School of Chemistry at Melbourne University. Her research interests are free-radical reactions in organic and bio-organic chemistry.*

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