

Acid tests for the Usanovich theory

John Gibson

A New View of Current Acid-Base Theories. By Harmon L. Finston and Allen C. Rychtman. Pp.216. ISBN 0-471-08472-7. (Wiley: 1982.) £39.50, \$66.50.

MOST chemical reactions and many life processes are carried out in a solvent, and closely connected with the properties of solvents is the behaviour of acids and bases. The acid-base concept has long had a unifying effect in chemistry and in modern times has a great bearing on solvation, compound solubility, the choice of a solvent for chemical synthesis, the understanding of nucleophilic and electrophilic reaction steps, and reaction mechanisms. In their *New View of Current Acid-Base Theories*, Finston and Rychtman review all the old theories, justify them within their limits but finally support the Usanovich theory as the most inclusive, giving experimental evidence for concerted proton and electron transfer, and for the relationship between oxidizing ability and acidity.

The evolution of the acid-base concept over the last three centuries was, at first, a shrinking process, continually reducing the number of substances regarded as acids and bases; it culminated in the restrictive electrolytic dissociation theory of the late nineteenth century, with its emphasis on protons and hydroxide ions in aqueous solution.

Brønsted and Lowry reversed this process in 1923 by omitting water as a requisite solvent and re-defining a base as any substance which can accept a proton. In his book *Valence and the Structure of Atoms and Molecules* published in the same year, G.N. Lewis proposed with complete generality "that a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom . . .". This throwaway line went largely unheeded for 15 years before he supported his alternative ideas in detail. In the meantime the Brønsted-Lowry theory grew strong and an independent theory, the solvent systems theory, became established for aprotic solvents. Only in the late 1930s did Lewis's theory gain currency. Lewis saw no reason for limiting acids to hydrogen-containing compounds and also objected to the over-emphasis of ions in the solvent systems theory. His definition of a base as "have pair, will share" incorporates the Brønsted-Lowry theory but his definition of an acid as an electron pair acceptor continues our enlargement process. The Lewis theory suffers from the disadvantage of being difficult to quantify, but this aspect has attracted attention from Mulliken, Klopman and Hudson, Pearson, Drago, Gutmann and others.

All of this comes over well in Finston and Rychtman's very readable book. Many

comparisons are made between the different theories, but the main message of the book comes in the penultimate chapter. This elaborates the very general definitions of Usanovich who matches the wide definition of base given by Brønsted and Lowry with an equally wide definition of acid, which now becomes capable of splitting off any cation. Moreover, since the electron is regarded as a base, redox reactions become a subclass of acid-base reactions. Thus oxidizing agents relate to acids, reducing agents to bases and quantitative comparisons arise through ionization energies and reduction potentials.

The last chapter is rather novel in that the authors describe some of their own experiments which were designed to test the Usanovich theory as applied to aqueous electrolytes. They carried out pH measurements and acid-base titrations to determine the acidity of the aqueous

oxidization agents dichromate, permanganate and ferric ion. Some support was found by analogous transfer mechanisms for protons and electrons; enhancement of acidity by oxidizing agents; and enhancement of the oxidizing power of a given redox couple with increasing acidity. I think that at this stage the authors would have us believe that our enlargement process is now complete. I take a more conservative view and suggest that some readers might like to repeat these experiments, and perhaps make the obvious extension to non-aqueous solvents, before we can consider the debate finished.

The book is well produced and makes interesting and convincing reading. It would be a good companion to a first-year university lecture course on this subject, but equally would be of interest to researchers in the traditional areas of chemistry and in biochemistry. □

John Gibson is a Senior Lecturer in the Department of Chemistry at Imperial College, University of London.

Unusual chain behaviour

Paul Calvert

Polymers and their Properties. Vol.1, *Fundamentals of Structure and Mechanics.* By J.W.S. Hearle. Pp.437. US ISBN 0-470-27302-X; UK ISBN 0-85312-033-1. (Halsted/Ellis Horwood: 1982.) \$94.95, £32.50.

IN AN established field the author of a textbook will usually play safe. He will repeat and update the contents of previous books and re-work only those areas which he knows well. Alternative and equally safe techniques are to be abstractly mathematical or to be light and descriptive. Hearle follows none of these courses and has produced a very original and personal book.

He starts with isolated polymer chains and discusses their conformations, energetics and response to stress. The rest of the book then traces the behaviour of the chains in successively more restrained states through melts and solutions, rubbers, glasses and crystals. There is no polymer chemistry, nothing about industrial plastics, no diversions into analytical techniques and not much mathematics, but there is a clear and consistent development of the main theme of chain behaviour. Hearle tries to give simple explanations or analogies for many aspects of chain behaviour and these are accompanied by many rough sketches of chains in various states of distortion.

Some of the questions which he raises have been quietly ignored by most other authors. I think that his explanations are

occasionally wrong but they are usually enlightening. An example is in the discussion of the origin of the β relaxation in polyethylene terephthalate where he draws an analogy between the flexible ethylene moiety and the soft segments of block copolymers. It is a nice idea but β relaxation also occurs in totally rigid molecules and cannot be attributed to a single chain segment.

Also, the final chapter in the book — which tries to relate the morphology of plastics and fibres to their mechanical properties — is not altogether satisfactory. I feel the author fails here because he does not keep a clear distinction between the highly oriented structures of fibres and the isotropic state of plastics where it is no longer fashionable to talk of "fringed micelles". Much of Hearle's own work has been on the structure and properties of fibres, however, so perhaps it is right that the deviations from the mainstream should be greatest here.

I would certainly recommend this book to someone seeking a first course on the physical properties of polymers. It provides a good framework either for more rigorous studies or for understanding the technology and applications of polymers. The small errors can be sorted out later, the overall structure will be of lasting value to a student. □

Paul Calvert is a Lecturer in Polymer Science in the School of Chemistry and Molecular Sciences, University of Sussex.