Atmospheric chemistry

Atmospheric Chemistry. By J. Heicklen. Pp. xiv+406. (Academic: New York and London, 1976.) \$38; £27.

In view of the rapid expansion in knowledge of the chemistry of the Earth's atmosphere in recent years, publication of a new volume on this topic is timely. *Atmospheric Chemistry* by Julian Heicklen, however, does not in any way achieve the standard of information collection, dissemination and presentation in the two notable publications on this topic in the early 1960s: Leighton's *Photochemistry of Air Pollution* and Junge's *Air Chemistry and Radioactivity*.

The reason for this failure mainly arises from the authors attempt to cover too much ground; indeed some of the topics discussed-such as the kinetics and mechanism of hydrocarbon combustion, the detailed effects of urban pollutants on plants and animals, and pollution control methods-are inappropriate to the field encompassed by the title. On the other hand there is inadequate coverage of the basic large-scale and local meteorological determining the transport factors mechanisms that are so important in defining the reactor in which the chemical reactions take place.

In addition, the overall emphasis is very much towards photochemistry. Although it is true that the absorption of solar radiation is the primary driving force for chemical reaction in the atmosphere, the chemical interactions of trace gases with precipitation elements and the wash-out and rain out processes have an important part to play in the overall atmospheric cycles, and these are hardly discussed at all. This lack of balance detracts from the overall usefulness of the work in presenting an overview of the science of atmospheric chemistry.

The author must be credited, however, with the collection of a large amount of photochemical and kinetic information on the chemical reactions which may occur in the atmosphere. In the chapters on chemistry of the upper atmosphere and on photochemical smog, simple model calculations are developed to demonstrate how the trace gas composition in each particular atmospheric region can be simulated using the chemical kinetic information. This is basically a useful presentation, but unfortunately the arguments tend to become too complex and difficult to follow. Also, the uncertainties in applying the results to real atmospheric situations are not emphasised. For example, in the discussion of a model photochemical smog

system, the reader is left with the impression that ozone concentration in sunlit exhaust-polluted atmospheres are governed solely by the photochemical reactions. The important and often dominant role of meteorology, in determining ozone concentrations is not mentioned.

The lack of emphasis on precipitation chemistry is very apparent in the chapter dealing with SO_2 chemistry. A comprehensive 10-page summary is given of laboratory data on SO_2 photochemistry, a process which is widely accepted as being of negligible importance in the atmospheric chemistry of SO_2 . The droplet-phase oxidation of SO_2 is, on the other hand, dealt with in a cursory fashion with no reference to some of the early classic work carried out on this important system.

In addition to the above mentioned chapters, there is a concise description of the chemistry of the ionosphere, a long chapter on atmospheric pollutants, which contains very little atmospheric chemistry and a lot of useless information on concentrations in US

Ion cyclotron resonance spectrometry

Ion Cyclotron Resonance Spectrometry. By T. A. Lehman and M. M. Bursey. Pp. xi+230. (Wiley-Interscience: New York and London, 1976.) £15.95; \$27.30.

ION CYCLOTRON RESONANCE (ICR) spectrometry has been widely used during the past 10 years for the study of the chemistry of ions in the gas phase. Although it has found many applications in the field of chemical physics, it has been used increasingly in studies of the structure and reactivity of organic ions and in the elucidation of reaction mechanisms which parallel those observed in solution. It is on the latter group of applications that this volume concentrates, and by far the longest chapter in the book is devoted to a discussion of such topics as gas-phase acids and bases, nucleophilic and electrophilic substitution reactions, and structures of ions. It is written from the viewpoint of a physical/organic chemist and a number of interesting comparisons are drawn with results obtained from studies of solution kinetics.

This illustrates one of the major problems in writing a book on a particular experimental technique: the subject of gas-phase ion chemistry is much bigger than ICR spectrometry and by confining themselves largely to examples based on ICR studies, it can be argued that the authors present an incomplete and selective view of the field. For example, results obtained from high pressure mass spectrocities and deleterious effects, together with a short but not very illuminating chapter on aerosol chemistry. A chapter entitled reactions of O_3 and singlet O_2 also contains a detailed discussion of NO_2 photolysis.

There are some misconceptions and inaccuracies which are unsatisfactory for a book of this kind. For example, it is stated that "The troposphere is a relatively quiescent region (of the atmosphere) where relatively little chemistry occurs . . . The global atmosphere chemical cycles can be summarised as mainly oxidation occurring in the stratosphere . . .". This statement is manifestly untrue. In fact, nearly all of the gaseous material emitted into the atmosphere from the Earth's surface fails to penetrate the tropopause. It is oxidised or otherwise scavenged in the troposphere where 80% of the atmospheric mass resides. R. A. Cox

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metry or by flowing afterglow and flowing after-drift methods have proved of considerable interest; and although comparisons are drawn between these results and those obtained by ICR spectrometry, discussion of them is necessarily brief.

The first two chapters of the book provide a very readable introduction to the technique in which the reader is encouraged to explore the possibilities of the technique without worrying too much about the finer points of its theory of operation. The chapter on reaction mechanisms is followed by a discussion of theoretical aspects of power absorption, linewidths and extraction of rate data together with a brief review of current theories of ion molecule reactions at near thermal energies. The final chapter briefly describes various applications of ICR spectrometry in the field of chemical physics. The book concludes with an extensive bibliography and two appendices.

The book provides a useful introduction to ICR spectrometry and to physical/ organic aspects of gas-phase ion chemistry but the chemical physicist will find little which is not adequately covered in review articles. The problem with any book on a particular technique is that it is necessarily limited in its scope; and although the reader will know quite a lot about ICR spectrometry, if he gets through this book, he will not be in a position to assess its advantages and disadvantages relative to other techniques used in the study of gas-phase ions.

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