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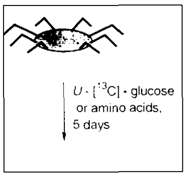
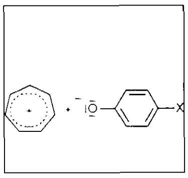
# Chemical Society Reviews

## Volume 22 Issue 1 Pages 1–72 February 1993



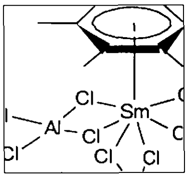
**NMR of Nature's Plastics and Spiders' Webs: Chemistry, Physics, or Biology?** *By Jeremy K. M. Sanders* (pp. 1–7)

Science is often divided into boxes with labels such as 'Chemistry', 'Physics', or 'Biology'; inside the Chemistry box are smaller boxes 'Organic', 'Inorganic', or 'Physical'. But is this the way science should be carried out? Do scientists always start with a clear question and then solve it in a logical manner? This article explores these questions, using as a case history the author's accidental discoveries, wrong conclusions, and outrageous NMR experiments in exploring the behaviour of PHB inside cells and of spider's web elasticity.



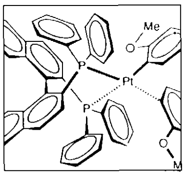
**Bond Cleavage Energies for Molecules and their Associated Radical Ions** *By Edward M. Arnett and Robert A. Flowers, II* (pp. 9–15)

Ordinary two-electron covalent bonds may be broken homolytically, to form free radicals, or heterolytically to form a cation and an anion. This article describes a simple approach employing reaction calorimetry and electrochemistry that can be applied to many ions that are stable in solution. Heats of heterolysis ($\Delta H_{het}$) are obtained immediately from the reverse process, the heat of reaction of the cation and the anion to form the covalent bond. $\Delta H_{het}$ values can be converted into heats of homolysis by determination of the oxidation potential of the anion and the reduction potential of the cation and extended to cleavage of radical ions.



**Zero Oxidation State Compounds of Scandium, Yttrium, and the Lanthanides** *By F. Geoffrey N. Cloke* (pp. 17–24)

The first stable zero oxidation state complexes of Sc, Y, and the lanthanides have been prepared by metal vapour synthesis. Whilst the tris-diimine complexes $[M(Bu^t\text{-}DAB)_3]$ are formally $M^0$ compounds, structural and spectroscopic data indicate that they are best regarded as $M^{3+}$ salts of the $Bu^t$-DAB radical anion. The sandwich compounds $[M(\eta\text{-}C_6H_3Bu^t_3)_2]$, however, have been shown to be genuine $f$-element (0) complexes from detailed magnetic and structural studies. The bonding in these complexes and some of their reaction chemistry is also discussed.



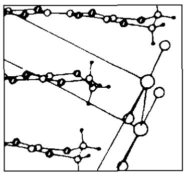
**TILDEN LECTURE. Selectivity and Mechanism in Catalytic Asymmetric Synthesis** *By John M. Brown* (pp. 25–41)

The utility of homogeneous catalysis in organic synthesis rests on a few key reactions, among which hydrogenation and other reductive procedures feature prominently. The review covers work on asymmetric hydrogenation, directed hydrogenation, transfer hydrogenation, and hydroboration carried out in Oxford in the last few years, and highlights the way in which mechanistic experiments can augment the synthetic utility of catalysis.

$x_B[G^*_{m,B} + RT\ln x_B]$
$+ x_B\ln x_B]$

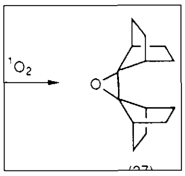
**Measurement, Analysis, and Utility of Excess Molar $-(\partial V/\partial p)_s$** *By G. Douhéret and M. I. Davis* (pp. 43–50)

The aim of this article is to demonstrate the importance of the quantity $-(\partial V/\partial p)_s$, by identifying the place that it occupies in the hierarchy of thermodynamic properties of liquid mixtures and by exploring its significance. After a brief survey of experimental techniques, emphasis is placed upon a procedure for examining its composition dependence for (amphiphile + water) mixtures. Detailed analyses of the excess molar quantity $[-(\partial V/\partial p)_s]^E$ and of other related properties of [amphiphile + water] systems have been performed by means of a segmented composition curve-fitting procedure. These reveal that even relatively small amphiphiles tend to adopt patterns of molecular aggregation that mimic those of their detergent homologues.



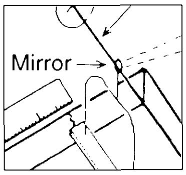
**HUMPHRY DAVY LECTURE. Halides Magnetic, Halides Superconducting** *By P. Day* (pp. 51–57)

Superconductivity and ferromagnetism are highly unusual states of matter, the more so when they are found in molecular inorganic and metal-organic compounds. Examples are halide-based salts, among which $(BEDT\text{-}TTF)_mX_nS_p$ (BEDT-TFF = bisethylenedithiotetrathiafulvalene, X = halide-containing anion, S = solvent) exemplify metals and superconductors, while $(RNH_3)_2CrX_4$ (X = halide, R = organic moeity) are ferromagnets. Structure–property relations in both series are surveyed, with special reference to the work of the author's group, while efforts to synthesize a magnetic molecular superconductor are summarized.



**The Photo-oxygenation of Olefins and the Role of Zwitterionic Peroxides** *By Charles W. Jefford* (pp. 59–66)

The article describes how olefins, particularly bridged bicyclic ones, react with singlet oxygen to give initially zwitterionic peroxides. Evidence for these fugitive species is obtained by trapping with alcohols and aldehydes. In the case of electron-rich mono-olefins, photo-oxygenation in the presence of aldehydes leads to 1,2,4-trioxanes and provides the mechanistic basis for a new methodology for preparing this hitherto unknown class of saturated oxygen heterocycles, certain members of which have potential as anti-parasitic agents.



**The Study of Surfactant Monolayers by Surface Pressure–Area Measurement** *By M. S. Aston* (pp. 67–71)

This review provides an introduction to the Langmuir Trough technique for studying insoluble surfactant monolayers, highlighting the scope of the method as well as pointing out some of the practical difficulties and pitfalls. The formation of gaseous, liquid, and close-packed surfactant films is discussed. The technique is shown to be a powerful tool for studying molecular interactions in mixed systems, but it is noted there is a need for further development of theories to explain experimental observations.

## *Articles that will appear in forthcoming issues include*

Scales of Solute Hydrogen-bonding: Their Construction and Application to Physicochemical and Biochemical Processes **M. H. Abraham**

How Do Diesel-fuel Ignition Improvers Work? **P. Q. E. Clothier, B. D. Aguda, A. Moise, and H. O. Pritchard**

Polymer–Micelle Interactions: Physical Organic Aspects **J. C. Brackman and J. B. F. N. Engberts**

Motion of Sorbed Gases in Polymers **W.-Y. Wen**

Thermodynamic and Related Studies of Amphiphile + Water Systems **M. I. Davis**

The Role of NMR in Boron Chemistry **D. Reed**

MELDOLA LECTURE. Reactions of Group 13 with Oxygen: From Carelessness to Chemistry **A. R. Barron**

The Solubility of Gases in Water–Alcohol Mixtures **R. W. Cargill**

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