

PREFACE

John Stuart Anderson (9 January 1908–25 December 1990)

For more than 40 years of his life Stuart Anderson (generally known as "JS") was a major player in the field of solid state chemistry: his death has left a void, particularly in the theoretical area, which shows no sign of being filled. Something of a legend, he stimulated several generations of solid state scientists with his enthusiasm and encyclopedic knowledge. In part his influence was widespread because he divided his working life between the United Kingdom (where he was born) and Australia (where he died). He spent 1926–1938 at Imperial College, London (B.Sc. 1928, Ph.D. 1931); 1938–1946 at the University of Melbourne; 1946–1954 at the AERE Harwell; 1954–1959 again at the University of Melbourne; 1959–1963 at the National Chemical Laboratory, Teddington; and 1963–1975 at the Inorganic Chemistry Laboratory of Oxford University; then, after "retiring," 1975–1982 at University College, Aberystwyth; and 1982–1990 at the Research School of Chemistry of the Australian National University in Canberra. Shorter periods were spent in other parts of the world, especially Germany, the United States, and India.

He was "an itinerant scholar," whose scientific career extended over more than 60 years, during which he accumulated many honors, including Fellowships of the Royal Society (in 1953) and of the Australian Academy of Science (in 1954), an Honorary Fellowship of the Indian Academy of Science, and numerous named Lectureships and medals. Until his final illness, when he was over 80, his practice was to be at the bench as much as possible, working with his own hands: he liked glass-blowing and vacuum techniques, even making his

own field-emission microscope (and ancillaries) in Melbourne in 1959, taught himself X-ray diffraction methods early in his career, and so on. During his life he witnessed many changes, in the world in general and in his own subject. He knew many of the prominent players—from Lord Cherwell, Klaus Fuchs, Gunnar Hägg, Hieber, and Paneth to L. Eyring, A. L. G. Rees, A. D. Wadsley, and others. Indeed he worked and published with many of them: Brockway (with whom he did a *gas* electron diffraction study of the structure of some nitrosocarbonyls in 1936 or 1937, 30 years before he started electron diffraction/microscopy on solids), Emeleus, and Penney. Many more were his students: J. G. Allpress, D. J. M. Bevan, N. N. Greenwood, T. A. O'Donnell; or colleagues: R. W. M. D'Eye, C. N. R. Rao, Tom Reed, L. E. J. Roberts, and R. J. D. Tilley (to mention only a few, mainly the older ones). And he had a profound effect on the many undergraduates to whom he lectured: while his lectures were not always easy for young minds to assimilate (or take notes from!), they were always crammed with up-to-date information and indications of important problems still needing solution: in a word they were stimulating.

Most people did not realize that he started as a coordination chemist, working on nickel carbonyl and related compounds at the Royal College of Science (Imperial College, London) and in Heidelberg (in 1931–1932, with Hieber). In fact he seems to have written the first review in English in that field ["Chemistry of the metal carbonyls," *Quart Rev.* 1 (1947), 331–357]. This was in the year *after* he had published the

paper for which he was most famous among solid state chemists, the one which established his early reputation in that field ["The conditions of equilibrium of 'non-stoichiometric' chemical compounds," *Proc. R. Soc. A* **185** (1946), 69–89]. Even more widely known than both of these was his influential book (with coauthor H. J. Emeleus), *Modern Aspects of Inorganic Chemistry*; invariably known as *Emeleus and Anderson*. The first edition was published in 1938, and two others were published in 1952 and 1960, before he relinquished his part in it: up to 1963 it was printed 16 times in English, and there were editions in German (the first in 1940!), Spanish, and Italian. It originated with discussion between the two young authors while they were demonstrating to second-year practical classes at Imperial College in 1936, both being dissatisfied with the classical inorganic texts which gave interminable facts, but made no attempt to fit them into a theoretical framework. Altogether he published over 160 papers and 5 books.

JS introduced solid state chemistry to England, pointing out its likely importance in the preface to the first edition of *Emeleus and Anderson* (which described Hägg's work on the tungsten oxides, etc.), and treating the field to an increasing extent in later editions. His own solid state research—stimulated by a lecture of J. D. Bernal and another by V. M. Goldschmidt in the mid-1930s, and no doubt also by his wide reading for *Emeleus and Anderson*—started in Melbourne in about 1940, and quickly came to dominate his scientific thought, certainly by the middle 1940s. (He also did a great deal of work on adsorption and reaction on solid surfaces, culminating in field emission and field ion microscopy until about 1970.) His development of solid state theory was stimulated by his noticing (as others had not) the early 1930s papers of Schottky and Wagner on native disorder in crystals, i.e., the classical "point defects."

(For this, his mastery of the German language would have been useful, perhaps even essential!) Coupling their ideas with those of Fowler and Lacher on "defect interaction," his 1946 paper (*loc. cit.*) was a general, statistical thermodynamic treatment of phase limits in binary, nonstoichiometric compounds. He later noted drily, "My [1946] paper does seem to have stimulated others. . . ." Certainly it stimulated him and his 1940s Melbourne group to work on SnS, PbS, Cu₂O, PrO_x—in the heroic age when, for example, praseodymia had to be prepared from mineral monazite.

Later, at Harwell, his group worked on the uranium oxides, and related ternary systems. He was peripherally involved in the (British, 1952) Montebello "atomic" tests (for he declined to work on military aspects of atomic energy); and he vividly remembered the shock of the first Russian nuclear explosion.

During his second period at Melbourne University, David Wadsley (who was also in Melbourne, but at the CSIRO Division of Mineral Chemistry) was developing and publishing his own radical ideas on "homologous series" of phases—principally "crystallographic shear" (CS) structures closely spaced in composition and closely related in structure, as an alternative explanation of at least some "nonstoichiometric solid solutions." These ideas were, of course, based on Wadsley's own X-ray work, and earlier and concurrent crystallographic work in Uppsala and Stockholm by Hägg, Magnéli, G. Andersson and S. Andersson, Kihlberg, and others on the oxides of W, Mo, V, Ti, etc. At the time, JS did not appear to be overtly enthusiastic about the new ideas, although it is obvious that he was well aware of the facts on which they were based (he documented them in the first three editions of *Emeleus and Anderson*). Indeed, somewhat ironically they included Bevan's work with him in Harwell (in 1953) on the cerium oxides.

The two sets of ideas being opposed, one supposes that there was controversy between their principal exponents, but no contemporary account has yet emerged. In 1962, at the ACS Meeting in Washington, Roland Ward arranged a symposium on nonstoichiometric compounds [subsequently published as *Nonstoichiometric Compounds* (Advances in Chemistry Series, Vol. 39), R. F. Gould (Ed.), American Chemical Society, Washington, DC], with Stuart Anderson and David Wadsley as plenary speakers—i.e., a deliberate and timely confrontation of views was deliberately engineered—the thermodynamicist *versus* the crystallographer. Later, JS recorded that their two papers showed a convergence of views: in both cases the picture of a disordered, defect solid was that of short-range instead of long-range order.

In the following years, JS developed more elaborate statistical thermodynamic treatments of disorder and nonstoichiometry [pp. 29–105 in *Modern Aspects of Solid State Chemistry*, C. N. R. Rao (Ed.), Plenum, New York, 1970; pp. 295–317 in *Solid State Chemistry* (Special Publication 364, N.B.S.), R.S. Roth and S. J. Schneider (Eds.), U.S. Dept. of Commerce, Washington, DC, based on microdomain textures and Terrell Hill's "small systems" thermodynamics, and driven by the results of W. L. Roth on wüstite, Willis on UO_{2+x} , etc. He was not entirely satisfied with the outcome, but his ideas were now much more sophisticated and realistic. He pointed out that:

(i) "Broad generalisations not infrequently turn into [i.e., come to be seen as] rather crude approximations as scientific knowledge advances. The point defect concept appeared at first to offer a rational interpretation for the structure and properties of inorganic solids. As can now be seen, this is no longer a tenable viewpoint."

(ii) On slightly reduced rutile: a $p(\text{O}_2)^{-1/6}$

law had been reported by Kofstad and others, "which extends into a composition range where . . . there is direct evidence that the real structure is quite different" from the point defect model from which the law was derived.

(iii) ". . . one must conclude that thermodynamic measurements do not suffice to discriminate between alternative structural models. . . ."

(iv) ". . . relaxation of the system [point defect in a crystal] may go far beyond a simple rebalancing of coulomb forces, and may effect a structural transformation of the 'solvent' crystal lattice."

(v) About the thermodynamic reversibility in the "swinging" region of TiO_x : "This is very remarkable, and contrary to all that one would intuitively foretell."

(vi) "One problem is that the preferred ultramicrostructure of defect solids shows a high degree of chemical specificity: elements from the same group of the Periodic Table may resolve the ordering and structure of defects in different ways. . . . Thus, in binary oxides of elements in Groups IV–VII of the Periodic Table, shear structures are formed by Ti and V in the rutile type . . . [but] . . . MnO_2 and the other rutile oxides are not known to form shear structures."

The (complex) theoretical situation has remained unchanged during the succeeding 20 years, so that these particular theoretical papers still warrant careful reading.

At about this time he had gone to Oxford. There he developed a model for the production of CS structures, and started electron microscopy (EM) studies (then new in chemistry) of ReO_3 -, MoO_3 -, and TiO_2 -related CS systems as well as thermodynamic studies of the last. This was a very prolific period in his career, especially the EM studies of oxidation and reduction of niobium oxides and related ternary systems in and by the EM ["Electron microscopy in

the study of solid state reactions,” *Chem. Scr.* **14** (1979), 129–139; Nobel Symposium 47 of the Royal Swedish Academy of Sciences, *Direct Imaging of Atoms in Crystals and Molecules*. And, reacting to the perhaps excessive emphasis on oxides he also started some work on carbides, etc.

The almost simultaneous discovery of “swinging CS” in reduced rutile and Bevan’s continuous sequence of fluorite-related, “vernier structure” yttrium oxyfluorides in the early 1970s undoubtedly led JS to his reification of the notion of “infinitely adaptive structures” [*J. Chem. Soc. Dalton Trans.*, 1107–1115].

His EM work in particular (and its publication) continued to flow strongly while he was at Aberystwyth after “retiring.” Subsequently, in Canberra, he was extremely active during the “warm superconductor” boom. In addition he resumed work on alkali uranates which had started in Melbourne 30 years earlier. He eased off only when (in 1989, at the age of 81) he developed cancer of the throat. His final illness, borne with characteristic stoicism, did not destroy his phenomenal memory, puckish humor, and sharpness of intellect: these persisted to the last days. Relief came on Christmas day, 1990. On 28 December he was cremated at a family ceremony, and a memorial service attended by many friends and colleagues was held at the Church of St. John the Baptist, Canberra, on 29 January 1991.

JS was an unusually private man, and evaluation of his character is therefore difficult. To many “he was the very model of a modern [i.e., 1880s] major-general”; casual

acquaintances held him in awe. Some recalled “the astonishing air of remote infallibility which surrounded him in our eyes”—and that was when he was still in his thirties! But he relished a good argument, and was famous for his aphorisms: “Extrapolation is an inexhaustible source of fallacious reasoning”; “Infinitely adaptive structures”; etc. [A nonscientific one that he liked came from a family trip by car to the Flinders Ranges in South Australia. In its dry, sheep-station country one station manager opined that “in this country a man can make a living off a thousand square miles.”] His *sang froid* was equally well known: One afternoon in Melbourne (in the 1940s) there was a violent thunderstorm during which a lightning bolt struck somewhere within the University, just as JS and two students were about to enter a glass-paneled research laboratory. There was a blinding flash of light through the glass and, almost simultaneously, a tremendous clap of thunder. The students recoiled in fright; JS simply commented, “Hm; about 500 feet, I would guess.”

But he impressed most by his first-rate intellect and remarkable memory and erudition, as well as his very fertile imagination and passion for science. He had a great appreciation of “Nature,” especially the Australian bush: in his younger days he walked over E and SE Europe and canoed down the Danube.

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